

Investigation of Gas Phase Composition During Carbon Nanotube Production

S. Yaglikci, B. Salgara, F. Soysal, B. Cicek

Abstract—Chemical vapor deposition method was used to produce carbon nanotubes on an iron based catalyst from acetylene. Gas-phase samples collected from the different positions of the tubular reactor were analyzed by GC/MS. A variety of species ranging from hydrogen to naphthalene were observed and changes in their concentrations were plotted against the reactor position. Briefly benzene, toluene, styrene, indene and naphthalene were the main higher molecular weight species and vinylacetylene and diacetylene were the important intermediates. Nanotube characterization was performed by scanning electron microscopy and transmission electron microscopy.

Keywords—Carbon nanotubes, chemical vapor deposition, GC/MS, species profile

I. INTRODUCTION

SINCE the discovery of carbon nanotubes (CNT's) in 1991 [1], these structures have become an interesting research topic for many researchers because of their promising mechanical, electrical and optical properties. For the production of carbon nanotubes, various techniques have been developed such as arc-discharge [2]–[4], laser ablation [5]–[7], and thermal chemical vapor deposition (CVD) [8]–[10].

Over the years, many researchers have investigated solid phase mechanism of carbon nanotube synthesis, but the events that take place in the gaseous phase yet to be clarified. Changes in gas phase have direct consequences on CNT diameter, length, purity, morphology etc. If we understand the gas phase behavior during nanotube production, we can have the possibility of producing nanotubes with desired properties. Gas phase events are as important as those occur in the solid phase. In recent years some few researchers intended to address the gas phase mechanism during the carbon nanotube production [11], [12].

In CVD method, carbon sources [13], [14]; such as solid, liquid or gaseous phase introduced into reaction zone over a catalyst surface. In this process transition metals (Fe, Ni, Co, etc.) are used as catalysts [15]–[17] and Si, Al, etc. are used as the substrate.

In this paper, we investigate the gas phase mechanism during the production of carbon nanotubes with CVD process,

identify the nature of the gas phase species, determine their concentration profiles over the length of the tubular reactor in order to comment on the dependence of rate on either reactant species or intermediates those formed in the reaction zone and explore the effects of the amount of catalyst on carbon nanotube production and gas phase species.

In the first step we studied the pyrolysis of acetylene without the introduction of catalyst into the reactor to identify species profiles when there is no CNT production. In the second step the main purpose was to provide same experimental conditions but to use a catalyst coated reactor instead. All gas phase samples along the length of the reactor were collected by a cooled sample probe and stored in heated loops at low pressure in order to prevent condensation of higher molecular weight products. Samples were then analyzed by an on-line GC/MS.

II. EXPERIMENTAL

A. Catalyst Preparation

Sol-gel method was applied to prepare suitable catalysts for CNT production. In this method $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ used as a catalyst precursor and TEOS was used to enhance the surface properties. Ethanol was added to the aqueous solution of the catalyst. The solution was mixed in a flask and ultrasonicated for 20 minutes. Quartz substrates and/or inner surface of the quartz reactor were then drop coated with the catalyst solution, calcined at 450 °C for 10 h under vacuum and reduced at 500 °C for 1 h under H_2 atmosphere.

B. Experimental Setup

In the first experimental setup a 40 mm inner diameter (i.d) and 600 mm long quartz tube was used as the reactor and placed in a tube furnace. The furnace temperature was set to 500 - 950 °C. Acetylene was used as the carbon source and Ar as the carrier gas. Reactor pressure was kept stable at 40 kPa (300 Torr). Gas flow rates were controlled by Alicat Scientific 16 series mass and volumetric flow controllers. Gases were mixed homogenously in a mixing chamber filled with steel wool and fed to the reactor.

In this setup the objective was to explore the experimental parameters such as temperature, pressure and flow rates of feed gases appropriate for CNT production. Temperature, pressure and gas flow rates were identified for CNT production. However in this setup surface to volume (S/V) was too low such that the effects of the surface reactions on the gas phase species distribution were extremely difficult to observe. In order to account for surface reactions the reactor was replaced with a 1.5 mm i.d. quartz tube and S/V ratio was increased 2.7 mm^{-1} . This ratio is very close to those usually obtained by monolithic porous reaction media and still lets us

B. Cicek is currently Full Professor in Chemical Engineering Department, Ankara University, Ankara, Turkey. (Corresponding author phone: +903122033306; fax: +9003122121546; e-mail: cicek@ankara.edu.tr).

