

The control of diameter of carbon nanotube over Co-loaded Zeolite Y

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Abstract—This study examined carbon nanotubes (CNTs) with various outer diameters produced by the catalytic decomposition of acetylene over Co-loaded zeolite Y. The CNTs were grown at differed reaction temperatures, reaction times, and acetylene concentrations. In addition, the effect of the amount of Co dispersed over zeolite Y used as a support was determined. The shape and diameter of the synthesized CNT were identified by SEM and TEM analyzers. As a result, CNTs with various outer diameters were synthesized successfully. The average outer diameter of the synthesized CNTs increased with increasing amount of Co dispersed over zeolite Y regardless of the reaction temperature and reaction time. The outer diameter did not change with acetylene concentration, and the acetylene concentration was fixed to 10 cm³/min. Most of the CNT had large surface areas, >400 m²/g. The surface area increased with increasing outer diameter of the CNT until the outer diameter reached 60 nm but decreased with further increases in outer diameter.

Key words: Co Loaded Zeolite Y, Carbon Nanotube, Acetylene Thermal Decomposition, Outer Diameter, Surface Area

INTRODUCTION

The preparation and characterization of nano-scale materials have attracted increasing interest because of their remarkable electronic, magnetic, optical, biological, and mechanical properties, which differ from bulk materials. In particular, carbon nanotubes (CNTs) are considered very useful for hydrogen adsorption. The largest challenge facing the hydrogen economy is the development of a viable hydrogen storage system. Hydrogen adsorption on carbon materials has been known for many years [1,2]. The level of adsorption on activated carbon has been reported to be approximately 0.5-wt% hydrogen at ambient temperature and 60-bar pressure. Recently, hydrogen storage on carbon nano structures has attracted attention because earlier results indicated large storage capacities. It was confirmed that the theoretical maximum hydrogen adsorption on nano structured carbon material was 8-wt% at ambient temperature [2].

Several methods have been developed for the synthesis of CNTs. However, these methods do not always result in the formation of CNTs with the same diameter. In addition, there is no chemical method that can separate according to size. Some efforts have been made to disperse CNTs obtained using supports with a regular structure. Recently, Co/silica and Fe/zeolite with a regular structure were found to be active in the catalytic growth of nanotubes, and methods for their separation from the catalyst particles have been developed [3-7] e.g. Fe-loaded mesoporous silica for the preparation of CNTs by decomposition of acetylene [3,8]. However, the effect of the zeolite pore structure on the diameter of the nano tubes formed catalytically has not been reported. Some researchers believe that the diameter of the nanotubes is controlled by the active metal particles from which the nanotube begins to grow [9-11]. In this point, it is believed that the size of the active metal particles might be altered by controlling the conditions used to synthesize the catalysts, such as reaction temperature, reaction time, catalyst precursor concen-

tration, etc. In addition, it is expected that CNTs could be applied to the storage of hydrogen if the diameter of CNTs can be controlled.

Therefore, this study examined the effect of the reaction conditions on the diameter of CNTs grown on Co-loaded zeolite Y with a large surface area, regular and thermal stable structure. The conditions examined were the amount of catalyst, reaction time, reaction temperature, and reactant concentration. In addition, the surface areas of the synthesized carbon nanotube at various diameters were compared.

EXPERIMENTAL

1. Catalyst Preparation

Reagents: Zeolite NaY, Aldrich chemical company; Co(NO₃)₂·6H₂O, Junsei chemical company, 98%; HF, J. T. Baker, 49%

Procedure: The three types of Co-loaded zeolite Y catalyst samples were prepared by impregnation with aqueous solutions of Co(NO₃)₂. Commercial NaY were reacted directly with 0.1 mol, 1.0 mol and 2.0 mol aqueous solution of Co(NO₃)₂ for 6 h. The resulting impregnated zeolite Y was filtered, washed, and calcined at 550 °C for 1 h. In this study, the impregnated zeolite Y is called Co_{0.1}ZY, Co_{1.0}ZY, and Co_{2.0}ZY. The prepared catalysts were identified by XRD and SEM analysis.

