A PARAMETRIC STUDY ON THE GROWTH OF SINGLE-WALLED CARBON NANOTUBES OVER CO-MO/MGO NANOCATALYST IN A FLUIDIZED BED REACTOR BY CCVD METHOD

Alimorad Rashidi*, Ehsaneh Fakhrmusavi, Roghayeh Lotfi, Mahmood Fatemi, Masoud Zare, and Maryam Rashtchi

Nanotechnology Research Center, Research Institute of Petroleum Industry (RIPI), Tehran, Iran

ABSTRACT

Single-walled carbon nanotubes (SWNTs) with high yield and quality were synthesized using chemical vapor deposition (CVD) over Co-Mo/ MgO nanocatalyst in a fluidized bed reactor. Different parameters such as temperature, the ratio of hydrocarbon source to hydrogen, the flow rate of gas, growth time, the size of catalyst particles, heating rate, and the kind of hydrocarbon source were examined to assess their effects on the SWNT synthesis. The influence of these parameters on the carbon nanotubes yield and quality is also reported. Single-walled carbon nanotubes were characterized by using different characterization techniques including thermo-gravimetric analysis (TGA), scanning electron microscopy (SEM), tunneling electron microscopy (TEM), Raman spectroscopy, and X-ray diffraction (XRD). Under the optimum operation conditions (900 °C, 30 min, rate of gas=1800 ml/min, heating rate of 7 °C/min, size of catalyst particle=212 μm, volumetric ratio of hydrocarbon source to hydrogen=1:1), single-walled carbon nanotubes with an average diameter of 0.9 nm and a yield of 300% (related to the catalyst) were produced.

Keywords: Chemical Vapor Deposition, SWNT, Electron Microscopy, Raman Spectroscopy, Thermo-gravimetric Analysis

INTRODUCTION

Carbon nanotubes have superior properties which can influence many different branches of science. The multi-walled carbon nanotubes (MWNT's) were first produced by Ijima in 1991 by the use of arc discharge method [1], while the single-walled carbon nanotubes were discovered in 1993 [2,3]. These materials have a variety of applications such as catalyst supports, adsorbents, microelectronic devices, filters, membranes, sensors, etc. [4].

Generally carbon nanotubes can be produced by the use of three different methods, including arc discharge method, laser ablation, and chemical vapor deposition (CVD) [4-9]. Among these methods, CVD is the best method for the large-scale production of CNT's, since it has the lower cost, higher efficiency, and also needs lower temperatures [10-15].

Use of fluidized bed reactors in the CVD method has the advantage of providing enough space for the growth of nanotubes as well as more efficient heat and mass transfer due to the

***Corresponding author**
Alimorad Rashidi
Email: rashidiam@ripi.ir
Tel: +98 21 4825 2323
Fax:+98 21 4825 7676

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uniform distribution of temperature and concentration. Furthermore, the residence times of the carbon nanotubes can be controlled more accurately in a fluidized bed reactor. Qian evaluated the production of carbon nanotubes by the use of Fe/Al_2O_3 catalyst in both fixed and fluidized bed reactors and reported that the latter is prior to the former [16]. Moreover, Hsieh et al. studied the synthesis of multi-walled carbon nanotubes by the catalytic dissociation of acetylene over the catalyst of Fe-Ni/ Al_2O_3 in the temperature range of 700-850 °C in a fluidized bed reactor and mentioned that, compared with CNT's grown in a fixed bed reactor, the CNT's grown in a fluidized bed reactor showed higher purity [17].

To examine the effect of different parameters on the growth of carbon nanotubes, it is necessary to perform a parametric study. Although some parametric studies on CNT's have been done previously [18-22], to the authors' knowledge, such a study has not yet been performed for the same system used in this work.

In the present study, Co-Mo/MgO nanocatalyst has been selected as the catalyst for carbon nanotube growth, because the MgO support can be eliminated easier than other supports such as alumina and silica [23]. In reality, one stage acid washing can eliminate MgO support completely, which leads to the reduction of purification costs.

In this work, the dissociation of methane and natural gas over Co-Mo/MgO nanocatalyst in a fluidized bed reactor was studied. The influences of different parameters such as temperature, hydrocarbon source to diluting gas ratio, gas flow rate, growth time, size of catalyst particles, heating rate, and type of inlet gas on the quality and yield of single-walled carbon nanotubes were investigated to find the optimum values of these parameters.

EXPERIMENTALS

The experimental set up for carbon nanotube growth is presented in Figure 1. The reactor is made of quartz with an inner diameter of 20 mm and a height of 1,400 mm. A porous quartz disc is used to distribute the gas and hold the catalyst particles. The flow rates of the different gases are regulated by mass flow meters. The gas enters the reactor after passing through the preheating section. The reactor is placed in a programmable vertical furnace.

