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Effect of sudden initiation and temperature on growth and diameter of carbon nanotubes synthesized by CVD method

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ABSTRACT

In this study, the synthesis of CNTs over MgO supported Co₃O₄ by chemical vapor deposition of acetylene at temperatures in the range of 500 °C - 975 °C have been investigated. The size of Co₃O₄ nanoparticles could be controlled by changing the concentration of cobalt nitrate in aqueous solution containing of MgO lightweight powder by impregnation method. The most important point is the fact that, without any pre-temperature of catalyst nanoparticles, the synthesis process of CNTs started suddenly, and then the effect of sudden initiation and conventional calcination processes on yield of CNTs was compared. The results suggest that this sudden initiation of synthesis process affects the carbon yield and morphology of CNTs. © 2013 Trade Science Inc. - INDIA

KEYWORDS

Carbon nanotubes;
Catalyst nanoparticles;
CVD method;
Impregnation.

INTRODUCTION

Since their discovery^[1], carbon nanotubes (CNTs) have attracted a great deal of interest from the research community due to their unique and useful chemical and physical properties^[2]. The chemical vapor deposition (CVD) method for production of carbon nanotubes is of great interest since it gives large quantity, good quality of CNTs^[3]. The product can easily be varied by changing the growth parameters, such as catalyst (size and kind of them)^[4], temperature^[5], substrate^[6], carbon source^[7] and pretreatment of catalyst^[8]. Transition metals, most frequently Fe, Ni or Co, supported on oxides or zeolites are the catalyst precursors^[9]. The most commonly used catalyst supports are silica, magnesium

oxide, zeolite and alumina^[9-11].

The advantage of CVD is that the morphology and microstructures of the carbon deposits can be easily controlled by adjusting the processing parameters. Recently, several papers dealt with the mechanism of the formation of carbon nanotubes. Particularly, the role of pretreatment^[12,13] and the size of catalyst's nanoparticles have been discussed^[14,15].

Researchers mostly attempt to produce CNTs with low diameters and high yield^[17,19,20]. The influence of metal loading on the final carbon productivity has been demonstrated in a few studies^[15,16]. The yield of CNTs depends significantly on the number of metal particles on supported catalysts. For high productivity, therefore, it has been suggested that the more metal the more

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carbon^[16-18]. Hence, in order to obtain a high productivity, one efficient way is to increase the catalyst metal loading, but with relatively high dispersion.

Some reports indicate that using high ratio of catalyst to support material can cause negative results^[15,21]. Therefore finding an appropriate way in which these conditions are satisfied is very essential and beneficial.

This present work deals with the effect of sudden entrance of catalyst nanoparticles into the center of CVD furnace, on growth of CNTs. The aim has been to enhance CNTs productivity with control of their diameters. We prepared cobalt oxide catalysts with four different metal loadings by impregnation method. Morphology and structural characteristics of CNTs have been investigated using scanning electron microscopy (SEM) and X-ray diffraction (XRD).

EXPERIMENTAL

Preparation of the catalyst

The MgO-supported Co_3O_4 catalyst nanoparticles ($\text{Co}_3\text{O}_4/\text{MgO}$) was prepared by means of homogeneous deposition – impregnation method, using cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Merck, >99% purity) as metal salt. In this method, at first 1gr of MgO light-weight powder was dispersed in 50 ml of ethanol and sonicated for 30 min. Then, the desired weight percent of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 25 ml ethanol. With constant magnetic stirring, at 75 °C, the solution of cobalt nitrate was added dropwise to the above solution through a dropping funnel. The rate of addition was kept at 0.5 ml/min. After completion of the cobalt nitrate, the mixture was stirred for 1 h and dried at 120 °C on a hot plate, followed by grinding in to a fine powder by means of using a mortar, until a uniform powder were achieved. As the last treatment, the sample was calcinated in an oven under 550 °C for 2 h (The temperature of the furnace was steadily raised from room temperature to 550 °C with an increment of 10 °C/min). $\text{Co}_3\text{O}_4/\text{MgO}$ catalytic substrates were prepared in four different concentration of Co_3O_4 (10 wt.%, 20 wt.%, 30 wt.% and 40 wt. %).

