THE EFFECT OF SYNTHESIS TEMPERATURE ON THE CARBON YIELD AND CHARACTERISTICS OF NANO COMPOSITE C-CNFs

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Abstract - Synthesis temperature is one of important factors influencing on characteristics of carbon nanostructured materials. In this article, the authors evaluate the change of properties of nano composite C-CNFs obtained by simultaneously synthesizing and decorating NFs on the surface of the carbon felt at different temperatures. The results have shown that the carbon yield increases from 5.55 %wt to 227.13 %wt by enhancing the growth temperature from 620ºC to 680ºC. The results from Raman spectrum analysis have indicated that when the temperature rises from 620ºC to 680ºC, the I_D/I_G ratio decreases from 0.932 to 0.728. The decrease of I_D/I_G ratio has affirmed the increase in the graphitization degree of the product. However, this ratio increases slightly to 0.749 when the temperature is at 710ºC. This result demonstrate formation of amorphous carbon at high temperature. Besides, the obtained C-CNFs are also analyzed by several techniques such as SEM, TEM, TGA and BET.

Key words - C-CNFs; LPG; SEM; TEM; BET; TGA; Raman

1. Introduction

Carbon nanostructured materials have received much attention of research communities in recent decades because of their outstanding properties and wide applications in many fields in the life [1, 2]. Depending on different applications, these materials could be synthesized by many methods such as arc discharge, laser ablation or chemical vapor deposition [3] with different carbon sources, for sample methane, acetylene or ethanol, methanol [4-6]. Nowadays, chemical vapor deposition (CVD) method is popular because operating temperature is lower than with other methods, as-product is high purity, cost is low [7]. After synthesis, carbon nano materials are nanoscale, so it causes a number of disadvantages, especially when they are used as adsorbent or catalyst support. In order to deal with these drawbacks, some researchers used adhesives to mount carbon nano materials into a macroscopic shape [8] or decorated it on surface of films or 3D structural materials [9]. Due to low specific surface area of almost 3D materials, their applications were limited. For instance, carbon felt was industrially produced and used in many fields such as energy, environmental applications [10, 11] because of their good electronic conduction, high mechanical strength, thermal stability, especially chemical inert property. However, their low specific surface area (ca. 1 m^2/g) is limited to be applied in chemical and environmental fields. Therefore, decorating carbon nanostructured materials on carbon felt's surface would increase specific surface area, so they would extend their applicability.

Generally, the quality and characteristics of the carbon nano materials mainly depend on operating conditions such as temperature, catalyst, carbon sources, synthesis time [12, 13]. In particular, temperature is one of the important factors that influence on yield and quality of product. So, it has been of great interest to researchers [4, 5, 14]. Aksak et al. investigated the effect of temperature on diameter of CNTs obtained over $Co/SiO_2/Si$ catalyst [4]. The authors used CH_4 as carbon source in a synthesis procedure implemented by CVD method. The results indicated that CNTs diameter decreased about 50 percent, from 20.4 to 10.5 nm when temperature increased from 850 to 925ºC. Similarly, Lee et al. also applied CVD method to synthesize CNTs over $Fe/SiO_2/Si$ catalyst and C_2H_2 as carbon source [5]. The results showed that the effect of temperature on the diameter was opposed to the Aksak's conclusion. In detail, CNTs diameter rose from 30 to 130 nm by increasing the growth temperature in the range 750-950ºC. Moreover, Lee's report also presented the temperature's effect on graphitization level of synthesis material. In the same direction as the two research groups mentioned above, the results of Hu et al. were completely different. They produced CNTs by CVD method over Ni/MgO/Cu catalyst and carbon source [14]. The results showed that diameter was quite homogeneous in the growth temperature range from 720 to 870ºC. And the results also revealed the influence of temperature on the properties of product, for example, the graphitization level increased (or I_D/I_G ratio decreased) with increasing the reaction temperature.

From above analysis, in this research, the authors focused on investigating the effect of temperature on the yield, characteristics of carbon nanofibers (CNFs) decorated on carbon felt. The as-product has been characterized by several techniques such as nitrogen isothermal adsorption - desorption using the Brunauer-Emmett-Teller method, Scanning Electron Microscopy, Transmission Electron Microscopy, Thermogravimetric Analysis and Raman scattering spectroscopy.