S. Yaglikci is currently pursuing his Masters Degree in Chemical Engineering Department, Ankara University, Ankara, Turkey. (e-mail: yaglikci@eng.ankara.edu.tr).

B. Salgara is currently pursuing his Masters Degree in Chemical Engineering Department, Ankara University, Ankara, Turkey. (e-mail: bsalgara@ankara.edu.tr).

F. Soysal is currently pursuing his Ph.D. Degree in Chemical Engineering Department, Ankara University, Ankara, Turkey. (e-mail: fsoysal@eng.ankara.edu.tr).

sample from the gas phase along the length of the reactor. In this second configuration gas phase sampling with a cooled probe from within the reactor became practically impossible thus a movable cooling jacket was placed around the reactor in order to limit the heated reaction zone to predetermined lengths. Being able to change the length of the heated zone allowed us to specify the residence time for CNT production and gas samples were collected from the downstream.

After gas flow rates and cooling jacket position were set, the gas mixture was sent to the reactor and gas phase samples were collected to different loops connected online to the reactor. Loop box contains 16 loops of 0.5 ml in volume and allowed us to collect 16 different samples along the length of the reactor in one experiment. Samples were kept at 150 °C and 40 kPa (300 Torr) in order to prevent condensation of higher molecular weight products. Loop box was also inline with the GC/MS system and analyses were performed following the sample collection. Schematic representation of our first experimental system was shown in Fig. 1 and second experimental system was shown in Fig. 2.

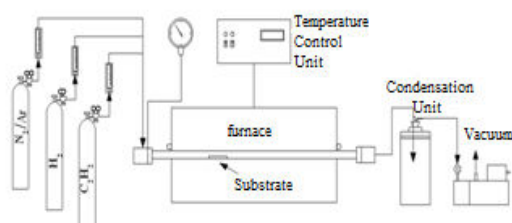


Fig. 1 Schematic representation of the first experimental setup

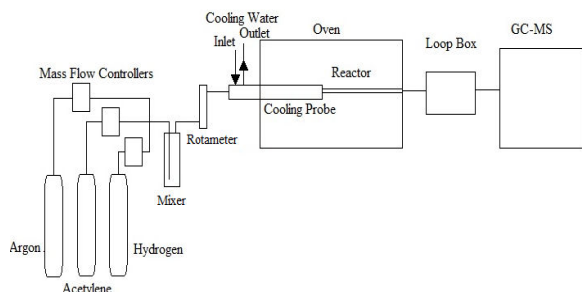


Fig. 2 Schematic representation of the second experimental setup

In this work our aim was to determine the gas phase species distribution during the production of CNT's and explore the effects of temperature, acetylene partial pressure in the feed stream and the amount of the catalyst coated on the reactor inner walls. Table I presents the experimental design applied.

TABLE I
EXPERIMENTAL PARAMETERS

No	C2H2 (SLPM)	Ar (SLPM)	Temperature (K)	Amount of catalyst [g, Fe(NO3) ₃ ·9H ₂ O]
1	0.17	0.83	923	0
2	0.17	0.83	923	1.4
3	0.17	0.83	1023	0

4	0.23	0.77	1023	0
5	0.23	0.77	1023	0.7
6	0.17	0.83	1023	1.4
7	0.23	0.77	1023	1.4

C. Gas Phase Species Analysis

Gas phase analyses were performed by Agilent 7890A GC and Agilent 5975C inert MSD using three different capillary columns namely HP-1 (60 m length, 0.25 mm i.d.), Plot-Q (30 m length, 0.53 mm i.d.) and Mol.s (30 m length, 0.53 mm i.d.).

HP-1 was used for the detection of higher molecular weight species such as benzene and above. Plot-Q was used for the detection of two to five carbon-containing species and Mol.s was used for Ar, N₂, H₂, CO, CO₂ etc. Fig. 3 shows the column configuration in the GC oven.

