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Effect of Synthesis Condition on the Growth of SWCNTs via Catalytic Chemical Vapour Deposition

(Kesan Keadaan Sintesis untuk Tumbesaran Tiub Nanokarbon Dinding Tunggal Melalui Pemendapan Wap Kimia Bermangkin)

SETAREH MONSHI TOUSSI, A. FAKHRU'L-RAZI*,
A. LUQMAN CHUAH & A.R. SURAYA

ABSTRACT

Single-walled carbon nanotubes (SWCNTs) were synthesized by catalytic chemical vapor deposition (CCVD) of ethanol (C_2H_5OH) over Fe-Mo-MgO catalyst by using argon as a carrier gas. The reaction conditions are important factors that influence the yield and quality of carbon nanotubes. The effects of temperature and flow rate of carrier gas were investigated to increase the yield of carbon nanotubes. The synthesized carbon nanotubes were characterized by scanning electron microscopy, transmission electron microscopy, X-Ray diffraction and thermo-gravimetric analysis. The results showed that the growth of carbon nanotubes was effectively influenced by the reaction ambience and the synthesis condition. The temperature and flow rate of carrier gas played a key role in the yield and quality of synthesized CNTs. The estimated yield of synthesized carbon nanotubes was almost over 70%.

Keywords: Carbon nanotubes (CNTs); catalytic chemical vapor deposition (CCVD); Fe-Mo-MgO catalyst; synthesis; yield

ABSTRAK

Tiub nanokarbon dinding tunggal (SWCNTs) telah disintesis melalui pemendapan wap kimia bermangkin etanol (C_2H_5OH) di atas pemangkin Fe-Mo-MgO menggunakan argon sebagai gas pembawa. Keadaan tindak balas adalah faktor penting yang mempengaruhi hasil dan kualiti tiub nanokarbon. Kesan suhu dan kadar aliran gas pembawa telah dikaji untuk meningkatkan hasil tiub nanokarbon. Tiub nanokarbon yang disintesis telah dicirikan melalui mikroskop elektron imbasan, mikroskop elektron transmisi, pembelauan sinar-X dan analisis termo-gravimetrik. Keputusan menunjukkan bahawa pertumbuhan tiub nanokarbon dipengaruhi oleh ambien tindak balas dan keadaan sintesis. Suhu dan kadar aliran gas pembawa memainkan peranan utama dalam hasil dan kualiti tiub nanokarbon yang disintesis. Anggaran hasil tiub nanokarbon yang disintesis hampir melebihi 70%.

Kata kunci: Endapan wap kimia bermangkin (CCVD); hasil; mangkin Fe-Mo-MgO; sintesis; tiub nanokarbon (CNTs)

INTRODUCTION

After the discovery of carbon nanotubes (CNTs) in 1991 (Iijima 1991), this new nanostructure material has received a great deal of attention because of its remarkable properties (Thess et al. 1996) and applications in various fields of materials research (Iijima & Ichihashi 1993). Due to its many unique properties, the synthesis of SWCNTs has become a significant subject of global research.

The discovery of CNTs via the arc-discharge method with low yield and a high-graphitic content made the production costs very high (Iijima 1991). For large-scale synthesis of CNTs, the decomposition of carbon containing material in the presence of catalysts seems to be more suitable (Li et al. 2004). Nowadays the catalytic chemical vapor deposition (CCVD) method appears to be a promising technique since it has the potential for a large-scale synthesis of high-quality single-walled carbon nanotubes (SWCNTs) at relatively low cost (Liu & Fang 2006).

It has been found that transition metals such as iron, cobalt and nickel are active catalysts for the growth of CNTs. The use of Fe, Co, and Ni with elements such as molybdenum and tungsten has led to an increase in the yield of CNTs under certain conditions (Landois et al. 2009; Mann 2006). It is believed that Mo not only improves catalyst activity and lifetime, but also decreases the activation energy for decomposition of the carbon source. Thus Mo is sometimes added as a promoter for the formation of CNTs (Pigos et al. 2006; Su et al. 2000).

The catalysts are generally supported on inorganic materials such as Al_2O_3 (Lamouroux et al. 2007), SiO_2 (Thiruvengadachari & Ajmera 2007), zeolite (Hernadi et al. 1996) and MgO (Tsoufis et al. 2007). Among these support materials much attention has been paid to MgO because it can be easily removed by acid treatment (Kang et al. 2008), while zeolite and Al_2O_3 supports require a harsh hydrofluoric treatment (Liu et al. 2004).