2. Experimental

2.1. Materials

In this research, $Ni(NO_3)_2.6H_2O$ (98.5% purity) supplied from Guangdong Xilong chemical Co.Ltd was used as catalyst precursor; carbonsource for synthesis process was liquefied petroleum gas (LPG) from PetroVietnam northern gas joint stock company; carbon felt supplied by CeraMaterialswas used as catalyst support; H_2 gas (from Cryotech company) was used to reduce catalytic oxide phase to corresponding metal and dilute LPG concentration; Ar gas was used to remove air from reaction system supplied by DAGASCO company. And Duc Giang chemicals group joint stock company supplied ethanol (99.5% purity).

2.2. Catalyst synthesis

Nickel was deposited on carbon felt via an incipient wetness impregnation method using a nickel nitrate solution as precursor ($Ni(NO_3)_2.6H_2O$), nickel loading was

fixed at 1 %wt. The impregnated solid was dried in an oven at 110°C for 14h and calcinated in air at 350°C for 2h in order to decompose the nickel nitrate into its corresponding oxide. The catalyst was further reduced under hydrogen flow at 400°C for 2h. The detail of catalyst synthesis process was performed in our previous publication [15].

2.3. Synthesis of nano composite material C-CNFs

The synthesis and decoration of carbon nanofibers on carbon felt was done at atmospheric pressure as follows: a known amount of catalyst (Ni/felt) was put into a quartz tube reactor located inside an electrical furnace controlled by thermocouple. All of the gas LPG, H_2, Ar were led through flowmeter to control flow and came in reactor. Firstly, Ar gas was used to remove air from the system within 60 minutes (100 mL/min), then the catalyst was reduced under a flow of hydrogen (100 mL/min) at 400°C for 2h. After reduction step, the reaction temperature increased from 400°C to the desired temperature with a heating rate of 5°C/min. When the system reached synthesis temperature, the H_2 flow was replaced by a LPG and H_2mixture (% LPG/H_2=30/70) with a flow rate of 100 mL/min. The synthesis process was implemented for 2h. After the synthesis, the reactor was cooled down to room temperature under an Ar flow. The as-product was discharged from the reactor. The CNFs yield is defined as the weight gain ratio of the carbon deposition to the starting catalyst materials, it was calculated by equation:

$$\boldsymbol{H = \frac{w1-w2}{w2} * 100} \quad (1)$$

With:

- H: CNFs carbon yield made and decorated on carbon felt's surface;
- w1: amount of sample after synthesis (gram);
- w2: amount of sample before synthesis (gram).

2.4. Characterization techniques

Firstly, the morphology of material was determined by scanning electron microscopy (SEM) using a JEOL 6010-FEG microscope. The HR-TEM (High Resolution Transmission Electron Microscopy), model JEM 2100, was used to provide information about the microstructure of the materials. Raman scattering spectroscopy equipment RENISHAW was used to evaluate structural defect level, quality of product. Thermogravimetric Analysis (TGA) was conducted inan oxygen flow of 20 mL/min witha heating rate of 3°C/min by the STA6000 apparatus (Perkin Elmer). Finally, specific surface area BET (Brunauer-Emmett-Teller) was carried out on ASAP 2020 equipment using nitrogen as adsorbent at liquefied nitrogen temperature.

3. Results and discussion

In this research, four samples were synthesized at the temperatures of 620°C, 650°C, 680°C and 710°C, while the other operating conditions were exactly the same as described in section 2.3. The samples were labeled M1, M2, M3 và M4, respectively.

After finishing synthesis, the as-product was discharged from the reactor, and yield was calculated by equation (1). Figure 1 shows the carbon yield at different synthesis temperatures. From this figure, we can see that the carbon yield at low temperature was low (5.55 %wt) and this rate dramatically increased with the increase of synthesis temperature, reached 205.77 %wt at 680°C. When temperature continued increasing from 680°C to 710°C, the carbon yield slowly increased. This result was in good agreement with previous reports in the literature [14, 16, 17].

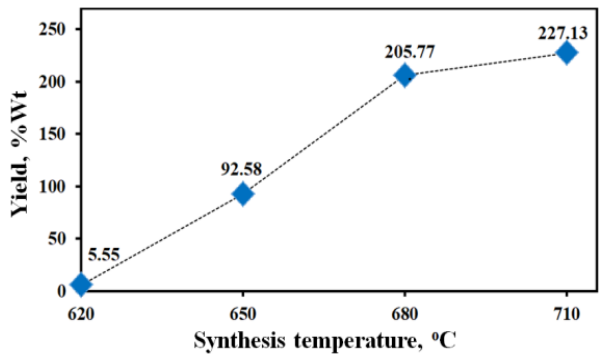

Figure 1. *Variation of carbon yield withreaction temperature*

In order to consider the formation of CNFs on carbon felt's surface, samples M1 and M2 were examined by SEM micrographs, the results were shown in Figure 2. It was clear that the carbon materials were formed and decorated on surface of carbon felt. However, in the case of sample M1, the amount of the material produced was very low (5.55 %wt), so it didn't decorate homogeneously on carbon felt's surface. For sample M2, the amount of product significantly increased to 92.58 %wt, and formed a dense and homogeneous interwoven coverage.