2. Synthesis of Carbon Nanotubes

Fig. 1 shows a schematic diagram of the reactor used to synthesize the carbon nanotubes. A quartz tube (outer diameter 13 mm, inner diameter 11 mm, length 480 mm) was used as the reactor and installed in a vertical electric furnace. 30 mg of the three types of Co_xZY samples were heated to >500 °C, respectively, in flowing helium (99.99%, Donga gas) and maintained at that temperature for 30 min to eliminate any water present. The samples were then heated to 650 °C, and an acetylene-helium mixture (10 cm³/min in helium) was passed over the catalyst bed at a rate of 100 cm³/min for 1-30 min. At this point, reduction of the catalyst by H₂ gas was not carried out because as reported in many paper, only the catalytic performance of Co_xZY was examined. The yield of deposited

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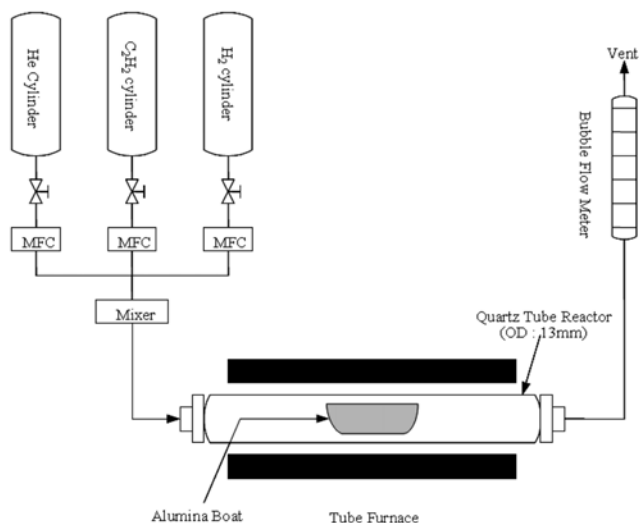


Fig. 1. Schematic diagram of the reaction apparatus.

carbon after the reaction was determined by subtracting the initial weight of the catalyst before the reaction from that after. After the reaction, CNTs on the Co_xZY were treated with a 20% HF solution for 2 h to eliminate the Co_xZY . The CNTs were then washed, filtered, and dried at 100 °C for 15 h.

3. Characterizations

The X-ray diffraction (XRD) patterns of these samples were recorded in the range of 2° to 50° 2θ . The experimental conditions are as follows. Diffractometer: Rigaku D Max IIA, Radiation: $\text{CuK}\alpha$, Filter: Ni, Power: 30 kV, 15 Ma, CPS: 2000, Scanning speed: 2 degree/min, Time constant: 1, Chart speed: 20 mm/min.

The size and shape of the CNTs were observed by a scanning electron microscope (SEM, JEOL-JSM35CF). The power and working distance were set to 15 kV and 39 cm, respectively.

The inner shape of the carbon deposits on the catalyst was determined using transmission electron microscopy (TEM, JEOL-3011). The specimens for the TEM observations were dispersed ultrasonically in alcohol, and then dropped onto holey grids. The power was set to 300 kV.

The BET surface areas of the synthesized CNTs were measured by nitrogen gas adsorption using a continuous flow method by chromatography equipped with a TCD detector at the liquid nitrogen temperature. A mixture of nitrogen and helium was used as the carrier gas using a GEMINI2375 model from Micrometrics. The sample was thermally treated at 200 °C for 1 h before the nitrogen adsorption tests.

RESULT AND DISCUSSION

1. Physical Properties of Co_xZY Catalysts

Fig. 2 shows the powder XRD patterns of the Co supported Zeolite Ys. As shown, the XRD pattern of Co_xZY showed the material to be a pure ZY molecular sieve with no evidence of an amorphous phase. Unfortunately, there was no peak that could be assigned to cobalt oxides. It is possible that the amount was very small. SEM revealed the pure zeolite Y sample to consist of relatively uniform and spherical particles approximately 1.0 μm in size. The size dis-

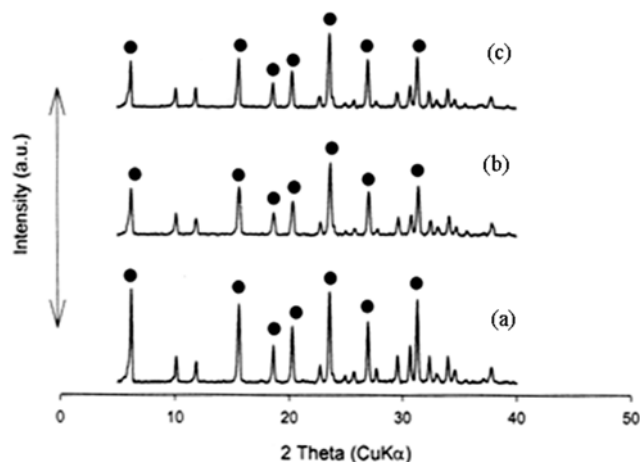


Fig. 2. XRD patterns of the Co-loaded zeolite Y catalysts. (a) $\text{Co}_{0.1}\text{Z-Y}$, (b) $\text{Co}_{1.0}\text{Z-Y}$, and (c) $\text{Co}_{2.0}\text{Z-Y}$.

