

# EFFECT OF H<sub>2</sub> REDUCTION ON CARBON NANOTUBE SYNTHESIS

Nazlı Çınar, Neslihan Yuca, Nilgün Karatepe

Energy Institute, Istanbul Technical University, 34469 Maslak, Istanbul, Turkey  
nazlicinar2004@yahoo.com, nyuca@itu.edu.tr, kmnilgun@itu.edu.tr

**Abstract:** Carbon nanotubes (CNTs) with their high mechanical, electrical, thermal and chemical properties are regarded as promising materials for many different potential applications. Chemical vapor deposition (CVD) is a common method for CNT synthesis especially for mass production. There are important parameters (synthesis temperature, catalyst and calcination conditions, substrate, carbon source, synthesis time, H<sub>2</sub> reduction, etc.) affecting the structure, morphology and the amount of the CNT synthesis. In this study, CNTs were synthesized by CVD of acetylene (C<sub>2</sub>H<sub>2</sub>) on magnesium oxide (MgO) powder substrate impregnated by iron nitrate (Fe(NO<sub>3</sub>)<sub>3</sub>•9H<sub>2</sub>O) solution. The synthesis conditions were as follows: at catalyst calcination temperatures of 400 and 550°C, calcination time of 0, 15 and 30 min, hydrogen concentrations of 0, 5, 10, 20, 50 and 100 % vol, synthesis temperature of 550°C and synthesis time of 30 minutes. The synthesized materials were characterized by thermal gravimetric analysis (TGA), transmission electron microscopy (TEM), and Raman spectroscopy. Effect of H<sub>2</sub> reduction on catalyst calcination and CNT synthesis were investigated.

**Key words:** H<sub>2</sub>, reduction, carbon nanotubes, CVD, synthesis, fluidized bed

## Introduction

Since the carbon nanotubes discovery of by Iijima in 1991 (Iijima,1991), Carbon nanotubes (CNTs) have attracted much attention due to their exceptional electrical, optical and mechanical properties. Therefore, they can be implicated to many fields such as electronics, chemicals, sensors, energy storage, and biotechnology. However, currently major obstacles are present in the application of carbon nanotubes. Specifically, the exact growth mechanism of CNTs and their resulting properties are not yet well understood. Hence, there has been an ongoing effort to understand the growth of CNTs. Various methods were used for carbon nanotubes growth, both single-walled and multi-walled nanotubes (SWNTs and MWNTs), including arc-discharge (ADE) (Maiti et al., 1994), laser beam evaporation (LBE) of graphite (Guo et al., 1996) and chemical vapor deposition (CVD) of carbon through catalytic decomposition of hydrocarbons (Hernadi et al.2000; Trimm,1977) . The catalytic chemical vapor deposition method is a very efficient technique for the large-scale and low-cost synthesis of carbon nanotubes. Recently, several groups have started academic and engineering researches on the CVD in the fluidized bed reactor process (Pérez-Cabero et al., 2003; Corrias et al., 2003; Qian et al., 2004) based on the catalytic decomposition of carbonaceous gases on a catalytic material that contains transition-metal nanoparticles. For large-scale production, the use of a fluidized bed reactor has been proposed as an alternative to avoid obstruction of the carbon deposited and damage to fixed bed reactor walls (Pérez-Cabero et al., 2003). There are different parameters (synthesis temperature, catalyst and calcination conditions, substrate, carbon source, synthesis time, H<sub>2</sub> reduction, etc.) affecting the structure, morphology and the amount of the CNT synthesised. In the growth of CNTs, it is clear that hydrogen is an essential element having been implicated in a number of surface morphology change of the catalyst. The activity of hydrogen with the hydrocarbon gas is also important. During recent decades, many studies have been reported in this subject (Chang Chung et al., 2004; Kim et al., 2006). In a study conducted with the effect of H<sub>2</sub> addition on synthesis yield of CNT was investigated and the relation between the reduction degree and reaction temperature, the ratio of H<sub>2</sub>/CO concentration in the synthesis was observed. It was reported that the high reduction degree of catalyst before synthesis is an essential condition for high yield of CNTs because low reduction degree means the insufficiency of an active catalyst required to make CNTs. Optimum gas flow rate of H<sub>2</sub> on CNT synthesis was determined. Also it was found that when content of H<sub>2</sub> was higher this critical value, the shapes of CNTs became worse due to transition into inactive surface of catalyst (Chang Chung et al., 2004). In another study, the effect of growth temperature on the CNT synthesis was examined with H<sub>2</sub> reduction. It was found that the H<sub>2</sub> reduced the iron oxide to different oxidation states, depending on the time of H<sub>2</sub> introduction. When H<sub>2</sub> was introduced at 200°C, very little growth was achieved. As the H<sub>2</sub> was introduced at 400°C and 600°C, the growth was curbed with very little CNTs resulting on the samples. When H<sub>2</sub> was introduced at 600°C, CNTs were seen only on the edges of the substrate (Kim et al., 2006).