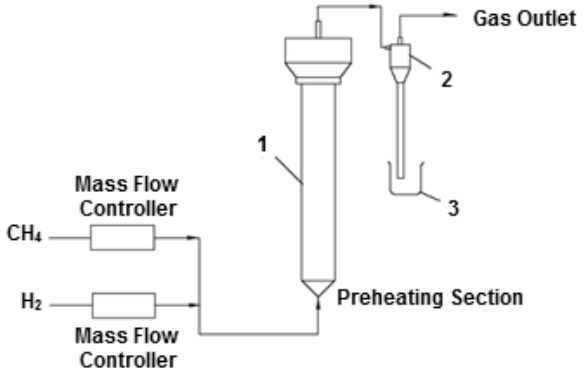

Figure 1: A schematic of the experimental setup; (1) fluidized bed reactor, (2) cyclone, and (3) product container.

As it was mentioned previously, in the present study, Co-Mo/MgO combination was used as the catalyst. This nanocatalyst was prepared by using our special sol-gel method [23]. To prevent the erosion of the catalysts inside the fluidized bed reactor, they were shaped in the form of spherical beads. After catalyst loading stage, they were reduced by the use of a mixture of hydrogen and nitrogen flow. When the reduction treatment was completed and the reactor temperature reached the desired operating temperature, the hydrogen flow was switched off and methane or natural gas with a diluter was introduced into the reactor. The reaction was taken place and the products exited from the cyclone continuously. At the end of the reaction, the methane or natural gas flow was switched off. The final product was washed with dense chloridric acid and, after filtration and

centrifuge, was dried in an oven at 120 °C. As-synthesized products were analyzed using thermogravimetric analysis (TGA), scanning electron microscopy (SEM), Raman spectroscopy and X-ray diffraction (XRD).

RESULTS AND DISCUSSION

Single-walled carbon nanotubes were prepared by the chemical vapor deposition of hydrocarbons on Co-Mo/MgO nanocatalyst in a fluidized bed reactor. At first, cold test was performed to determine the fluidization parameters of the catalyst. Then, the effects of various parameters such as temperature, growth time, heating rate, gas flow rate, type of gas, the ratio of hydrocarbon source to hydrogen, and size of catalyst particles were examined on the yield and quality of the produced nanotubes. The method requires the definition of the lower and higher bounds of parameters which can be based on the experience. Table 1 shows the bounds of the parameters used in this work. In order to understand the role of different parameters in the carbon nanotube growth, the experiments are designed using Plackett-Burman design. Table 2 shows the design matrix used in the present work.

Table 1: Examined parameters and their ranges

Parameter	Low limit	High limit
Temperature (°C)	900	1000
Gas flow rate (ml/min)	1800	3600
Heating rate (°C/min)	7	10
CH_4/H_2	1/4	1/1
Catalyst bulk size (mesh)	70	200
Reaction time (min)	30	60
Gas type	Natural gas	Methane

XRD analysis is important to quantify the as-synthesized CNT's and it was performed on all of the samples mentioned in Table 2. Typically carbon nanotube peaks appear in 2θ=25-26° and 2θ=43° [24]. The result for the optimum sample is shown in Figure 2.

Table 2: Plackett-Burman design matrix

Run	Temperature (°C)	Gas flow rate (ml/min)	Heating rate (°C/min)	Ratio of carbon source to carrier gas	Particle size of catalysts (mm)	Reaction time (min)	Type of carbon source
1	1000	1800	7	1:1	0.212	30	Methane
2	900	1800	10	1:1	0.212	60	Natural gas
3	1000	3600	7	1:4	0.212	60	Natural gas
4	1000	1800	10	1:1	0.075	30	Natural gas
5	900	3600	10	1:1	0.212	60	Methane
6	1000	3600	7	1:1	0.075	60	Natural gas
7	1000	1800	10	1:4	0.075	60	Methane
8	1000	3600	10	1:4	0.212	30	Methane
9	900	3600	10	1:4	0.075	30	Natural gas
10	900	3600	7	1:1	0.075	30	Methane
11	900	1800	7	1:4	0.075	60	Methane
12	900	1800	7	1:4	0.212	30	Natural gas

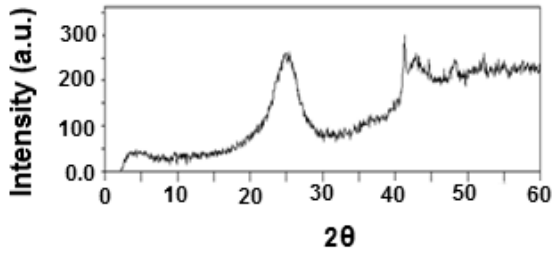

Figure 2: XRD patterns of the sample grown in the fluidized bed reactor under the optimum conditions

Furthermore, the Raman spectra are employed for understanding the quality and diameter distribution of carbon nanotubes. Figure 3 represents the Raman spectra results for the samples. It should be noted that the D band at 1344 cm^{-1} is attributed to the amorphous carbon or deformation vibrations of a hexagonal ring, while the G band at 1590 cm^{-1} wave length is assigned to a single crystallite of graphite. The G* band appears at 2670 cm^{-1} and shows the ordered graphite structures [25]. The ratio of G band intensity to D band intensity (I_G/I_D) indicates the quality of products. The higher the ratio is, the higher the quality of products become. This ratio is calculated for various samples in all the experiments and the results are shown in Table 3. As it can be seen, the first experiment has the highest quality.