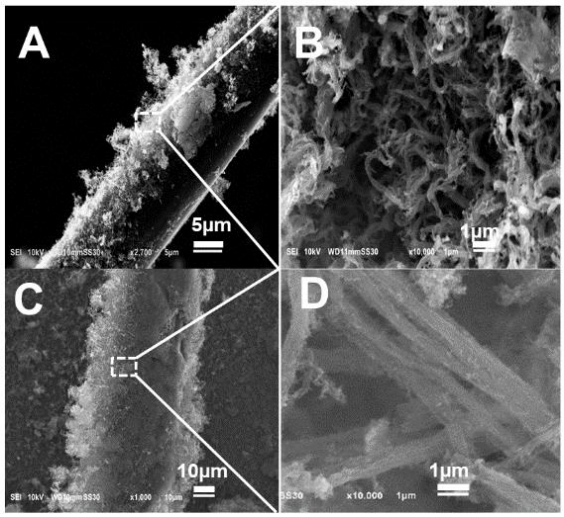

Figure 2. *SEM micrographs of samples; A, B: M1; C, D: M2(*) ((*) the results were published in reference 11)*

In order to get information about the microstructure and diameter of CNFs, the morphology of M1, M2 samples were observed by TEM with different magnifications as shown in Figure 3. The TEM images confirmed that the used method led to the formation of carbon nanofibers (CNFs). The CNFs diameters of the two samples synthesized in the narrow temperaturerange were nearly uniform about 20 nm.

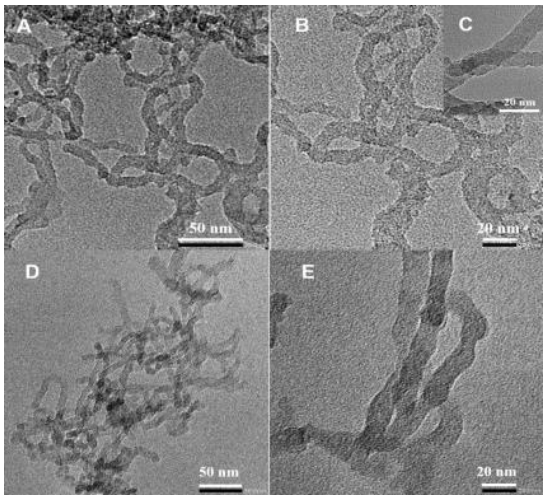

Figure 3. *TEM microghaphs of CNFs; A, B, C: M1; D, E: M2*

The specific surface area of the C-CNFs was obtained by the measurement of N_2 adsorption at 77 K. Temperature dependence of the BET values of the samples was shown in Figure 4. This figure also presented the synthesized CNFs's BET value which was calculated by equation (2).

$$\mathbf{BET_{C\text{-}CNFs}x(100+H)=BET_{carbon\ felt}x100+BET_{CNFs}xH} \quad (2)$$

With, $BET_{C\text{-}CNFs}$, $BET_{carbon\ felt}$, BET_{CNFs} were BET values of C-CNFs, carbon felt and CNFs, respectively; H: The yield of product.

Hypothesizing that BET value of C-CNFs was equal the total BET value of each other material and was linear with weight percentage.