tribution of the cobalt-incorporated samples was the same as pure zeolite Y, as expected. The surface area of the Co_0 , $\text{Co}_{0.1}$, $\text{Co}_{1.0}$, and $\text{Co}_{2.0}$ zeolite Y samples were 650, 630, 600, and 580 cm^2/g , respectively.

2. CNTs Synthesis Under Various Conditions

In CNT formation, various supports, such as HY, NaY, ZSM, and SAPO, have been used with transition metals, such as Ni, Fe, and Co. In particular, transition metal/Y catalyst produce better results than the other supports. In addition, samples impregnated with transition metals are better materials than those of incorporated and ion exchanged samples. Therefore, Co impregnated zeolite Y was selected in this study.

Fig. 3 shows SEM images of the synthesized CNTs over a Co_xZY catalyst with various cobalt concentrations. The reaction conditions were the same as shown in this figure. CNTs with various shapes were synthesized successfully by the thermal decomposition of acetylene. The diameter of the synthesized carbon nanotubes increases with increasing cobalt content in the Co_xZY catalysts. In addition, the amount of synthesized CNTs also increased with increasing impregnated cobalt concentration. This was attributed to cobalt playing a key role in the acetylene thermal decomposition, such that with cobalt, the rate of thermal decomposition was faster resulting in more deposited carbon.

Fig. 4 shows XRD patterns of the synthesized CNTs over the Co_xZY catalyst with various cobalt concentrations. The reaction conditions were the same as shown in Fig. 3. A band at approximately 20° 2θ was observed, which was attributed to an unstable base line not a peak. Surprisingly, the broad band increased with increasing CNT diameter. On the other hand, a small peak at approximately 26° 2θ [002] was observed, which was assigned to the level of CNTs graphitization. In addition, the peak intensity as well as the amount and diameter of the CNTs increased with increasing cobalt concentration.

As shown in Fig. 5 (TEM image of carbon nanotube), Co_xZY catalysts can produce regular bulky tubes with an average outer diameter of 20-30 nm and a length of at least 10 nm. As shown, most of the nanotubes were tubular-like and a relatively wide hollow core was surrounded by a thinner carbon wall. In addition, the CNTs were