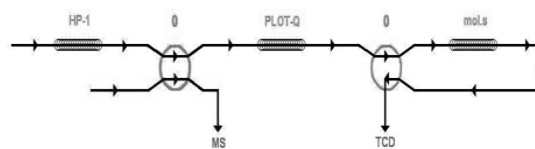


Fig. 3 Column configuration

D. Carbon Nanotube Characterization

Characterization of CNTs were performed by Jeol Jem 1010 Transmission Electron Microscopy (TEM) and Jeol Jsm 7001F Scanning Electron Microscopy (SEM).

III. RESULTS AND DISCUSSION

A. Carbon Nanotube Characterization

Fig. 4 shows SEM and TEM images of the CNT samples produced with the first experimental setup. Mean diameter of the CNTs grown on quartz substrates is 35 nm. Almost all of the CNTs observed in the images are multi walled. These experiments were performed to verify that the techniques utilized for catalyst preparation are appropriate for CNT growth. Same procedure is applied to coat the inner walls of the 1.5 mm i.d. quartz tube.

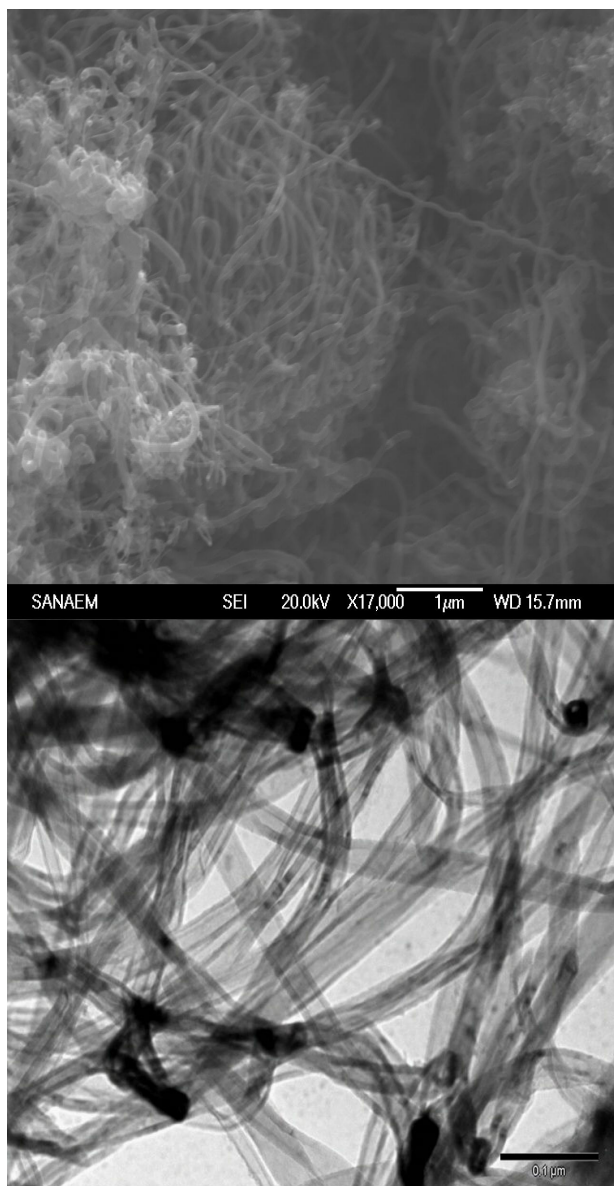


Fig. 4 SEM and TEM images of carbon nanotubes

B. Species Observed in Gas Phase

Species identified in the gas phase pyrolysis of acetylene can be summarized as hydrogen, carbon dioxide, methane, acetylene, acetone, propyne, propene, vinyl acetylene, diacetylene, benzene, toluene, styrene, indene. All of the species detected were the result of pyrolysis reactions except acetone. Acetone comes together with acetylene as an unavoidable impurity from the cylinder. All species we have found in the gas phase are shown in Table II. In Table II indicate detected species but only acetylene and benzene concentration profiles generate in this paper.