The use of ethanol (C_2H_5OH) as the carbon source in the CVD method exhibits positive effects, like lower reaction temperature, high purity of the products and the possibility of large-scale production at lower costs (Liu & Fang 2006; Maruyama et al. 2002). With Fe-Mo-MgO catalyst, most researchers have used methane and acetylene as the carbon source.

Experiment

For the preparation of Fe-Mo-MgO catalyst, the right amount of iron nitrate ($Fe(NO_3)_3 \cdot 9H_2O$), ammonium molybdate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$), magnesium nitrate ($Mg(NO_3)_2 \cdot 6H_2O$), and citric acid with Fe: Mo: MgO = 0.7: 0.1: 10 molar ratio were dissolved in a minimum amount of distilled water. After mixing, the solution was sonicated at room temperature to obtain homogeneous impregnation of salts in support. After one hour in sonication, it was heated until 150°C with stirring and then dried at 200°C for 24 h in an oven. Then the obtained material was ground in mortar to break the chunks into powder (Niu & Fang 2006; Ouyang et al. 2008).

The growth of CNTs was obtained by catalytic chemical vapor deposition (CCVD) by ethanol (C_2H_5OH) with Fe-Mo-MgO as catalyst. The CVD reactor consisted of a horizontal alumina ceramic tube (100 cm long, 4 cm in diameter) placed in a cylindrical furnace 80 cm long. A Pyrex flask containing the source of carbon is connected to the tube. About 200 mg of the catalyst powder was dispersed on alumina boat which was placed in the middle of the ceramic tube. The reactor was purged with Ar until the reactor reached 750°C. Argon gas was switched to ethanol vapour when the temperature stabilized. The flow of ethanol vapour was maintained for 30 min. The reactor was cooled down in argon flow to room temperature after reaction.

Different temperatures and argon flow rates were used in order to obtain optimized growth condition catalyzed by Fe-Mo-MgO.

The carbon deposits (CD) for each experiment was calculated by the following formula:

$$CD\% = \left[\frac{m_{ar} - m_b}{m_{br}}\right] \times 100, \quad (1)$$

where m_{ar} is the sample mass after reaction (catalyst + carbon deposited), m_{br} is the initial weight of catalyst before the reaction, and m_b is the catalyst mass after the blank experiment (Biris et al. 2008; Méhn et al. 2004). It can be assumed that the carbon nanotube yield is closely related to the carbon deposits yield (Ago et al. 2006).

The synthesized CNTs were characterized by Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), X-Ray diffraction method (XRD) and Thermo-Gravimetric Analysis (TGA).

Results and Discussion

SWCNTs were catalytically synthesized from the decomposition of ethanol (C_2H_5OH) on a bi-metallic catalyst system Fe-Mo supported on MgO.

Three flow rates of carrier gas (Ar = 50, 100 and 150 mL/min) were chosen in this part of the experiment. The purpose was to find a better flow rate in order to obtain better yields of CNTs. For this set of experiment, the temperature of 800°C was employed.

Based on the results of the experiment (Figure 1), for 50 mL/min flow rate of Ar, very little CNTs was formed, because the low flow rate of Ar could not carry enough ethanol vapors through the reactor to be deposited on the catalysts. It was found that the best flow rate for carrier gas is 100 mL/min because with this flow rate, Ar can carry enough carbon sources (ethanol) into the reactor. Besides, with this rate, the carbon source has enough time for decomposition and deposition on the catalysts. With the high flow rate of Ar (150 mL/min), most of the carbon source was carried out through the outlet of the reactor, and again it could not be deposited on the catalyst, thus a little carbon nanotubes was formed.