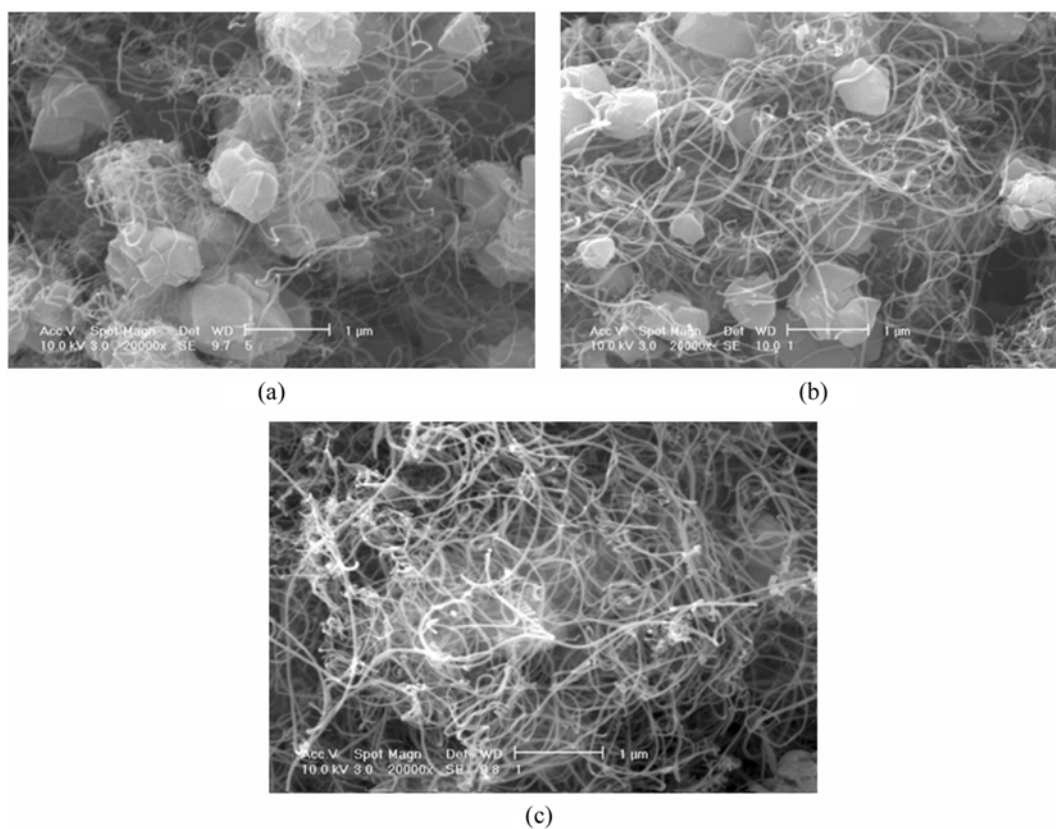


Fig. 3. SEM images of the CNTs synthesized over Co_xZY catalysts. Reaction conditions; reaction temperature 650°C , reaction time 5 min, and acetylene concentration $10\text{ cm}^3/\text{min}$. (a) $\text{Co}_{0.1}\text{ Z-Y}$, (b) $\text{Co}_{1.0}\text{ Z-Y}$, and (c) $\text{Co}_{2.0}\text{ Z-Y}$.

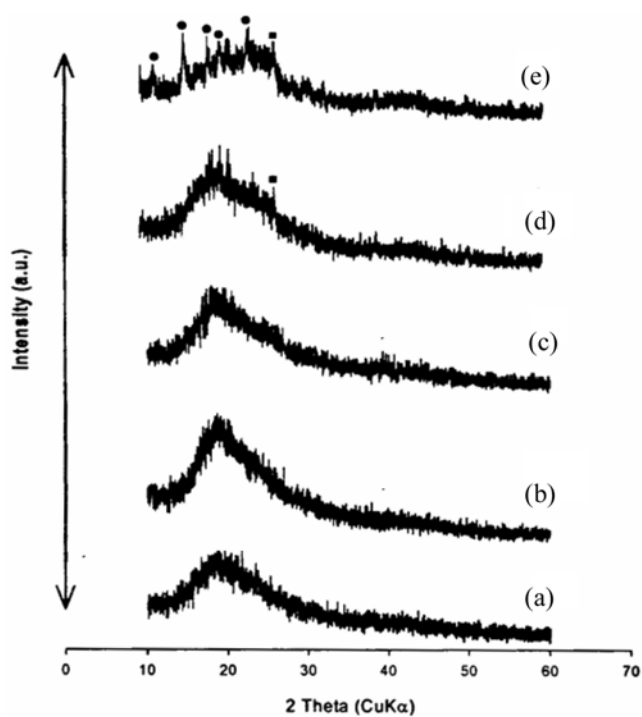


Fig. 4. XRD patterns of the CNTs over $\text{Co}_{1.0}\text{ZY}$ catalyst in various reaction conditions. (a) 650°C , 5 min, $10\text{ cm}^3/\text{min}$; (b) 650°C , 10 min, $10\text{ cm}^3/\text{min}$; (c) 750°C , 10 min, $10\text{ cm}^3/\text{min}$; (d) 650°C , 30 min, $10\text{ cm}^3/\text{min}$; (e) 650°C , 120 min, $10\text{ cm}^3/\text{min}$.