TABLE II
LIST OF SPECIES FOUND IN GAS PHASE

Molecule	Formula	Molecule	Formula
Hydrogen	H ₂	Di acetylene	C ₄ H ₂
Methane	CH ₄	Vinyl acetylene	C ₄ H ₄
Water	H ₂ O	1,3-Butadiene	C ₄ H ₆
Acetylene	C ₂ H ₂	1-Butene	C ₄ H ₈
Nitrogen	N ₂	Acetone	C ₃ H ₆ O
Carbon monoxide	CO	1,3-Cyclopentadiene	C ₅ H ₆
Oxygen	O ₂	Furan	C ₄ H ₄ O
Argon	Ar	Benzene	C ₆ H ₆
Propyne	C ₃ H ₄	Toluene	C ₇ H ₈
Propene	C ₃ H ₆	Styrene	C ₈ H ₈
Cyclopropane	C ₃ H ₆	Indene	C ₉ H ₈
Carbon dioxide	CO ₂	Naphthalene	C ₁₀ H ₈
Acetaldehyde	C ₂ H ₄ O		

Benzene was the important molecular weight species through the reactor. In the light of current literature it is quite reasonable to anticipate that acetylene loses one of its hydrogens to form ethynyl radicals. Recombination of ethynyl radicals yield a stable species namely diacetylene. Depending on the availability of hydrogen atoms vinyl acetylene can also form. Further reactions of diacetylene with ethynyl radicals can lead in the ring closure. C₂ radicals can combine with methyl to provide 3 carbon species observed in our experiments. Methyl radical on the other hand reacts with benzene to release a hydrogen atom by forming toluene or simply recombines to a phenyl group. Group linked the benzene and formed toluene. Vinyl acetylene precursor, C₄H₅ radicals linked with each other and formed styrene also H₂ formed this reaction. Formation of toluene has triggered the formation of indene. Acetylene reacts with toluene and formed indene. Also benzene and vinyl acetylene linked and naphthalene formation complete.

In both catalyst and pyrolysis experiments benzene was the important species but pyrolysis resulted in more benzene formation. In the presence of catalyst, toluene, styrene and indene formations were non-negligible but formation of other low carbon-containing species decreases considerably.

These results indicate that gas phase behavior during the CNT production is very important. Although acetylene is fed to the reactor, CNT production is thought to be because of other carbon containing species resulting from acetylene. We think the different formation of benzene concentration between the pyrolysis and catalyst experiments showed benzene was the influential species for the CNT production.

C. The Effect of the Amount of Catalyst on Carbon Nanotube Production

After GC/MS analyses the percentage of acetylene and benzene was calculated along the reactor length.

The analyses started from point zero of the reactor which means that the cooling probe was placed all around the reactor and there were no heated zones in the reactor. GC/MS analyses supported that acetylene decomposition could not take place at point zero.

Cooling probe position was then shifted and a heated zone emerged where the decomposition could take place. Further

shifting of the cooling probe increased the reaction zone. This procedure was repeated until the reaction zone length got through 30 cm. Fig. 5 shows the percentage of acetylene decomposition at 750 °C and 23 % C_2H_2 feedstock condition.

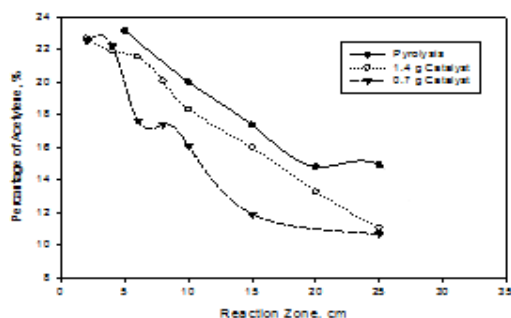


Fig. 5 Percentage of acetylene along the length of reaction zone at 750 °C and 23 % C_2H_2 feedstock

As shown in Fig. 5, percentage of C_2H_2 decreases along the length of reaction zone. Amount of catalyst seems to be also effective in the decomposition of acetylene. Acetylene decomposition was less without a catalyst and the experiment in which the most decomposition took place was the one having 0.7 g catalyst. In pyrolysis, acetylene decomposition is affected by temperature only. However, in the presence of iron catalyst, decomposition of acetylene is affected by both temperature and the catalytic activity.