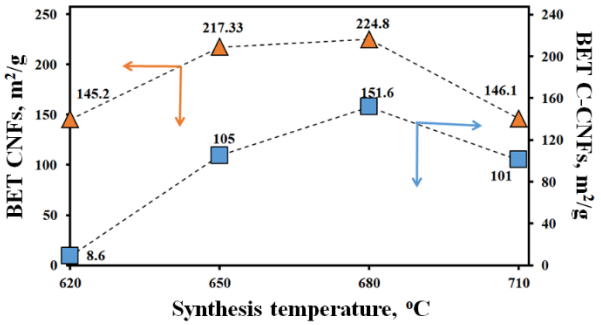

Figure 4. *Variation of BET value with growth temperature*

As seen in Figure 4, the temperature dependence of the BET values of C-CNFs and CNFs had the same trend. When the temperature increased from 620°C to 680°C specific surface area quickly rose from 145.2 m^2/g to 224.8 m^2/g. However, it strongly decreased to 146.1 m^2/g when the temperature reached 710°C. According to the results reported in the literature [14, 17, 18], when reaction temperature was not high enough, the decomposition rate of carbon source and catalyst activity were low, so the yield of amount product was also small. When the operating temperature increased, the decomposition rate of carbon source and catalyst activity were high, so the formation rate of CNFs also increased. Therefore, both yield and specific surface area dramatically rose. Nevertheless, when growth temperature was over optimal temperature, the decomposition rate of carbon source was higher than the formation rate of CNFs on carbon felt's surface. Carbon atoms which were formed from carbon source's decomposition but not exposed on active phase could be carried out with gas flow or combined together into kinds of carbonaceous. On the other hand, when temperature continued increasing from 680°C to 710°C, the agglomeration of active phase of catalyst became obvious. So metal particle size increased, which resulted in lower surface contact between carbon source and active phase of catalyst. So the excess carbon was accumulated on the surface of catalysts to form carbonaceous particles [14, 18].

Raman scattering spectroscopy is widely used to examine the quality and micro-structures of carbon nanomaterials due to its ability to characterize materials from molecular vibrations. In general, the Raman spectra of carbon nanomaterials are characterized by three main bands: The D-band at around 1356 cm^{-1}, the G-band at around 1592 cm^{-1} and the 2D-band appearing at around 2700 cm^{-1}. The shapes, the positions and the intensities of peaks of the spectra revealed the information of their micro-structures and quality. Results reported in literature indicated that D-band represents for structural defect level on material's surface and appearance of carbonaceous such as amorphous carbon, G-band featured for crystal structural lattice of product [19, 20]. Therefore, the ratio of I_D/I_G (I_D and I_G are the peak intensity at D- and G-band) is an important parameter to investigate the defect level. The greater the ratio, the higher the defect level and vice versa.

Raman spectra of the synthesized C-CNFs at different reaction temperatures were shown in Figure 5A. In order to determine the intensity of peaks as accurately as possible, OriginPro 8.5.1 software was used to deconvolute peaks, the spectra diagram of deconvolution of sample M2 was shown in Figure 5B. This result revealed that peaks of Raman spectroscopy followed Lorentz distribution with the features indicated in Table 1 (the results of other samples were similar). The change of the ratio between intensity at peak D and intensity at peak G were also shown in Figure 6.

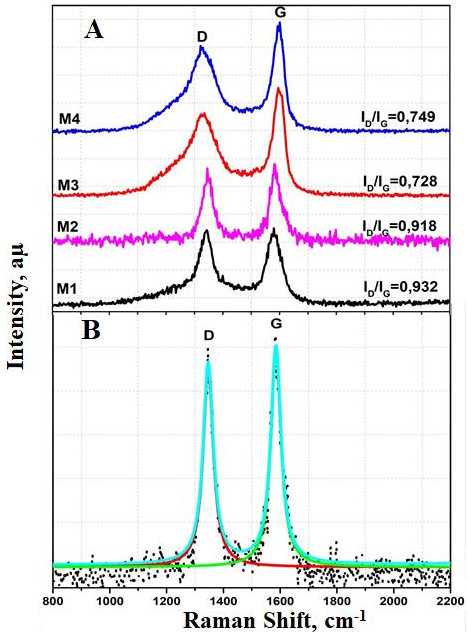

Figure 5. *Raman spectra of as-prodcuts atdifferent growth temperatures (A); Deconvolution of the Raman spectrum of sample M2 (B)*

Table 1. *Features of peaks in Raman spectroscopy*

T, ^oC	Peak	Peak distribution	Peak position (cm^{-1})	Peak height ($a\mu$)
620	D	Lorentz	1340	454
	G	Lorentz	1579	487
650	D	Lorentz	1347	462
	G	Lorentz	1585	503
680	D	Lorentz	1326	550
	G	Lorentz	1597	756
710	D	Lorentz	1328	543
	G	Lorentz	1596	725

As shown in Figure 5A, the ratio of I_D/I_G decreased from 0.932 to 0.728 by enhancing the growth temperature between 620^{o}C and 680^{o}C. The results proved that the graphitization degree would progressively improve as reaction temperature increased. This result matched with results reported in literatures [10, 12]. However, when synthesis temperature continued going up to 710^{o}C, the value of I_D/I_Glightly rose. As aforementioned, formation of amorphous carbon occurring simultaneously with forming CNFs was the reason so as that I_D/I_G value increased [18].