Synthesis and purification process of carbon nanotubes

CNTs were synthesized by the catalytic decompo-

sition of acetylene at different temperatures (500 °C - 975 °C) over $\text{Co}_3\text{O}_4/\text{MgO}$, using CVD method at atmospheric pressure. To synthesize CNTs, 50 mg of catalyst powder was dispersed uniformly on a quartz boat. Two procedures for synthesis of CNTs was used. In first method, the conventional method^[9,10,12,15], the catalyst was placed in the center of a quartz tube (i.d. 50 mm, length 1200 mm). The quartz tube, mounted in an electrical tube furnace, was heated to 925 °C in the air atmosphere. Subsequently, argon was fed at a flow rate of 300 sccm for 15 min. A mixture of acetylene (15 sccm) and carrier gas (150 sccm) was introduced into the quartz tube and maintained at the reaction temperature for 15 min before the furnace was cooled down to room temperature under Ar protection. In secant method, the one in this paper, while keeping constant Ar carrier gas flow at 150 sccm in the quartz reaction tube, the temperature of the furnace was raised to desired temperature for the growth of CNTs. Then the quartz boat (contain of catalyst powder) was placed directly in the middle of the furnace as acetylene gas was flowing simultaneously (with flow rate of 15 sccm), and synthesis process of CNTs started suddenly. The synthesis of CNTs was carried out by pyrolysis of the acetylene feed gas for 15 min. After synthesis of CNTs, the reactor was turned off and cooled down to room temperature under Ar gas atmosphere.

Structure and morphological analysis

The prepared catalyst was characterized by X-ray diffraction (XRD, GBC, $\text{Cu}(\text{K}_\alpha)$ radiation, $\lambda = 1.54 \text{ \AA}$), scanning range $2\theta = 10-90^\circ$ to analyze the phases and average size of particles. The resulting CNTs were characterized by scanning electron microscopy (SEM, Philips, MAG 15 kV, 30000 X, SE Detector Microscope).

RESULTS AND DISCUSSION

In order to investigate the effect of catalyst sudden initiation in to the reaction zone of CVD furnace on growth of CNTs, carbon yield in two different methods mentioned was compared. The result of four different weight percentages (10 wt. %, 20 wt. %, 30 wt.%, and 40 wt.%) are shown in Figure 1. Comparing diagrams 1a and 1b, it can be seen that carbon yield in

second method (sudden initiation of catalyst) is considerably higher than the first one (conventional method). This is indeed a remarkable result which hasn't been much attention from researchers. In other hand, for temperatures higher than 800 °C and contents more than 30 wt.%, carbon yield decreases rapidly in first method compared to the second one in which higher carbon yield is achieved.

This can be a result of thermal shock caused by sudden entrance of catalyst in the reaction zone with high temperature which then crumbles the aggregated catalyst nanoparticles. This in fact increase the number of nanoparticles implied for CNTs growth and also the carbon yield. Whereas, in first method, catalyst maintenance in that high temperature of furnace causes more aggregation of catalyst nanoparticles which then form bigger particles and therefore less carbon yield. According to the different results achieved from both