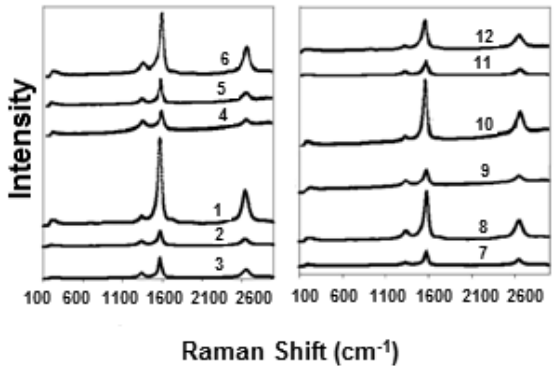

Figure 3: Raman spectra of carbon nanotubes grown under different conditions

In addition to CNT quality, Raman analysis can help to estimate the diameter of nanotubes. The Raman spectra in lower intensities (RBM) of the optimum sample are shown in Figure 4. The estimates of the tube diameters can be made according to ωRBM = 234/*dt* + 12.5 where *dt* is the nanotube diameter (nm) and ωRBM stands for the RBM frequency (cm^{-1}) [26]. The nanotube diameters are reported in Table 3 for all of the experiments.

Table 3: Result of Raman spectra for the SWNT's samples

Run	I_G/I_D	SWNT Diameter (nm)
1	9.75	0.92
2	3	0.95
3	3.5	0.93
4	1.6	0.94
5	3.4	0.98
6	5.0	0.94
7	3.8	1.04
8	5.1	0.99
9	2.0	0.94
10	7.0	0.93
11	3.5	0.98
12	4.7	0.99

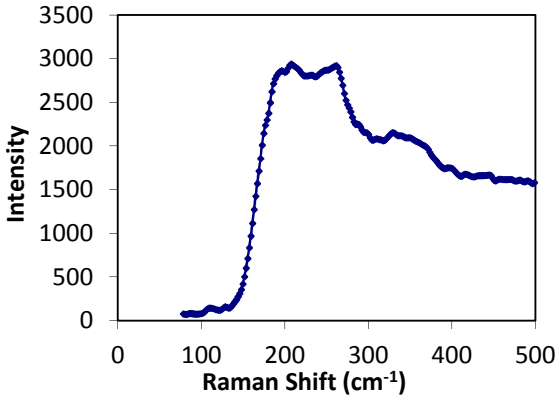

Figure 4: Raman spectra of carbon nanotubes grown under optimum conditions for Raman shifts below 500 cm^{-1}

As it is obvious from the results, the diameter of single-walled carbon nanotubes in different tests does not change greatly. Therefore, it can be concluded that the selected parameters in the mentioned range have no significant effect on the diameter of CNT's. In fact the major factors controlling diameters can be related to the catalyst synthesis parameters and thermal conditions of reduction.

To determine the purity of products, TGA analysis was used. The samples were heated in

the oxygen atmosphere up to 800 °C. Amorphous carbons disappeared at 450 °C. Also, the temperature of SWNT's removal was in the range of 500-600 °C, while MWNT's disappeared at about 700 °C. Thus the percentage of different carbon materials can be obtained to determine the purity of CNT's in various experiments. As it is shown in Figure 5, under the optimum conditions, the amount of SWNT and amorphous carbon in the product are respectively 91 and 8.2 percent; this was obtained from the related temperatures in the TGA analysis. The remaining part includes the metallic impurities.

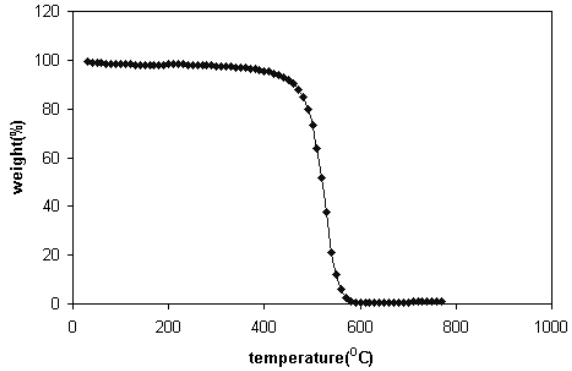

Figure 5: TGA analysis graph for the best SWNT's sample

The yield of carbon nanotube growth can be calculated through the following formula:

$$yield = \frac{W_{Cat\ and\ CNT} - W_{Cat}}{W_{Cat}} \quad (1)$$

where, $W_{Cat\ and\ CNT}$ is the total weight of catalyst and CNT and W_{Cat} represents the weight of catalyst. The optimum case had a yield of 300%.