These results indicated that the optimal reaction temperature was 680^{o}C to obtain the high yield of C-CNFs with the highest surface area, low defects.

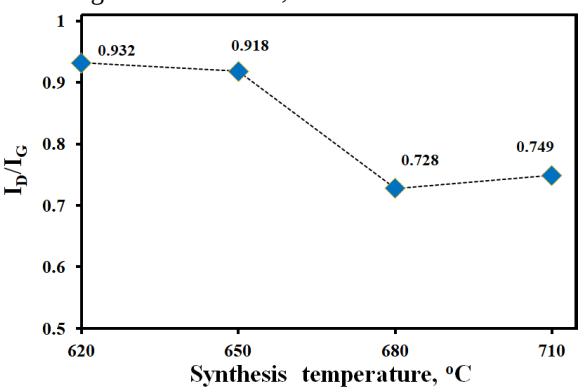

Figure 6. *Variation of ratio of I_D/I_Gwithsynthetsis temperature*

In studies of Zhiqiang et al. and Siang-Piao et al. using CH_4 as carbon source over the different catalysts, the optimal temperature in Zhiqiang's research was 850^{o}C when they synthesized CNTs over Mo-Co-MgO catalyst [16]. Meanwhile, with CoO-MoO/Al_2O_3 catalyst, Siang-Piao et al's result has shown that the optimal reaction temperature was 700^{o}C [17]. Therefore, we can see that each study with different catalysts and carbon sources, the temperature to obtain high yield with high quality is not the same.

To evaluate the effect of temperature onthe oxidation stability of C-CNFs, the samples were also analyzed by thermogravimetric analysis method (TGA), the results were shown in Figure 7.

Accordingly, the decomposition of the samples underwent 2 stages with 2 peaks, respectively as Figure 7A and 7B. The peak at lower temperature represented decomposition of CNFs, the second one was attributed to the decomposition of the carbon felt [11]. As seen in Figure 7C, the decomposition temperature rose with the growth reaction temperature. In detail, when synthesis temperature enhanced from 620^{o}C to 710^{o}C, the decomposition temperature of CNFs increased from 512^{o}C to 560^{o}C. The results from analysis Raman spectrum showed that the obtained product was higher purity as the growth temperature increased. Therefore, the oxidation stability was improved. The results were similar to the results published by Chen et al [12].

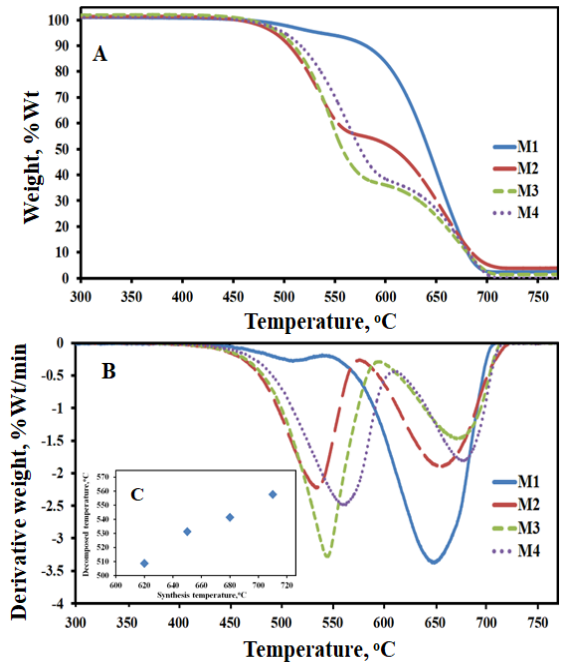

Figure 7. *Thermogravimetric analysis diagram, A: The weight loss, B: Derivative weight; C: Variation of degradation temperature of CNFs with operating temperature*

4. Conclusion

This research revealed the effects of the synthesis temperature on the carbon yield and properties of C-CNFs. In the range of the investigated temperature, the results showed that the carbon yield increased with enhancing the reaction temperature. The quality and graphitization of carbon atoms in the graphic network were improved by increasing the growth temperature. However, when the operating temperature was too high, the carbonaceous materials were formed. So, the quality of product declined. According to the results of this work, as well as the works from the other results reported in literature, the range of optimal temperature to synthesize the carbon nanomaterials which has high yield and high quality depends on many factors such as implemented temperature, carbon source, catalyst (active phase and catalyst support).

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