In this study, the effects of H<sub>2</sub> reduction on catalyst calcination and multi-walled carbon nanotubes (MWCNTs) synthesis were investigated. MWCNTs were produced by CVD of (C<sub>2</sub>H<sub>2</sub>) on magnesium oxide (MgO) powder substrate impregnated by iron nitrate (Fe(NO<sub>3</sub>)<sub>3</sub>•9H<sub>2</sub>O) solution. While catalyst calcination and CNTs synthesis, parameters such as calcination temperature and time, H<sub>2</sub>% concentration in catalyst calcination and CNT synthesis were optimized to investigate the effects on the carbon efficiency and quality of CNTs. The synthesized materials were characterized by thermal gravimetric analysis (TGA), transmission electron microscopy (TEM), Raman spectroscopy.

## Experimental Study

### Synthesis of Carbon Nanotubes

Multi-wall carbon nanotubes were synthesized by the fluidized-bed CVD synthesis of acetylene ( $C_2H_2$ ) on a magnesium oxide (MgO) powder impregnated with an iron nitrate ( $Fe(NO_3)_3 \cdot 9H_2O$ ) solution which has MgO to Fe weight ratio of 5%. The system was composed of a "Protherm" furnace that can operate up to 1100°C and a quartz reactor with a diameter of 2.5 cm and length of 94.5 cm. In the middle of the reactor is a nano porous silica disc allowing gas flow. The furnace is placed vertically and the quartz reactor is placed in it with the nano porous silica disc placed in the middle of hot region of the furnace. MWCNT synthesis was held on the 5 to 10 cm length region around the quartz disc of the reactor. To fluidize the bed a certain flow rate of gas was necessary for a given substrate catalyst mixture. For this purpose argon was used as carrier and inert gas and acetylene was used as carbon source. The gas was fed to the system through the bottom of the reactor and it left the system from the top. A magnesium oxide ( $100 \text{ m}^2 \cdot \text{g}^{-1}$ ) supported iron oxide powder produced by impregnation in an iron nitrate ethanol solution is used as precursor powder. To get a precursor with a MgO to Fe weight ratio of 5%, MgO were suspended in ethanol and iron nitrate ( $Fe(NO_3)_3 \cdot 9H_2O$ ) previously dissolved in 100 ml ethanol was stirred together and sonicated for 20 min in order to homogenize the mixture. Afterwards the precursor was dried and grinded into a fine powder. The catalyst and substrate mixture was placed homogeneously on the disc. For MWCNT synthesis while heating the system to calcination temperatures of 400°C and 550°C by an increase of 10°C/min, 100 ml/min argon was fed to the system to maintain inert atmosphere and to make flow of other gases existing in the system. As the temperature reached calcination temperature,  $H_2$  flow started with argon to form reduction on iron oxide catalyst. To investigate the effect of  $H_2$  reduction in calcination, hydrogen concentrations in gas mixture were varied as 0, 5, 10, 20, 50 and 100 % vol. Calcination times were selected as 0, 15 and 30 min. After calcination, the furnace was heated to the synthesis temperature (550 °C). The synthesis was started with the introduction acetylene mixed with argon and different  $H_2$  concentrations (0,5, 20 and 50 % vol) for 30 min. After synthesis, the MWCNTs were cooled in inert gas (argon). The total experimental time varied from 2 to 3 h with duration of actual growth stage 45 min. All experimental conditions were given in Table 1.