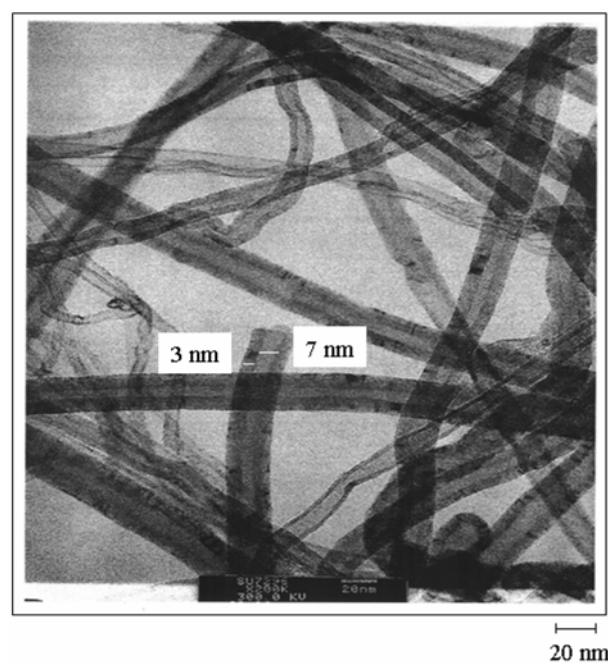


Fig. 5. TEM images of the CNTs synthesized over $\text{Co}_{1.0}\text{ZY}$ catalyst in the same condition with Fig. 3.

composed of two parts: an inner layer, which grows catalytically from the cobalt catalyst particle; and the outer part, which grows

from decomposed carbon deposited on the catalytic part. Ultrafine Co particles were trapped in the caps of the tubes, which indirectly confirmed the growth mechanism of these carbon nanotubes. First,

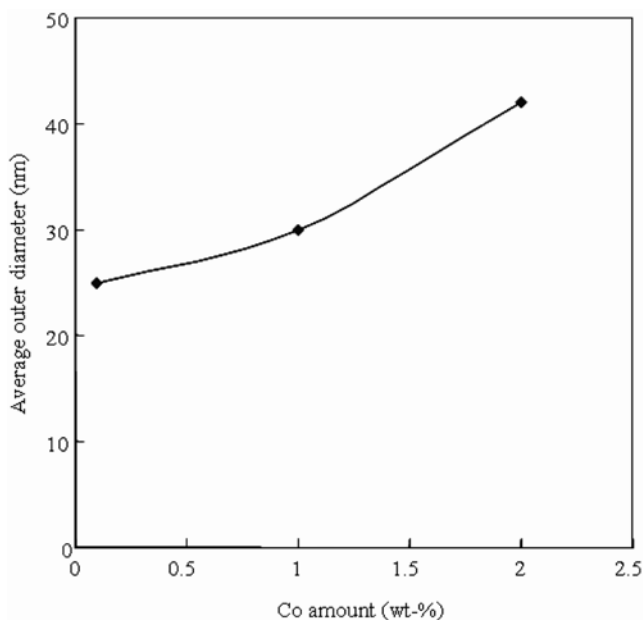


Fig. 6. Relationship between the average outer diameter of the CNTs and the amount of Co dispersed over zeolite Y.

cobalt ions, which are derived from thermal decomposition of acetylene, agglomerate and form catalyst particles of certain sizes through collision and coalescence. Subsequently, precipitation of carbon begins and CNTs are formed.

Fig. 6 shows the relationship between the outer diameter of the synthesized CNTs and the amount of Co impregnated in the Co_xZY catalysts. At 0.1, 1.0, and 2.0 mol% cobalt, the average outer diameters of the synthesized CNTs were 26, 30, and 43 nm, respectively. This data was calculated from the distribution of CNTs, as shown in Fig. 7.

In Fig. 7, the outer diameter range ranged from 10–40 nm. In particular, the distribution was sharper on the $\text{Co}_{1.0}\text{ZY}$ catalyst than on the other catalysts. On the catalyst with the lower amount of Co amount, CNT growth was unaffected by steric effects resulting from the smaller Co amount. This observation was attributed to the inhomogeneous dispersion of cobalt particles over zeolite Y which resulted in a larger size distribution of the CNTs. As shown in Fig. 4, amorphous carbon was observed on the lower Co containing sample. These results showed that the average outer diameter increased with increasing amount of cobalt.