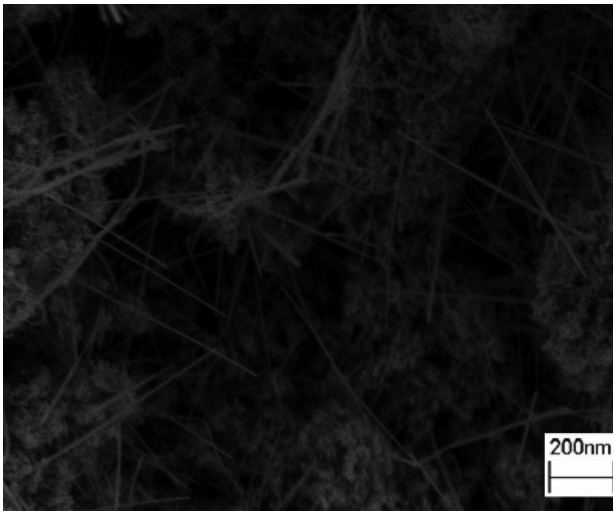

FIGURE 1. SEM image of CNTs at 100 mL/min flow of Ar as carrier gas

In the previous part of experiment, it was found that the best flow rate for carrier gas (Ar) was 100 mL /min. Since the yield of CNTs for low flow rate (50 mL / min) and high flow rate (150 mL /min) of carrier gas (Ar) was very little, the 100 mL/ min flow rate of Ar was chosen for the this part of experiment testing the effect of temperature on the growth of CNTs. In this experiment, to observe the impact of temperature, the process was continued by applying 100 mL/min flow rate of Ar. Because the previous experiments were at the temperature of 800°C, the new set of the experiment were carried out with temperatures lower and higher than 800°C.

When the temperature was decreased from 800 to 750°C, the yield of CNTs decreased. So the higher temperatures were examined. The results showed that by increasing the temperature, the yield of CNTs increased. Therefore, it can be concluded that the activity of catalysts decreases as lower temperature was used and vice versa.

Figure 2 shows the SEM images of as-prepared CNTs at 900°C, and Ar flow rate of 100 mL/min. The SEM images showed that very straight and high-purity carbon nanotubes were formed by catalytic decomposition of Ethanol over the Fe-Mo-MgO catalyst at 900°C. The yield increased as the temperature increased. It indicates that the catalysts were more active at higher temperatures resulting in better growth of CNTs.

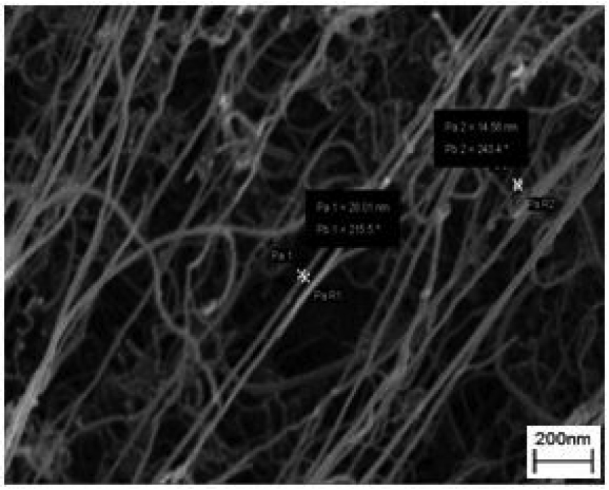

FIGURE 2. SEM image of CNTs at 900°C

As can be seen in Figure 3, which is the SEM of CNTs synthesized at 950°C, the yield of CNTs increased. Figure 4 shows the percentage of carbon deposit (CD %) calculated by Eq. (1) or yield of synthesized CNTs at different temperatures. It can be seen that the yield is low at lower synthesis temperatures, but as the temperature increased, the yield of CNTs increased. When the temperature was increased to higher degrees (more than 900°C), a layer of amorphous carbon was found to cover the surface of carbon nanotubes. Based on the findings, despite the fact that at higher temperatures (950°C and above), the percentage of carbon deposit increased, the quality of synthesized CNTs decreased.

The XRD result of CNTs samples synthesized at 900°C without purification is displayed in Figure 5. The peak around 2θ = 26° (Chen et al. 2008), as indicated by "C" in the XRD pattern was sharp indicating few defects in the structure of CNTs. The Fe_2C, Mo_2C and MgO phases can also be observed confirming that the Fe and Mo phases were converted to these phases because carbon atoms were continuously dissolved by the catalyst after Mo and Fe were deoxidized.