Table 1. Calcination and synthesis experimental conditions

Exp. No	Calcination Experiments					Synthesis Experiments			
	Ar flow rate (ml/min)	$H_2$ flow rate (ml/min)	Calcination temp. (°C)	Calcination time (min)	$C_2H_2$ flow rate (ml/min)	Ar flow rate (ml/min)	$H_2$ flow rate (ml/min)	Synthesis time (min)	Synthesis temp. (°C)
1	410	0	400	30	41	369	0	30	550
2	410	0	550	30	41	369	0	30	550
3	0	0	550	0	41	369	0	30	550
4	410	0	550	15	41	369	0	30	550
5	369	41	550	15	41	369	0	30	550
6	328	82	550	15	41	369	0	30	550
7	205	205	550	15	41	369	0	30	550
8	0	410	550	15	41	369	0	30	550
9	369	41	550	30	41	369	0	30	550
10	328	82	550	30	41	369	0	30	550
11	205	205	550	30	41	369	0	30	550
12	0	410	550	30	41	369	0	30	550
13	369	41	400	15	41	369	0	30	550
14	328	82	400	15	41	369	0	30	550
15	205	205	400	15	41	369	0	30	550
16	0	410	400	15	41	369	0	30	550
17	369	41	400	15	41	369	0	30	550
18	328	82	400	15	41	369	0	30	550
19	205	205	400	15	41	369	0	30	550
20	0	410	400	15	41	369	0	30	550
21	0	410	550	30	41	348,5	20,5	30	550
22	0	410	550	30	41	287	82	30	550
23	0	410	550	30	41	164	205	30	550
24	0	0	550	30	41	348,5	20,5	30	550
25	0	0	550	30	41	287	82	30	550
26	0	0	550	30	41	164	205	30	550

### Characterization of Materials

The synthesized MWCNTs were characterized by transmission electron microscopy (TEM) -FEI-Tecnai-G2 F-20 instrument, raman spectroscopy-Horiba Jobin-YVON HR 800UV instrument and thermogravimetric analyzer (TGA)-TA-Q600 SDT instrument.

## Results and Discussion

### Structure Characterization of Multi Wall Carbon Nanotube

By the synthesis temperature of 550°C at a fixed iron content of 5%, a synthesis time of 30 min. and acetylene as carbon source the yield was obtained in multi-wall nanotube type. TEM image of this yield was given in Fig. 1. It has obviously been seen from Fig. 1 that the diameter of the CNTs is 10 nm and their appearance is darker in the picture. One possible explanation for the dark parts is a result of the impurities within the structure. This observation lead to a conclusion: in the temperature of 550°C MWNTs were grown.



Fig.1. TEM images of MWNTs

Raman spectroscopy is a powerful technique for the characterization of the structure of carbon nanotubes. Fig. 2 shows Raman spectrum for carbon deposits excited by 633 nm laser. As seen from Fig. 2, the spectrum in RBM band which is a characteristic of SWNT was also observed in the sample. The reason of this spectrum which was observed at MWCNT is that the innermost tube diameter was below 2 nm.

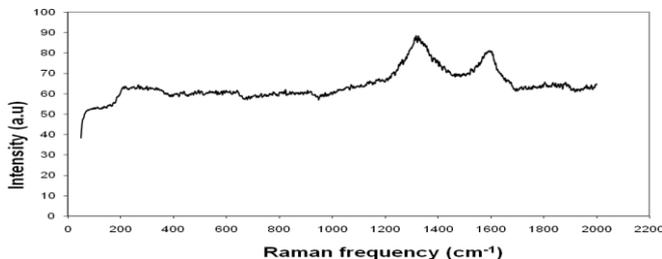


Fig. 2. Raman spectra of MWNT

### Effect of Hydrogen Reduction

The effects of H<sub>2</sub> reduction were investigated into two parts: catalyst calcination and MWCNT synthesis. The carbon efficiency of the synthesized MWCNTs was calculated according to TGA measurement. In order to eliminate any differences which may be caused due to moisture content of synthesized samples, in the calculations the initial temperature was selected as 200°C to have the dry weight percent and the final temperature was taken as 800°C to have the same temperature value for all samples. The formula of carbon efficiency is:

$$\text{Carbon efficiency (\%)} = \frac{\text{Weight\%}(200^\circ\text{C}) - \text{Weight\%}(800^\circ\text{C})}{\text{Weight\%}(200^\circ\text{C})} \times 100 \quad (1)$$

Thermogravimetric (TG) analysis is used to characterize the total carbon loading and determine the residual metallic catalyst. The amorphous carbon is completely oxidized at temperatures below 350 °C and graphite burns above 750 °C. The oxidation temperatures of the CNTs depend on the nanotube type and MWCNTs is generally oxidized at the temperatures above 400 °C. In this study, the TG analysis of MWNTs was conducted in air atmosphere with a ramp of 10 °C/min between 200 and 800°C. Carbon efficiency (%) of the MWCNTs were obtained from TG analysis. TGA results were given in the Table 2.