The effect of the reaction temperature on the decomposition of acetylene over the $\text{Co}_{1.0}\text{ZY}$ catalyst was examined. As shown in Fig. 8, a higher temperature is favorable for the formation of a graphite wall structure. The amount of CNTs increased with increasing temperature. At temperatures $<600^\circ\text{C}$, there was a considerable amount of amorphous carbon. However, above 800°C , good qual-

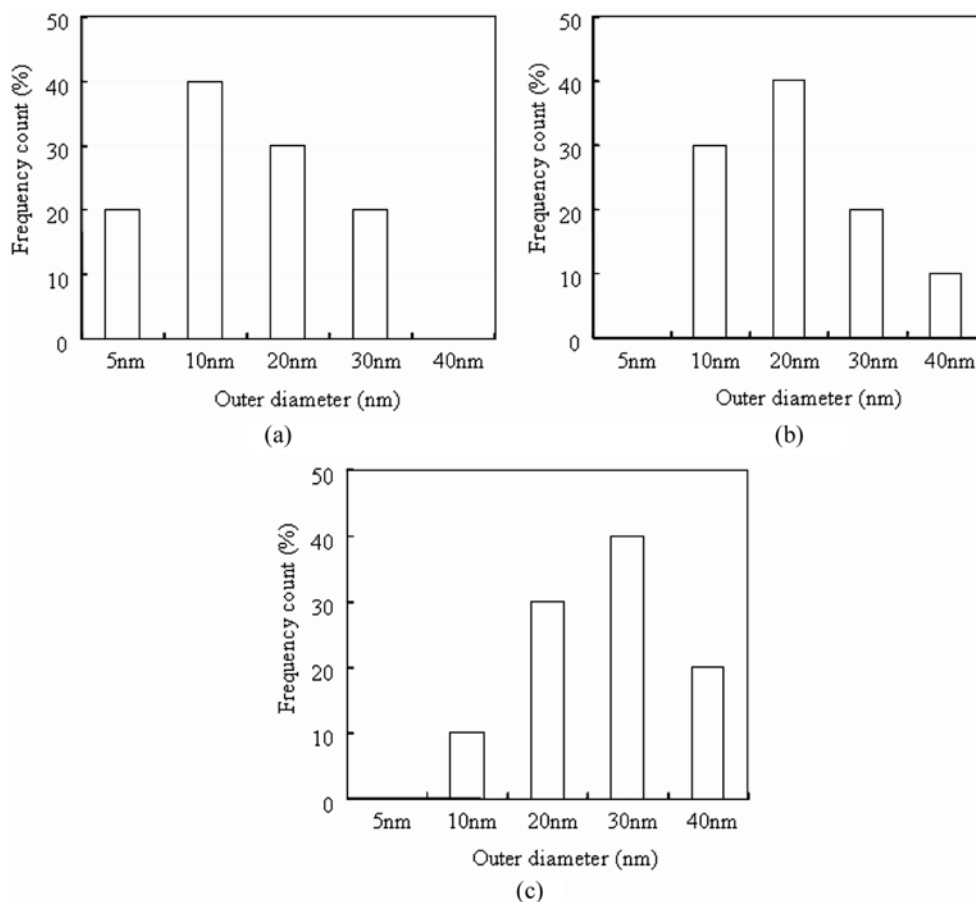


Fig. 7. Distribution of the average outer diameter of the CNTs over the Co_xZY catalysts. (a) $\text{Co}_{0.1}\text{ZY}$, (b) $\text{Co}_{1.0}\text{ZY}$, and (c) $\text{Co}_{2.0}\text{ZY}$.

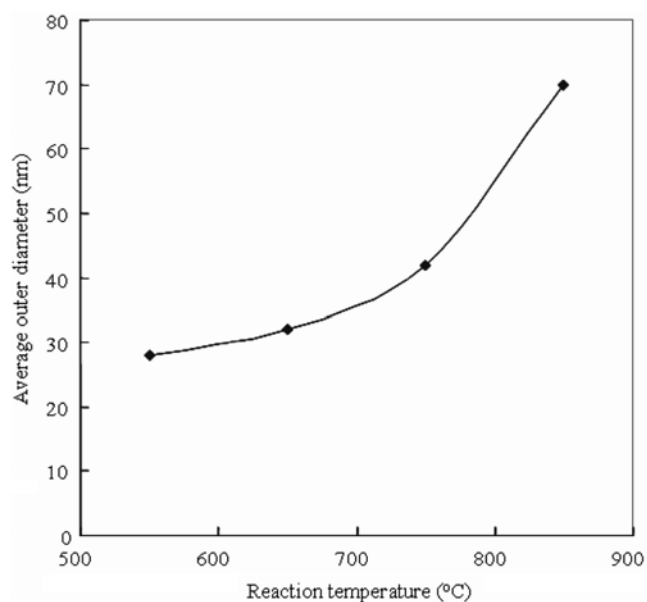


Fig. 8. Relationship between the average outer diameter of the CNTs and the reaction temperature. Reaction conditions; reaction time 5 min, acetylene concentration 10 cm³/min, catalyst Co_{1.0}ZY.