Figure 6 shows the SEM image of the best sample without removal of the catalyst. As it can be seen high quality CNT's are grown over the nanocatalyst.

To determine the diameter and the type of carbon nanotubes, TEM analysis was used. Figure 7 shows the TEM of the optimum sample; it is obvious that CNT's are single-walled. Furthermore, it can be deduced that CNT's are grown in the form of single tubes or bundle of tubes. The TEM results reported that the outer diameter of CNT's was 3 nm, while the inner one was 1 nm, which was consistent with the Raman results (Figure 3).

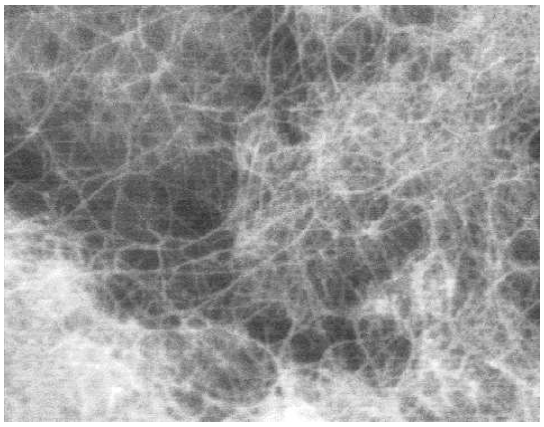

Figure 6: SEM photograph of the best SWNT's sample

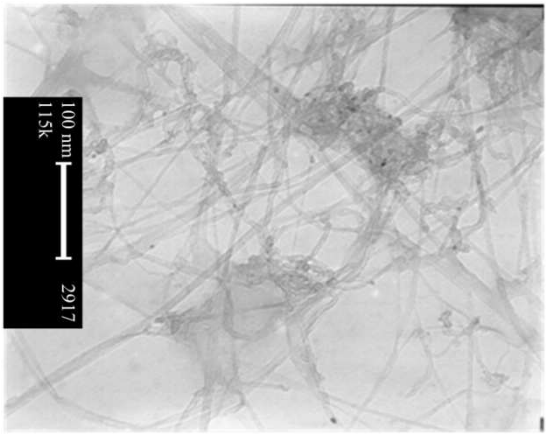

Figure 7: TEM photograph of the best SWNT's sample

Finally, according to all of the analyses used herein, the following results can be concluded:

1- The temperature was assessed in the range of 900-1000 °C and it was inferred that, since at higher temperatures the crystalline structure was formed better and also the probability of defect formation was reduced, the produced CNT's had higher quality and yield;

2- The gas flow rate was tested in the range of 1800-3600 ml/min according to the need for the minimum flow rate conserving the fluidity characteristics. At lower flow rates

the results were more acceptable because of increased growth time and the existence of enough time for the growth of carbon nanotubes;

3- Two hydrocarbon resources, namely methane and natural gas, were tested. Methane gas showed better results because of higher purity;

4- Heating rate was evaluated in the interval of 7-10 °C/min. Lower rates were preferred because of providing more time for catalyst reduction;

5- Reaction time was tested for 30 to 60 minutes and shorter times showed better performance, since it reduced the amount of coke and increased the quality of the product;

6- Catalyst mesh was in the range of 75-212 micrometer. Larger catalyst grains had better performance because of better fluidity and control of growth time;

7- The ratio of hydrocarbon to hydrogen was selected in the range of 1:1 to 1:4 and the 1:1 ratio led to better products.

The optimized parameters for SWNT's nanotube growth were a temperature of 1000 °C, a growth time of 30 minutes, a gas flow rate of 1800 ml/min, methane gas as the source, a heating rate of 7 °C/min, a catalyst particle size of 212 micrometer, and the ratio of hydrocarbon source to hydrogen equal to 1.

CONCLUSIONS

The role of different parameters on the quality and yield of products were evaluated and the optimum value of each parameter was reported. The parameters included temperature, ratio of hydrocarbon source to hydrogen, flow rate of gas, growth time, the size of catalyst particles, heating rate, and the kind of hydrocarbon source. The experiments were carried out according to Plackett-Burman experimental design and the optimum values of the parameters were reported based on the various analyses conducted on the samples. Moreover, it was deduced that the mentioned parameters had no significant effect on the diameter of CNT's.

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