

## Effects of Bimetallic Catalyst Composition and Growth Parameters on the Growth Density and Diameter of Carbon Nanotubes

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**Abstract**—Multi-wall carbon nanotubes (MWNTs) were synthesized by catalytic decomposition of acetylene over Fe, Ni and Fe-Ni bimetallic catalysts supported on alumina under various controlled conditions. The growth density and diameter of CNTs were markedly dependent on the activation time of catalysts in  $H_2$  atmosphere, reaction time, reaction temperature, flow rate of acetylene, and catalyst composition. Bimetallic catalysts were apt to produce narrower diameter of CNTs than single metal catalysts. For the growth of CNTs at 600 °C under 10/100 sccm flow of  $C_2H_2/H_2$  mixture, the narrowest diameter about 20 nm was observed at the reaction time of 1 h for 20Fe : 20Ni : 60Al<sub>2</sub>O<sub>3</sub> catalyst, but at that of 1.5 h for 10Fe : 30Ni : 60Al<sub>2</sub>O<sub>3</sub> catalyst. It was considered that the diameter and density of CNTs decreased with the increase of the growth time mainly due to hydrogen etching. The growth of CNTs followed the tip growth mode.

Key words: Carbon Nanotubes, Fe-Ni/Al<sub>2</sub>O<sub>3</sub> Catalyst, CVD, Acetylene, Growth Density

### INTRODUCTION

Recently, carbon nanotubes (CNTs) have attracted much research interest because of their extraordinary electronic properties and hydrogen storage capacities [Hassanien et al., 1998; Chen et al., 1999]. These diverse physical and mechanical properties of CNTs arise from their different diameter, length and chirality, which enable CNTs to be an ultimate alternative material applicable for portable electronics and future electrical vehicles. However, the growth of high quality and large amount of CNTs is essential for their practical application. The available methods for synthesis of CNTs such as arc-discharge, laser vaporization, etc., can produce well-graphitized products, but they also include various disordered carbonaceous deposits. These methods have no sufficient controlling factor to eliminate the growth of unwanted deposits and to change the diameter of CNTs.

Recent research has been focused on chemical vapor deposition (CVD) technique because the structure of CNTs or carbon nanofibers (CNFs) can be controlled by varying growth parameters such as chemistry and nanomorphology of catalysts, reaction temperature and time, carbon source concentration, etc. [Li et al., 1996; Hernadi et al., 1997; Park et al., 1997; Thaib et al., 1999; Anderson and Rodriguez, 1999; Mo et al., 2000; Kibria et al., 2000]. The growth of large amount of CNTs is the most typical advantage of CVD technique over the conventional synthetic methods. In the CVD growth, Fe-Ni bimetallic catalysts show a dramatic impact on the production of tubes, which is not obtained by single metal catalysts [Park et al., 1997]. Besides, supported bimetallic catalysts produced markedly narrow tubular CNFs with various geometries

and crystallinities differently from the case of unsupported catalysts [Anderson and Rodriguez, 1999]. However, till now, there are no available reports to explain whether supported bimetallic catalysts are, or are not, able to grow narrower CNTs with a high growth density than the case of corresponding single metal supported catalysts. To speed up the CNTs growth technology, it was necessary to clarify this fact. Moreover, the merit of supported bimetallic catalysts may be uniquely applicable to CVD method to synthesize large quantities of CNTs or CNFs with controlled size.

The present study aims to synthesize CNTs over Fe, Ni and Fe-Ni catalysts supported on Al<sub>2</sub>O<sub>3</sub> using  $C_2H_2/H_2$  mixtures under controlled conditions, and to compare the catalytic activity of each catalyst for the growth of CNTs. The structural properties of the grown CNTs were investigated by using scanning electron microscopy (SEM), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), and Raman scattering measurements.