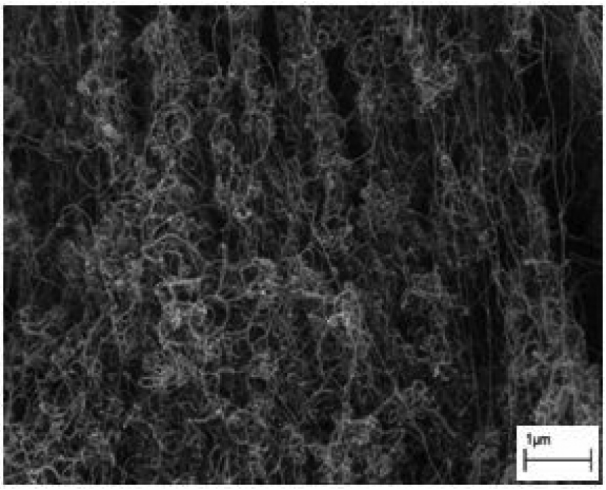

FIGURE 3. SEM image of CNTs at 950°C

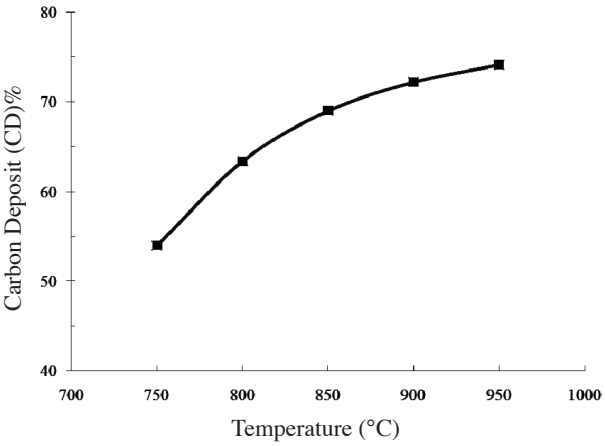

FIGURE 4. The effect of temperature on the percentage of carbon deposit

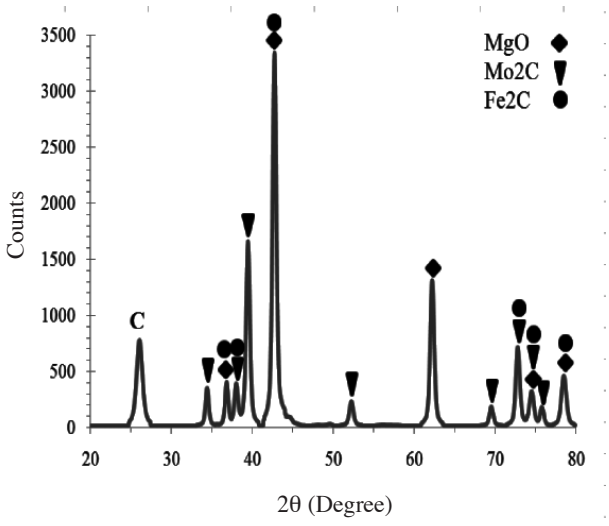

FIGURE 5. XRD pattern of the synthesized CNTs

Thermo-gravimetric analysis (TGA) for CNTs was performed to characterize the thermal behaviour of

the CNTs synthesized at different conditions. Figure 6 illustrates the TGA curves for the CNTs synthesized at 900°C and 100 mL/min flow rate of Ar. Kitiyanan et al. (2000) and Tang et al. (2001) reported that the oxidative temperatures were around 330°C for amorphous carbon, 500-600°C for SWCNTs, and 700°C for MWCNTs, respectively (Kitiyanan et al. 2000; Tang et al. 2001).

The weight loss was due to the combustion of carbon atoms in the samples by O_2. The residual weight at high temperatures was due to metal oxides from the catalyst. From the TGA curve, it is obvious that there was no weight loss before 550°C and after 740°C. The amorphous carbon usually started to burn at about 300°C, and there was no corresponding peak of amorphous carbon in the TGA curve. TGA analysis was performed to identify the different types of carbon species, and the one step TGA graph shows about 70% weight loss in between 540 to 740°C and indicates that the synthesized carbon nanotubes were dominated by SWCNTs and MWCNTs (Shajahan et al. 2003).

The TEM image of the sample as shown in Figure 7, confirmed the presence of high purity isolated SWCNTs.

Niu and Fang (2006) synthesized SWCNTs with lower quality as compared to this work (by comparing with the TEM and XRD results). Kang et al. (2008) also have obtained SWCNTs by using Fe-Mo-MgO catalysts but with lower quality as compared with the SWCNTs which were synthesized in this work (by comparing the SEM results). Note that the above mentioned researchers both used CH_4 as a carbon source in their experiment rather than ethanol used in the present research.