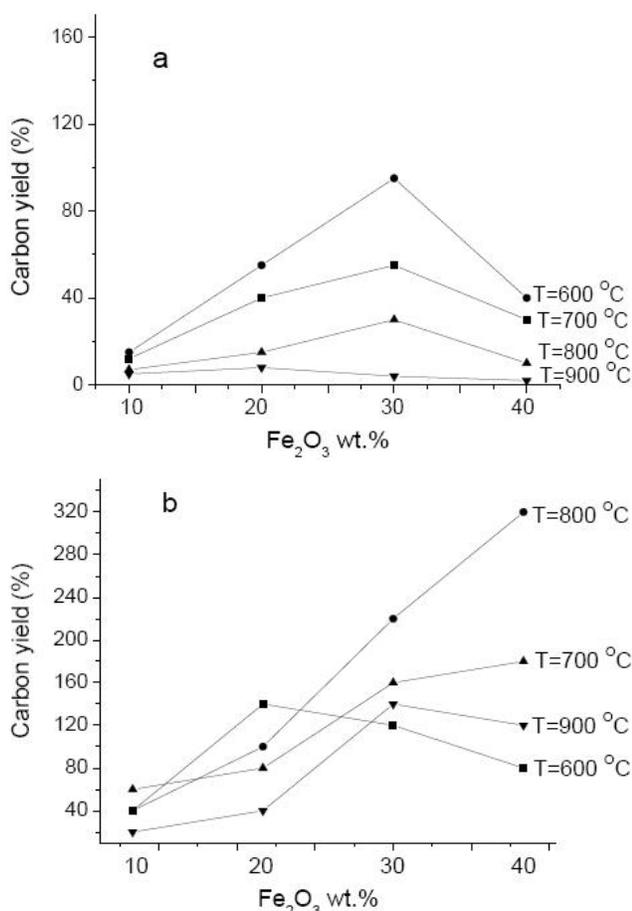


Figure 1 : Carbon yield (%) as a function of Co_3O_4 loadings (wt.%) at different temperatures; a) synthesis on calcinated of catalyst in CVD reactor for 15 min (conventional method), b) the synthesis process of CNTs started suddenly.

methods, the effect of temperature on growth of CNTs for 10 wt.% and 30 wt.% of Fe oxide nanoparticles using second method was also investigated.

Figure 2 shows the XRD patterns of nanoparticles synthesized for 10 wt.% and 30 wt.% of Co_3O_4 supported by MgO powders. The maximum peak belongs to Co_3O_4 nanoparticles in $2\theta=36.8^\circ$ becoming sharper by increasing the content of cobalt oxide from 10wt.% to 30 wt.% respectively. According to scherrer's equation^[21], the average size of nanoparticles for two contents, 10 wt.% and 30 wt.% are 11 nm and 16 nm respectively.

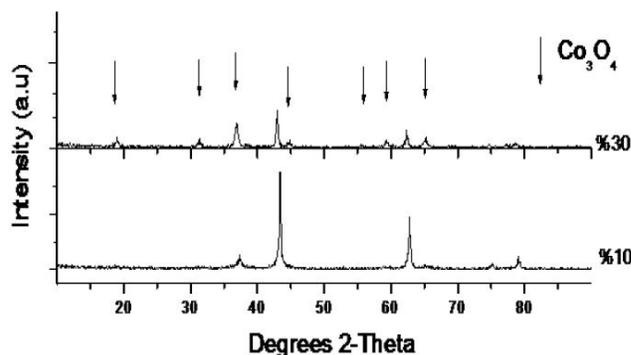


Figure 2 : The XRD pattern of $\text{Co}_3\text{O}_4/\text{MgO}$ catalyst for 10 wt.% and 30 wt.%.

SEM (Figures 3, 4 and 5) studies reveal that, CNTs were produced over $\text{Co}_3\text{O}_4/\text{MgO}$ catalysts prepared under experimental conditions cited above. In 500 °C, there was no carbonaceous product C on the surface of catalyst (we did not show the SEM results here). This result indicates that cobalt oxide nanoparticles aren't absolutely active at 500 °C. By increasing temperature to 550 °C, however, the decomposition process of acetylene gas and release of carbon atoms occurred, but all products were carbon impurities covering the catalyst's surface and no CNTs was seen in SEM images (Figures 3). A possible explanation of the low activity below 550 °C for synthesis of CNTs is that the catalytic components, cobalt and MgO, have strong interaction that make the metal reduction difficult at low temperatures^[20,23].

The existence of CNTs in figure 4, indicates that 600 °C is the appropriate temperature for reduction of cobalt oxide nanoparticles and the catalyst activity both weight percents of catalyst (10 wt.%, 30 wt.%) is high and they are intertwined together. In addition, no tubular structure, such as fibers, with abnormal and