Table 2. TGA results of MWCNTs

Exper. No	Calcination Temp. (°C)	Calcination Time (min)	H <sub>2</sub> % in calcination	H <sub>2</sub> % in synthesis	Carbon Efficiency %
1	400	30	0	0	42
2	550	30	0	0	45
3	550	0	0	0	49
4	550	15	0	0	44
5	550	15	10	0	23
6	550	15	20	0	35
7	550	15	50	0	41
8	550	15	100	0	39
9	550	30	10	0	32
10	550	30	20	0	37
11	550	30	50	0	38
12	550	30	100	0	53
13	400	15	10	0	40
14	400	15	20	0	44
15	400	15	50	0	41
16	400	15	100	0	43

17	400	30	10	0	40
18	400	30	20	0	46
19	400	30	50	0	49
20	400	30	100	0	42
21	550	30	100	5	58
22	550	30	100	20	59
23	550	30	100	50	55
24	550	0	0	5	54
25	550	0	0	20	57
26	550	0	0	50	64

**Effect of H<sub>2</sub> Reduction on Catalyst Calcination**

*Calcination Temperature*

The effect of calcination temperature on carbon efficiency was examined for 100 % H<sub>2</sub> and two calcination times (15, 30 min). The selected calcination temperatures were 400 and 550°C. Carbon efficiency (%) of these synthesized materials from TG analysis are shown in Fig. 3. It is seen that there is a tremendous increase in carbon efficiency (from 42% to 53%) of 30 min calcination time whereas there exists a slightly decrease in carbon efficiency of 15 min calcination time (from 43% to 39%). With this result it can be said that with the increase in calcination time there becomes an increase in the carbon efficiency. In summary the order of the carbon efficiency of given temperature of 400°C for 100% H<sub>2</sub> concentration is 30 min > 15 min, whereas for 550°C it is 30 min > 15 min.

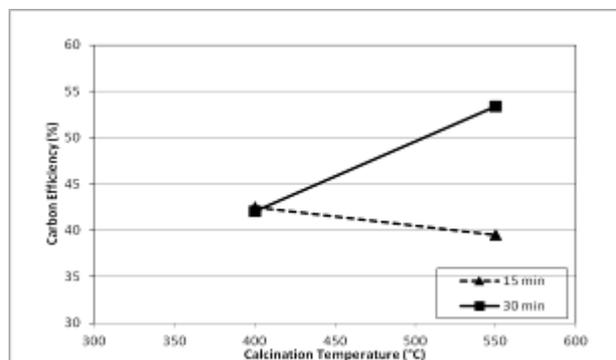


Fig. 3. Calcination temperature vs. carbon efficiency for 100 % H<sub>2</sub>

*Calcination Time*

The effect of calcination time on carbon efficiency was examined for 100 % H<sub>2</sub> and two calcination temperatures (400°C, 550°C). The calcination times were selected 15 and 30 min. Carbon efficiency (%) of these synthesized materials from TG analysis are shown in Fig. 4. It is seen that there is a tremendous increase in carbon efficiency (from 39% to 53%) of 550°C calcination temperature whereas there exists a decrease in carbon efficiency of 400°C calcination temperature (from 43% to 42%). With this result it can be said that with the increase in calcination temperature there becomes an increase in the carbon efficiency. In summary the order of the carbon efficiency of given time of 30 min for 100% H<sub>2</sub> is 550°C > 400°C, whereas for 15 min it is 400°C > 550°C.