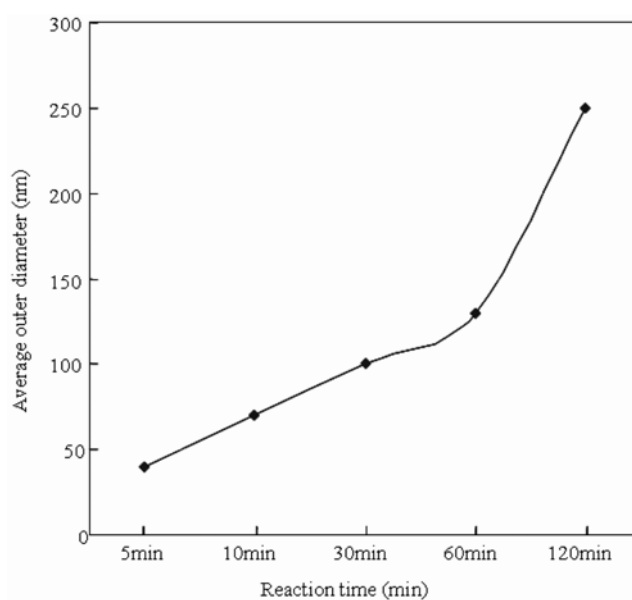
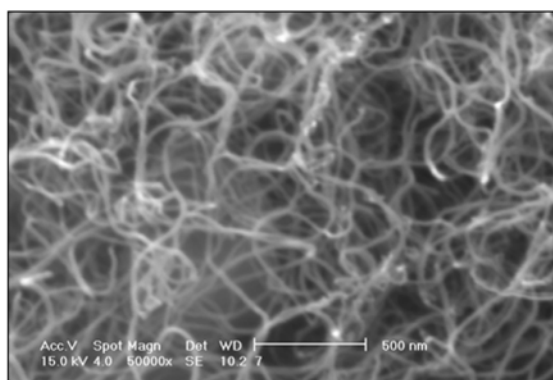
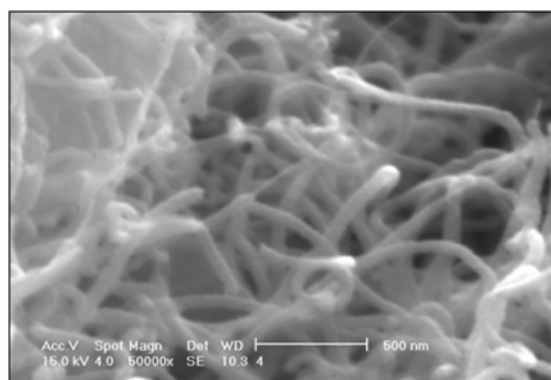


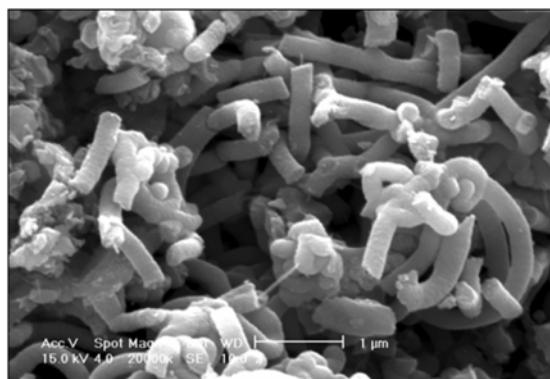
Fig. 9. Relationship between the average outer diameter of the CNTs and the reaction time. Reaction conditions; reaction temperature 650 °C, acetylene concentration 10 cm³/min, catalyst Co_{1.0}ZY.



(a)



(b)



(c)

Fig. 10. SEM images of the CNTs synthesized over Co_xZY catalysts at different reaction times under the same conditions shown in Fig. 9. (a) 5 min, (b) 10 min, and (c) 120 min.

ity graphite walls (nanotube) without amorphous carbon deposition were observed. It is believed that the reactant decomposes more

homogeneously higher temperatures.

The effect of the reaction time on CNT growth was examined.