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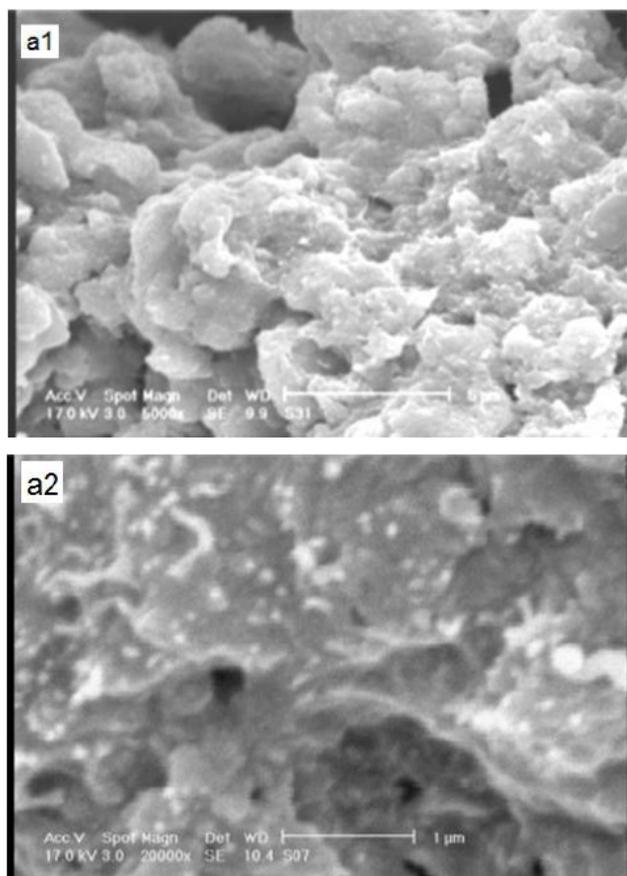


Figure 3 : The SEM images of experiments results at 550 °C with C_2H_2 over Co_3O_4/MgO for 10 wt.% (a₁), and 30 wt.% (a₂) of cobalt oxide.

large diameters was seen. This indicates that there can be a uniform distribution in diameters of the initial catalyst nanoparticles prepared in this research. Comparing nanotubes grown at 600 °C (Figures 4a₁, 4a₂) with those grown at 700 °C (Figures 4b₁, 4b₂), 800 °C (Figures 4c₁, 4c₂) and 900 °C (Figures 4d₁, 4d₂) indicates that a lower temperature corresponds to thinner and less impurity ascribable, while a high temperature was for thicker diameter CNTs and increase carbon impurities, because of the increase in size of nanoparticles and faster reaction rate. CNTs reduced amount was attributable to the catalyst partial surface deactivation. These results are in accordance with those reported by other researchers^[20,23].

At higher temperature (975 °C) (Figures 5b₁, 5b₂), CNTs growth did not occur as a consequence of the full deactivation of the catalytic active particles encapsulated by amorphous carbon. Different factors causing the catalyst deactivation could be taken into account. In general, during the CNTs growth, acety-

lene molecules decompose on the catalyst nanoparticles surface and then these carbon atoms diffuse into catalyst particles. As widely reported with regard to the non-catalytic pyrolysis of acetylene, the deactivation mainly occurs through the formation of amorphous carbon encapsulating the active catalytic particles which prevent the diffusion of acetylene into the surface of catalyst, formation of metal carbide for nucleation of CNTs^[20,23,24].

The authors suggest that, a possible factor of the increase in deactivation as the temperature raises could be the breaking of the whole catalyst structure (Co_3O_4 nanoparticles supported on MgO micro-particles) caused by the thermal shock of nanoparticles, with suddenly putting catalyst from environment's temperature to the center of hot furnace without any pretemperature. The breaking of the catalyst-support structure on one hand will increase the exposure of the active surface, but on the other hand will decrease the catalytic activity of the metal particles through the failure of the interaction with the support at higher temperatures.

In contradiction to reported literatures^[16,25], efficient CNTs production can be achieved when pretemperature procedure is not used. We believe that if we don't heat the nanoparticles before synthesis of CNTs, the production might be improved by keeping Co_3O_4 nanoparticles active for nucleation. Using this process for high percent of catalysts resulted in CNTs with low diameters and high yield without any negative effects reducing the production rate, this is what we were trying to achieve.