Amount of the catalyst also seems to be influential to acetylene decomposition. Decomposition of acetylene decreased while the amount of catalyst increased. This phenomenon could be related to catalyst particle diameter. Probability of agglomeration of iron particles rises, when there are more particles present at the reactor walls. Likewise, when there are less particles, probability of agglomeration should be low. Acetylene decomposition is thought to be promoted, because of the resultant relative high surface area when less catalyst is used.

Fig. 6 shows percentage of benzene at 750 °C and 23 % C_2H_2 feedstock condition.

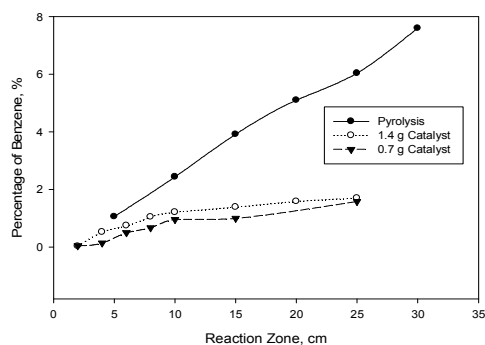


Fig. 6 Percentage of benzene along the length of reaction zone at 750 °C and 23 % C_2H_2 feedstock

As shown in Fig. 6, formation of C_6H_6 is also related to the quantity of catalyst. Although, benzene concentration increases along the reaction zone in pyrolysis, its concentration changes slightly when catalyst is present. The majority of benzene formed could be used for CNT production. Moreover, acetylene decomposition was more rapid but benzene formation rate was slower when less catalyst was used. This may be due to more CNT growth.

D. Effect of Carbon Feedstock Percentage

Carbon feedstock is another parameter that can be explored during the CNT production process. In Fig. 7 and Fig. 8, decomposition of acetylene and formation of benzene are shown with different acetylene feedstocks at 750 °C and 1.4 g catalyst.

In Fig. 7, experiments begin with different initial feedstock rates, their final acetylene concentration is nearly the same. This shows that it is possible to gain much more carbon source for CNT production with higher feedstock rates. In Fig. 8, benzene formation data supports this idea. Final benzene percentages are 1.5 % when 17 % acetylene feedstock was used and 1.7 % when 23 % acetylene was used. This indicates benzene formation is not affected from the initial acetylene feedstock rate and it is possible that the difference between the acetylene feedstocks goes to CNT growth process.

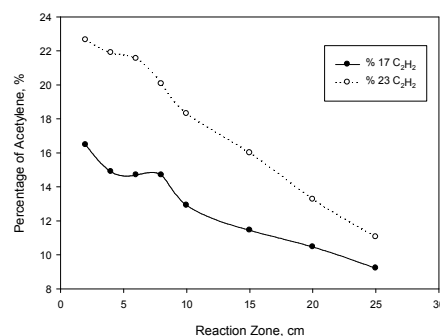


Fig. 7 Difference of acetylene percentage along the length of reaction zone in 1.4 g catalyst experiment at 750 °C

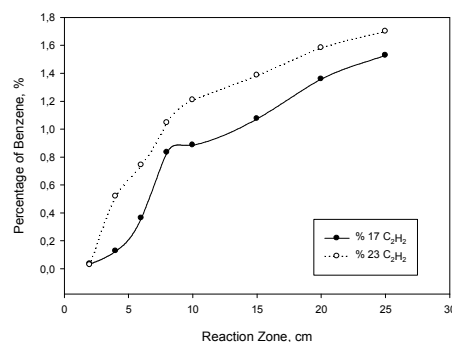


Fig. 8 Difference of benzene percentage along the length of reaction zone in 1.4 g catalyst experiment at 750 °C

E. Effect of Temperature

Reaction temperature is one of the most important parameters in CNT production process.

Fig. 9 and Fig. 10 show the decomposition rate of acetylene depending on reaction temperature with 17 % C_2H_2 feedstock in pyrolysis and in 1.4 g catalyst experiments respectively. Fig. 12 shows the formation rate of benzene depending on reaction temperature with 17 % C_2H_2 feedstock in pyrolysis and in 1.4 g catalyst experiments respectively.

Decomposition of acetylene was expected to increase with increasing temperature in both pyrolysis and catalyst experiments, because, the reaction rate constant is affected exponentially from temperature. Fig. 9 and Fig. 10 shows the decomposition rate of acetylene is increased with increasing temperature.