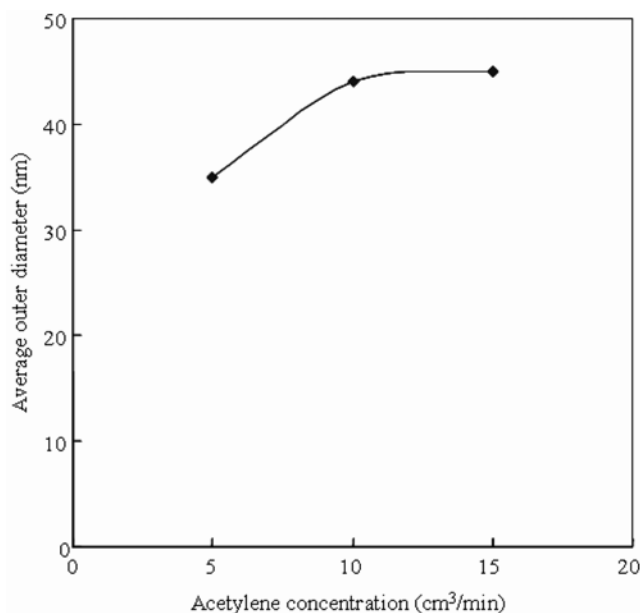


Fig. 11. Relationship between the average outer diameter of the CNTs and the acetylene concentration. Reaction conditions; reaction temperature 650 °C, reaction time 5 min, and catalyst Co_{1.0}ZY.

Acetylene decomposition was carried out for 1, 5, 10, 30, 60, and 120 min at 650 °C over a Co_{1.0}ZY catalyst. Fig. 9 shows the relationship between the average outer diameter of the CNTs and the reaction time. The amount of carbon deposition was quite low after 1 min but CNTs could already be observed. As shown in this figure, until 5 min, the catalysts were shown with CNTs. However, after that, pure CNTs were synthesized successfully.

As an additional explanation, Fig. 10 shows the SEM images of the CNTs synthesized for 10, 30, and 120 min, respectively. As shown, up to approximately 30 min, the amount and diameter of the CNTs increased without the formation of amorphous carbon. However, the tube length decreased to approximately 1-3 mm after 60 min (Fig. 9), and the diameter of the tube increased remarkably (Fig. 10). This effect is partly due to the deactivation of catalytically active sites as a function of the reaction time and the increasing surface area, which is favorable for the homogeneous decomposition of the reactant.

In order to determine the optimum acetylene concentration, the reactions were carried out at flow rate of 5, 10, and 15 cm³/min. Fig. 11 shows the relationship between the average diameter of the CNTs and the acetylene concentration. The outer diameter increased until 10 cm³/min. However, at higher flow rates, the diameter remained relatively constant at 45 nm. From this result, it was confirmed that the acetylene concentration was most suitable at 10 cm³/min. This result was attributed to the deactivation of catalytically active sites and the non-homogeneous decomposition of such a large amount of reactant.

Table 1 shows the relationship between the outer diameter of the CNTs and the BET surface area. The synthesized CNTs have large

Table 1. Average outer diameter and surface area of the CNTs

Catalyst	Reaction condition	Outer dia-meter (nm)	BET surface area (m²/g)
Co _{1.0} ZY	650 °C, 5 min	28	442
	650 °C, 10 min	60	583
	650 °C, 30 min	108	692
	650 °C, 60 min	148	486

surface areas >400 m²/g. The surface area increased with increasing outer diameter until 60 nm but decreased at larger outer diameters. From 28 nm to 108 nm, the length of the CNTs increased but decreased to approximately 1-3 mm with the 148 nm CNTs.

CONCLUSION

This study examined the growth of nanotubes with various diameters by acetylene thermal decomposition over Co loaded zeolite Y. CNTs with various diameters were synthesized. The outer diameter of the synthesized nanotubes increased with increasing amount of cobalt dispersed over the zeolite Y support, reaction temperature, and reaction time. The outer diameter increased until reactant concentration reached 10 cm³/min but remained relatively constant at approximately 45 nm at higher concentrations. The synthesized CNTs had large surface areas, >400 m²/g. The surface area increased with increasing outer diameter until 60 nm but decreased with further increases in outer diameter. Consequently, it confirmed that the outer diameters of the CNTs on the Co loaded zeolite Y can be controlled by the reaction conditions.

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