The result demonstrates that the catalyst powders with two different contents of Co_3O_4 showed similar behavior during the synthesis process, in different temperatures. In addition, not only the density of CNTs but also their diameter can be controlled by adjusting the growth temperature. As the temperature increases, the migration rate of catalyst nanoparticles increases to facilitate the agglomeration of Co_3O_4 particles^[26,27]. As a result of more significant agglomeration at higher temperatures, larger size Co_3O_4 particles are formed with low density and broad diameter distributions. The size of catalytic particles usually determines the diameter of CNTs in CVD growth^[27]. Therefore, the CNTs with larger diameter and lower density can be grown by raising the growth temperature. There is the additional

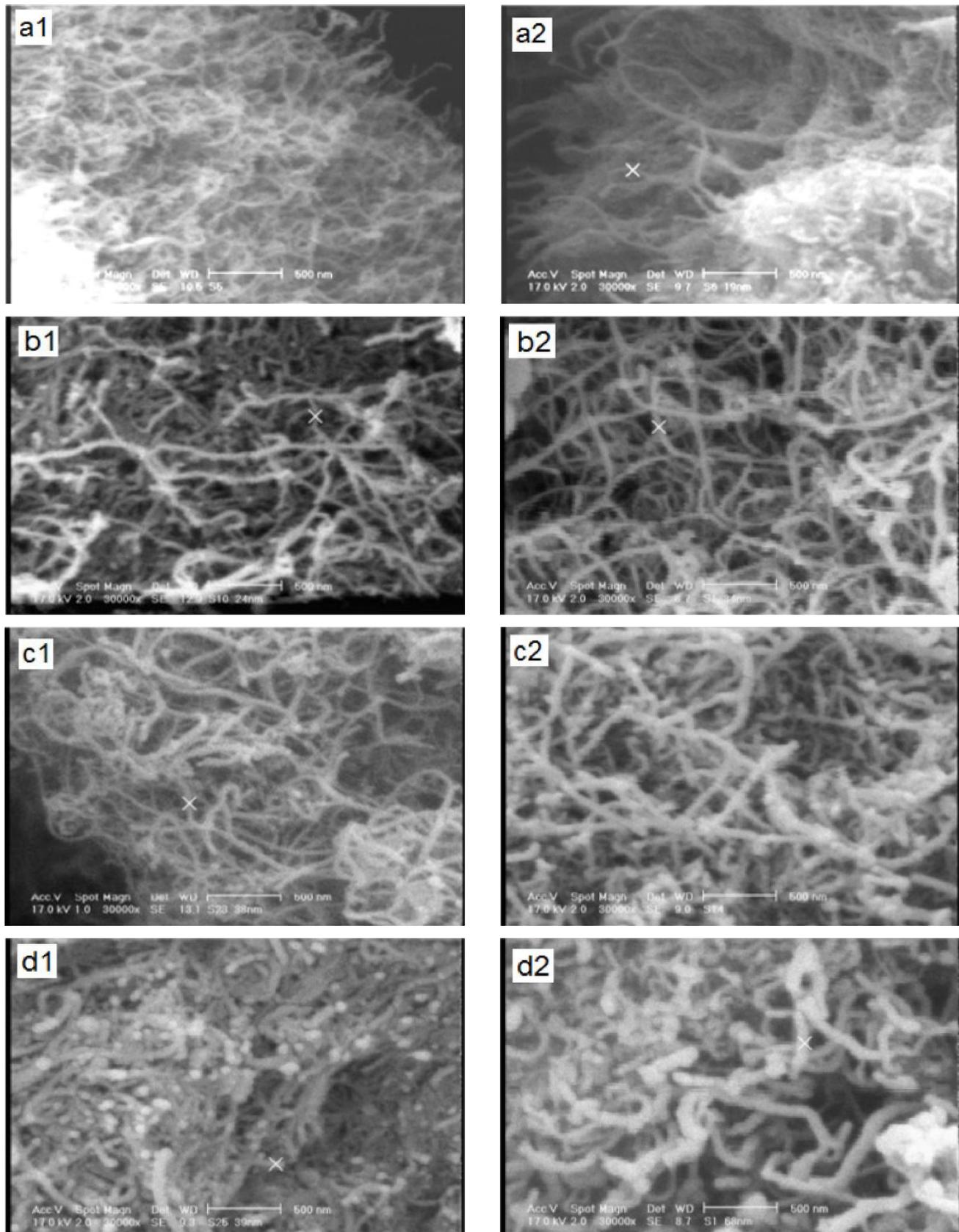


Figure 4: The SEM images of synthesized CNTs at 600 °C (a₁, a₂), 700 °C (b₁, b₂), 800 °C (c₁, c₂), and 900 °C (d₁, d₂) with C₂H₂ over Co₃O₄/MgO for 10 wt.% (indexed by 1) and 30 wt.% (indexed by 2).