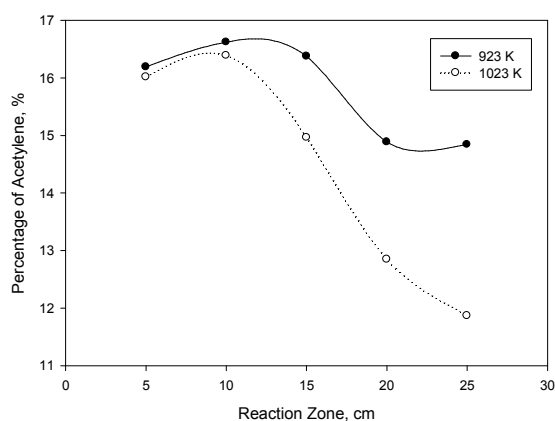


Fig. 9 Difference of acetylene percentage along the length of reaction zone in pyrolysis experiment at 17 % C_2H_2 feedstock

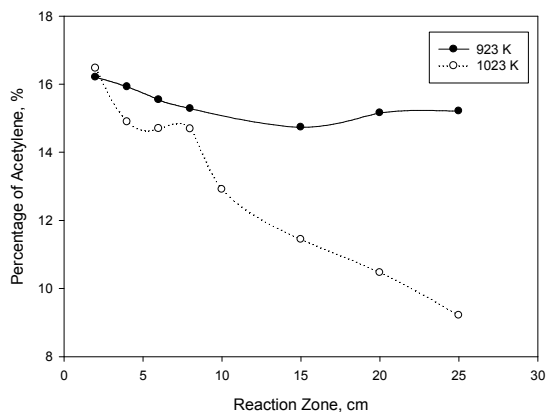


Fig. 10 Difference of acetylene percentage along the length of reaction zone in 1.4 g catalyst experiment at 17 % C_2H_2 feedstock

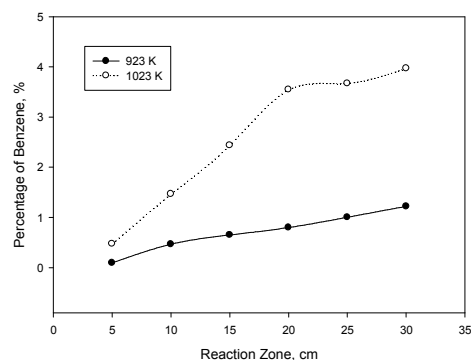


Fig. 11 Difference of benzene percentage along the length of reaction zone in pyrolysis experiment at 17 % C_2H_2 feedstock

Fig. 11 and Fig. 12 show the benzene formation rate depending on temperature. In both cases, benzene formation rate increases with increasing temperature. When the temperature increases, decomposition rate of acetylene increases and the concentration of the radicalic groups in the reaction media increase. Thus, radicalic groups increase the possibility of formation of new compounds in higher temperature.

Also, in catalyst experiment, rate of the benzene formation is lower than the pyrolysis experiment because some of the carbon source is used for CNT production in catalyst experiment.

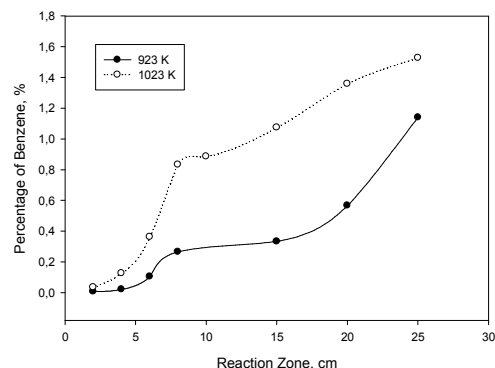


Fig. 12 Difference of benzene percentage along the length of reaction zone in 1.4 g catalyst experiment at 17 % C_2H_2 feedstock

IV. CONCLUSION

Our studies reveal the difference between pyrolysis of acetylene and CNT production using acetylene. Benzene is the main decomposition product and may be responsible for CNT growth. Investigation of gas phase during CNT production is as important as the investigation of solid phase. If we completely understand the gas phase and solid phase, only then we can control the CNT production process in the strict sense.