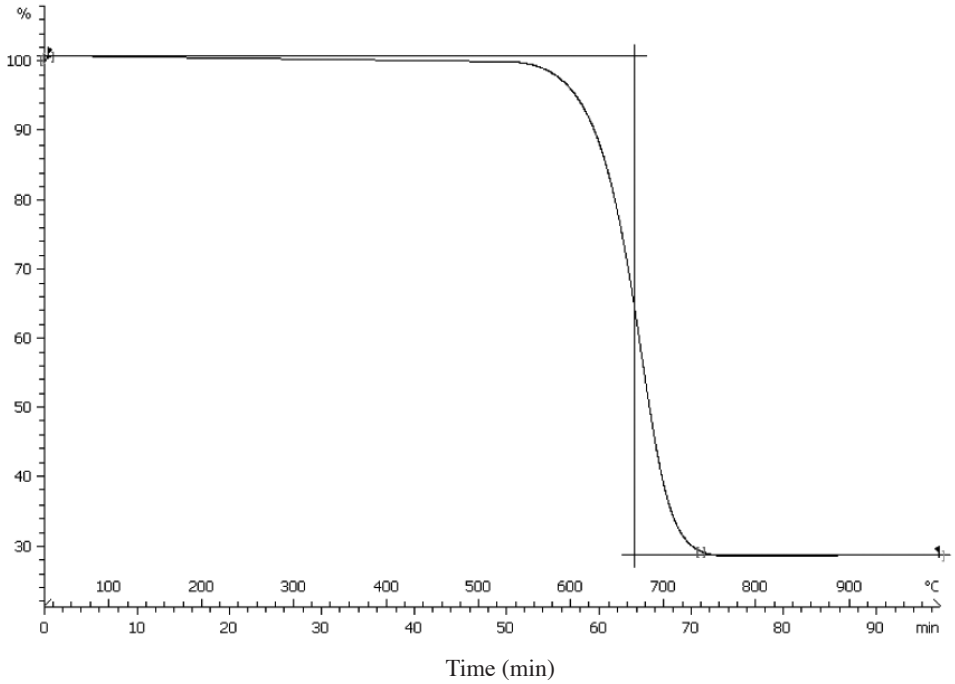

FIGURE 6. TGA graph of CNTs

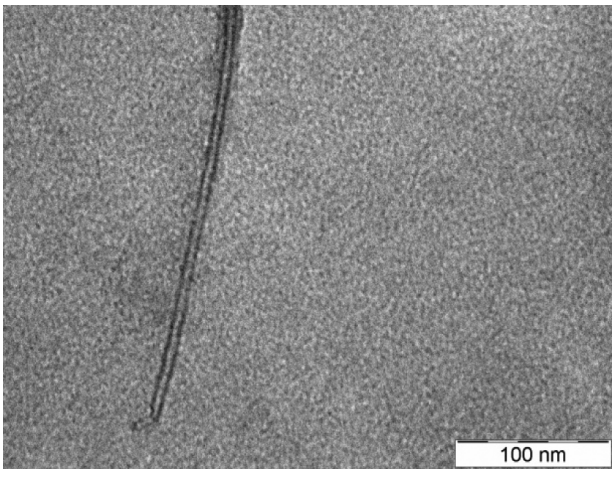

FIGURE 7. TEM image of synthesized SWCNTs

CONCLUSION

It was found that the best flow rate for carrier gas was 100 mL/min. For the flow rate lower or higher than this, very few CNTs were formed. In the synthesis of CNTs by CCVD method, the temperature plays a key role. The results showed that the yield of CNTs was low at lower synthesis temperatures and as the temperature increases, the CNTs yield increases correspondingly. It can be concluded that in this work, the best temperature for the growth of CNTs was about 900°C. These parameters affect the formation and yield, and quality of the carbon nanotubes.

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Setareh Monshi Toussi
Advanced Materials & Nanotechnology Laboratory
Institute of Advanced Technology
Universiti Putra Malaysia
Serdang 43400, Selangor D.E.
Malaysia

A. Fakhru'L-Razi*, Luqman Chuah A. & A.R. Suraya
Department of Chemical and Environmental Engineering
Universiti Putra Malaysia
Serdang 43400, Selangor D.E.
Malaysia

*Corresponding author; email: fakhrul@eng.upm.edu.my

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