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possibility of non-catalytic pyrolysis of acetylene on CNTs sidewalls, leading to thickening of the tubes. This behavior on the surface of CNTs can be seen perfectly in figure 4d₂.

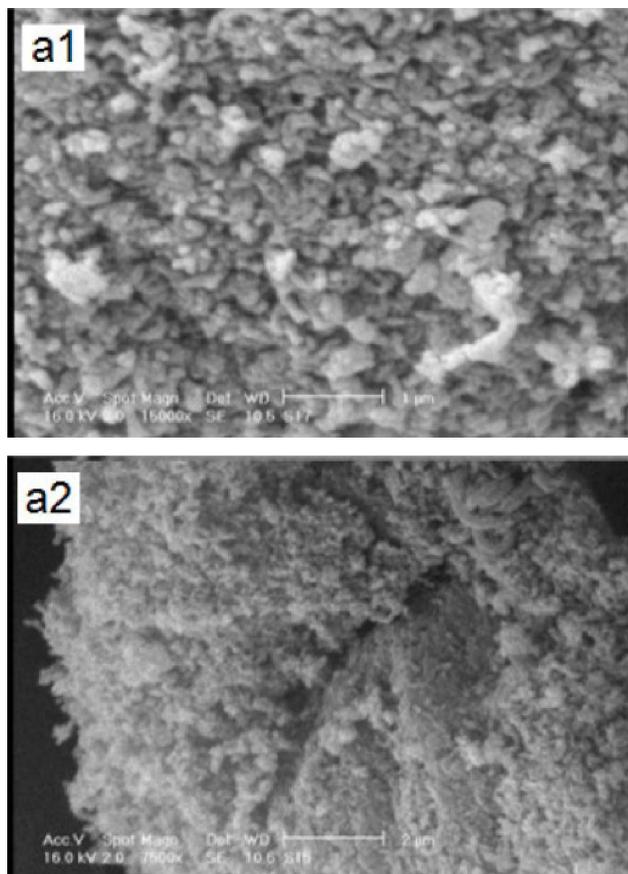


Figure 5 : The SEM images of experiments results at 975 °C with C₂H₂ over Co₃O₄/MgO for 10 wt.% (a₁), and 30 wt.% (a₂) of cobalt oxide.

The results indicate that the temperature has the dual effect of increasing both the diffusion coefficient and the solubility of carbon in the metallic nanoparticles. Consequently, high temperatures improve CNTs growth by increasing the rate-limiting step of carbon diffusion; however, the temperature

Can't be arbitrarily high due to accelerated thermal decomposition of hydrocarbon supplying more carbon than can be dissolved and transported at a given temperature, which precipitates as unwanted amorphous carbon.

The average diameter of CNTs is found to be 13 nm, 21 nm, 27.5 nm and 37.5 nm for 10 wt.%, and 19 nm, 27.5 nm, 52.5 nm and 62.5 nm for 30 wt.% at 600 °C, 700 °C, 800 °C and 900 °C, respectively. Then, the

average diameter of CNTs increases from ~13 nm at 600 °C to ~37.5 nm at 900 °C for 10 wt.%, and also from 19 nm to 62.5 nm for 30 wt.%. Figure 6 show the scattered temperature-diameter data between 600 °C and 900 °C with C₂H₂ over Co₃O₄/MgO for 10 wt.% and 30 wt.%. A wide range of CNTs diameters can be effectively synthesized over a range of temperatures. This scattered temperature-diameter data had shown a positive diameter- temperature relationship between 600 °C and 900 °C. It can be seen that the increasing rate of diameter is much more rapid in the range of 700 °C - 800 °C compared to other temperature intervals, and this change is more obvious for 30 wt.%. This happens because of the difference in the diffusion rate of catalyst nanoparticles into each other in different temperature ranges. In 900 °C although the diffusion rate is high, but large size of nanoparticles results in low catalyst activity.