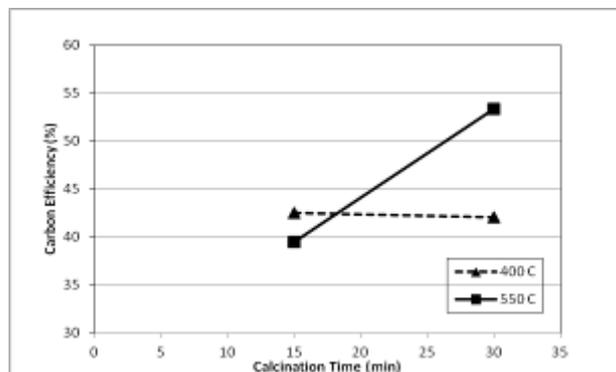


Fig. 4. Calcination time vs. carbon efficiency for 100 % H<sub>2</sub>

*H<sub>2</sub> Concentration (%) in Calcination*

The effect of H<sub>2</sub> concentration on carbon efficiency was examined for calcination time of 30 min and calcination temperatures of 400 and 550°C. The H<sub>2</sub> concentrations were selected as 10, 20, 50 and 100 % vol. Carbon efficiency of these synthesized

materials from TG analysis are shown in Fig. 5. It is seen that there is a tremendous increase in carbon efficiency (from 32% to 53%) at 550°C whereas there exists an increase in carbon efficiency at 400°C (from 40% to 42%). With this result it can be said that with the increase in H<sub>2</sub> concentration % there becomes an regular increase in the carbon efficiency for 550°C of calcination temperature. Besides this for 400°C calcinations temperature , carbon efficiency increased between 10% and 50% H<sub>2</sub> concentration , then a decrease was found between 50% and 100% H<sub>2</sub> concentration. Depending on these results, it was examined that the highest carbon efficiency % was obtained with 100% H<sub>2</sub> concentration, 30 min calcination time at 550°C calcination temperature.

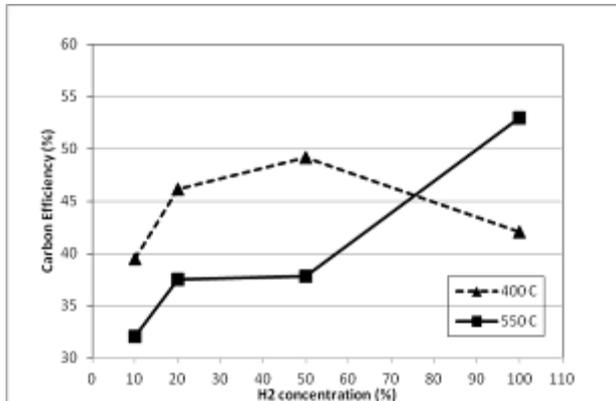


Fig. 5. H<sub>2</sub> concentration vs. carbon efficiency

### Effect of H<sub>2</sub> Reduction on CNT Synthesis

According to the TGA results of experiments which were carried out without H<sub>2</sub> reduction (0%) in CNT synthesis, the highest carbon efficiency values were obtained as 49% and 53% at 550°C calcination temperature for 0% and 100% H<sub>2</sub> calcination, respectively (Table 2). To examine the effect of H<sub>2</sub> reduction in CNT synthesis, H<sub>2</sub> was added into synthesis gas with three different concentrations of 5, 20 and 50% vol for 0 and 100% H<sub>2</sub> calcination. Carbon efficiency (%) of these synthesized materials from TG analysis are shown in Fig.6. According to the H<sub>2</sub> concentrations of 5, 20 and 50% vol in the CNT synthesis for 0% H<sub>2</sub> calcination there is a regular increase (from 49 % to 64 %) in carbon efficiency. Also TG analysis showed that for 100% H<sub>2</sub> calcination, there is an increase (from 58% to 59%), then a decrease (from 59% to 55%) in carbon efficiency. As a result of these values, it was found that H<sub>2</sub> concentration (%) in the CNT synthesis is important for increasing of carbon efficiency and this results are consistent with other studies found in literature (Uoo-Chang Chung et al., 2004). In the study of Uoo-Chang Chung et al., they investigated the shapes and structures of CNTs with H<sub>2</sub> addition in CO using a cheap iron oxide catalyst for CNTs synthesis. They found that the synthesized carbon weight increased with H<sub>2</sub> addition, and the value showed maximum in the H<sub>2</sub> gas with a flow rate of 0.7 L/min at 680°C with CO gas of 0,3 L/min. When H<sub>2</sub> value was higher than 0.7 L/min, carbon weight decreased as H<sub>2</sub> contents increase. Also it was found that when content of H<sub>2</sub> was higher than this critical value (0.7 L/min), the shapes of CNTs became worse due to transition into inactive surface of catalyst. It was also found that H<sub>2</sub> addition had an influence considerably on the shape and structure of CNTs.