REFERENCES

- [1] S. Iijima, "Helical microtubules of graphitic carbon", *Nature*, 354; 56-58, 1991.
- [2] D. S. Bethune, C. H. Kiang, M. S. de Vries, G. Gorman, R. Savoy, J. Vazques, R. Beyers, "Cobalt-catalyst growth of carbon nanotubes with single-atomic-layer walls". *Nature*, 363; 605-607, 1993.
- [3] S. J. Lee, H. K. Baik, J. Yoo, J. H. Han, "Large scale synthesis of carbon nanotubes by plasma rotating arc discharge technique". *Diamond and Related Materials*, 11; 914-917, 2002.
- [4] X. Sun, W. Bao, Y. Lv, J. Deng, X. Wang, "Synthesis of high quality single-walled carbon nanotubes by arc discharge method in large scale". *Materials Letter*, 61; 3956-3958, 2007.
- [5] R. E. Smalley, D. T. Colbert, A. Thess, P. Nikolaev, T. Guo, "Catalytic growth of single-walled nanotubes by laser vaporization". *Chemical Physics Letters*, 243; 49-54, 1995.
- [6] M. Zhang, M. Yudasaka, S. Iijima, "Single-wall carbon nanotubes: a high yield of tubes through laser ablation of a crude-tube target". *Chemical Physics Letters*, 336; 196-200, 2001.
- [7] E. Munoz, W. K. Waser, A. M. Benito, G. F. de la Fuente, M. T. Martinez, "Single-walled carbon nanotubes produced by laser ablation under different inert atmospheres". *Synthetic Metals*, 103; 2490-2491, 1999.
- [8] M. J. Yacaman, M. M. Yoshida, L. Rendon, J. G. Santiesteban, "Catalytic growth of carbon microtubules with fullerene structure". *Appl. Phys. Lett.*, 62; 202-204, 1993.
- [9] J. Ting, S. Lin, "Growth and characteristics of carbon nanotubes obtained under different C₂H₂/N₂/NH₃ concentrations". *Carbon*, 45; 1934-1940, 2007.
- [10] M. J. Bronikowski, "Longer nanotubes at lower temperatures: The influence of effective activation energies on carbon nanotube growth by thermal chemical vapor deposition". *J. Phys. Chem. C*, 48; 17705-17712, 2007.
- [11] T. C. Schmitt, A. S. Biris, D. W. Miller, A. R. Biris, D. Lupu S. Trigwell, Z. U. Rahman, "Analysis of effluent gases during the CCVD growth of multi-wall carbon nanotubes from acetylene". *Carbon*, 44; 2032-2038, 2006.
- [12] H. Li, D. He, T. Li, J. Bai, M. Genestoux, "Chemical kinetics of catalytic chemical vapor deposition of an acetylene/xylene mixture for improved carbon nanotube production". *Carbon*, 48; 4330-4342, 2010.
- [13] J. Kong, A. M. Cassell, H. Dai, "Chemical vapor deposition of methane for single-walled carbon nanotubes". *Chemical Physics Letters*, 292; 567-574, 1998.
- [14] Y. Chen, B. Wang, L. Li, Y. Yang, D. Ciuparu, S. Lim, G. L. Haller, L. D. Pfefferle, "Effect of different carbon sources on the growth of single-walled carbon nanotube from MCM-41 containing nickel". *Carbon*, 45; 2217-2228, 2007.
- [15] J. H. Hafner, M. J. Bronikowski, B. R. Azamian, P. Nikolaev, A. G. Rinzler, D. T. Colbert, K. A. Smith, R. E. Smalley, "Catalytic growth of single-wall carbon nanotubes from metal particles". *Chemical Physics Letters*, 296; 195-202, 1998.
- [16] B.K. Singh, H. Ryu, R. C. Chikate, N. D. Hoa, S. J. Park, S. Kim, J. R. Lee, "Growth of multiwalled carbon nanotubes from acetylene over in situ formed Co nanoparticles on MgO support". *Solid State Communications*, 139; 102-107, 2006.
- [17] M. Ritschel, A. Leonhardt, D. Elefant, S. Oswald, B. Büchner, "Rhenium-Catalyzed Growth Carbon Nanotubes" *J. Phys. Chem. C*, 24; 8414-8417, 2007.