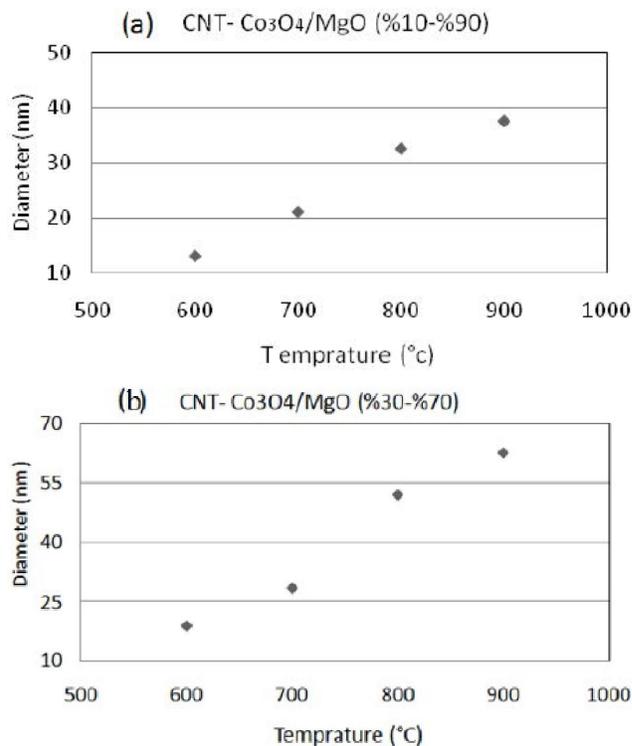


Figure 6 : The scattered temperature-diameter data from 600 °C - 900 °C with C₂H₂ over Co₃O₄/MgO for 10 wt.% (a), and 30 wt.% (b).

X-ray diffraction study and texture properties of CNTs

To verify the effect of growth temperature on size of nanoparticles and crystallinity of graphitic sheets, XRD patterns were obtained. Figure 7 shows XRD patterns

of the produced CNTs, for 30 wt.% of cobalt oxide, at 600 °C - 900 °C. The diffraction patterns normally present sharp, graphitic (002) reflections at about 26.5°, indicating a high degree of structural order of CNTs. The other peaks are always broad which might contain the overlapped diffractions of MgO, C, or possible Co₃C.

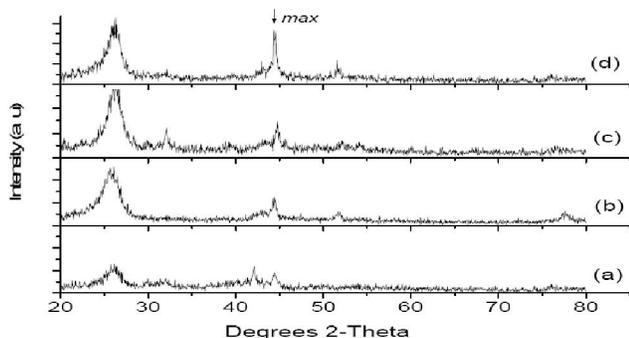


Figure 7 : The XRD pattern of synthesized CNTs from 600 °C- 900 °C with C₂H₂ over Co₃O₄/MgO for 30 wt.%.

The maximum peak belong to cobalt oxide at $2\theta = 44.8^\circ$, becoming sharper by increasing the growth temperature caused by migration of nanoparticles which increases the agglomeration of Co₃O₄ particles. Regarding scherrer's equation, the average size of the catalyst particles increases. As a result of more significant agglomeration, the CNTs diameter was found to increase with temperature increase due to changes in metal catalyst particle size.

CONCLUSIONS

We proved that both Co₃O₄/MgO are good catalysts in the generation of CNTs from acetylene via CVD. The sudden initiation with temperature and percent of cobalt oxide, played an important role in producing CNTs. The studies indicated that sudden synthesis process of CNTs resulted in high density, high yield and low impurity. Resulting from rapid growth of CNTs taking place just before the new aggregation of crumbled catalyst nanoparticles under thermal shocking. We have also observed that the highest CNTs densities resulted from un-pretemperature at 600 °C - 900 °C, therefore favoring the growth of CNTs.

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