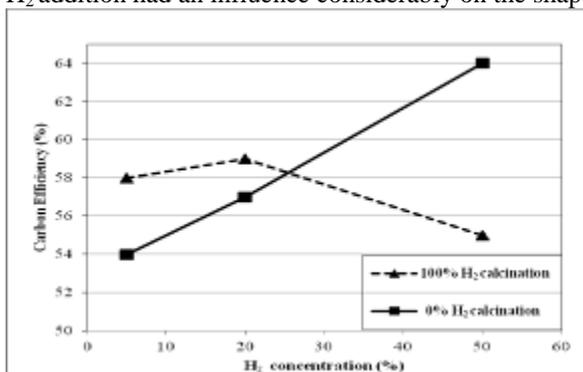


Fig. 6. H<sub>2</sub> concentration vs. carbon efficiency

### Conclusions

The present study has shown that calcination temperature, calcination time and H<sub>2</sub> concentration (%) are important parameters in catalyst calcination and MWCNT synthesis. As a result of TGA measurements, at highest calcination temperature (550°C), carbon efficiency (%) was increased with calcination time (15, 30 min) and H<sub>2</sub> concentrations (10, 20, 50, 100%). In addition to these results, with increase in H<sub>2</sub> concentration (5, 20, 50%) in synthesis gas, higher carbon efficiencies were obtained. Experimental evidences and measurements showed that the carbon efficiencies of synthesized MWCNTs are positively affected with increase the calcination temperature, calcination time and H<sub>2</sub> concentration (%) in CNT synthesis.

## References

- Chang Chung, Uoo.(2004). Effect of H<sub>2</sub> on formation behavior of carbon nanotubes. *Bull. Korean Chem. Soc*,25,1521-1524
- Corrias,M.,Caussat,B.,Ayrat,A.,Durand,J.Kihn,Y.,Kalck,Ph.,Serp,Ph.(2003).Carbon nanotubes produced by fluidized bed catalytic CVD: first approach of the process. *Chem. Eng. Sci*,58,4475–4482.
- Guo,T., Nikolaev,T.P.,Thess,A.(1996). *Chem.Phys.Lett*,260,471.
- Hernadi,K, Fonseca,A., Nagy,J.B.,Siska,A., Kiricsi,I.(2000). *Appl.Catal.A*,199,245.
- Iijima, S.(1991).Helical microtubules of graphitic carbon. *Nature*, 354,56-58
- Kim, Jin Suk Calvin.(2006).The role of hydrogen in the growth of carbon nanotubes: a study of the catalyst state and morphology, Massachusetts Institute of Technology,B.Sc.Thesis.
- Maiti,A.,Brabec,C.J.,Rol,C.M.,Bernhole,J.(1994). *Phys.Rev.Lett*,73,2468.
- Pérez-Cabero,M.,Rodríguez-Ramos, I., Guerrero-Ruiz,A.(2003).Characterization of carbon nanotubes and carbon nanofibers prepared by catalytic decomposition of acetylene in a fluidized bed reactor. *J. Catal*, 215,305-316.
- Piao,Lingyu.,Li,Yongdan.,Chen,Jiuling.,Chang,Liu.,Lin,Jerry.Y.S.(2002).Methane decomposition to carbon nanotubes and hydrogen on an alumina supported nickel aerogel catalyst, *Catalysis Today*,74,145-155.
- Qian ,W., Liu,T.,Wang,Z.,Wei,F.,Li,Z.,Luo,G.,Li,Y.(2004).Production of hydrogen and carbon nanotubes from methane decomposition in a two-stage fluidized bed reactor. *Appl. Catal. A*,260,223-228.
- Trimm, D.L.(1977). *Catal. Rev Sci. Eng*,16,155.
- Uoo-Chang C. (2004). Effect of H<sub>2</sub> on Formation Behavior of Carbon Nanotubes. *Bull. Korean Chem. Soc.*;25,10:1521