### EXPERIMENTAL

We prepared four bimetallic and two single metallic catalysts having weight proportions of 30Fe : 10Ni : 60Al<sub>2</sub>O<sub>3</sub>, 20Fe : 20Ni : 60Al<sub>2</sub>O<sub>3</sub>, 10Fe : 30Ni : 60Al<sub>2</sub>O<sub>3</sub>, 15Fe : 15Ni : 70Al<sub>2</sub>O<sub>3</sub>, 40Fe : 60Al<sub>2</sub>O<sub>3</sub> and 40Ni : 60Al<sub>2</sub>O<sub>3</sub> using impregnation method. High metal loading was chosen in order to ensure their homogeneous dispersion over the support and to get longer catalytic activity [Kibria et al., 1992]. The average size of the used  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> powder was 0.3  $\mu$ m. To prepare the catalysts, stoichiometric amounts of Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and/or Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O were dissolved in deionized water. Required amounts of Al<sub>2</sub>O<sub>3</sub> powders were mixed in the prepared solutions, which were stirred for about 1 h at 60 °C. As a result, pastes of impregnate metal salts in the Al<sub>2</sub>O<sub>3</sub> support were obtained. The metal

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salt impregnate pastes were then dried in an oven at 100 °C for 12 h. Then these were calcined in air at 400 °C for 4 h to convert the supported metal salts to supported metal oxide catalysts. Finally, the obtained supported metal oxide catalysts were reduced to supported metal catalysts under 100 sccm of hydrogen flow at 450 °C for 3 h.

Approximately 40 mg of a catalyst sample was uniformly dispersed in the base area of a quartz plate and placed in the central region of a horizontal quartz tube reactor. The length and diameter of the quartz tube reactor were 18 cm and 4.5 cm, respectively. The catalyst was activated at 900 °C in 100 sccm H<sub>2</sub> flow and CNTs were grown at temperatures between 500 and 700 °C by flowing 10/100 sccm of C<sub>2</sub>H<sub>2</sub>/H<sub>2</sub> for different time periods. The effects of activation period and C<sub>2</sub>H<sub>2</sub> flow rate on the growth of nanotubes were also investigated. The synthesized CNTs structure and morphology were determined by using SEM, FT-Raman spectroscopy, TEM and HRTEM.

## RESULTS AND DISCUSSION

The optimization of the catalyst activation condition was investigated to obtain the best growth of CNTs. The 20Fe : 20Ni : 60Al<sub>2</sub>O<sub>3</sub> catalyst was activated by using hydrogen at 900 °C for different time periods of 5 min, 0.5, 1.0 and 1.5 h, and CNTs were grown over the catalyst at 600 °C for 1 h under 10/100 sccm of C<sub>2</sub>H<sub>2</sub>/H<sub>2</sub> flow. It was observed that an increase of the activation time up to 1 h markedly increased the growth density and concurrently decreased the tube diameter, whereas the 1.5 h activation showed an opposite ef-

fect, i.e., tube growth density decreased and tube diameter increased. At present, we speculate that this is solely due to the change of catalyst morphology with the heat treatment in hydrogen. Fig. 1(a) and (b) show SEM images of the CNTs grown after activating for 5 min and 1 h, respectively. With the longer activation time of 1 h, the growth density of CNTs increased almost twofold, whereas the nanotube diameter decreased threefold to be about 20 nm. This indicates that the 1 h activation treatment generates smaller-sized metal crystallites and also converts any bulk metal oxides to active metal in favor of growing CNTs with narrower diameter [Yudasaka et al., 1997]. For the further activation time of 1.5 h, the metal crystallites show an agglomerating tendency. As a result, the tube density decreased and the diameter increased. In the present case, the activation time of 1 h seems to be sufficient to form small metal crystallites to grow nanotubes with narrow diameters.

After the catalyst activation time was chosen, the effect of temperature and reaction time on the CNT growth was also investigated at the same gas flow rate as used above. The growth of CNTs was observed at 600 and 700 °C, but not at 500 °C. It is considered that a temperature of 500 °C is not enough for the formation of fluidized metastable metal carbide eutectic from catalytic decomposition of acetylene, which is the key species for the CNTs growth [Parmon et al., 1996]. Fig. 2(a) and (b) show SEM images of the CNTs grown over 30Fe : 10Ni : 60Al<sub>2</sub>O<sub>3</sub> catalyst for 1 h at 600 and 700 °C, respectively. The growth density at 600 °C is much higher than that at 700 °C. Additionally, the diameter of the CNTs grown at 600 °C is about three times narrower than that grown at 700 °C. At 700 °C, the decrease in CNTs density and increase in diameter occurred pro-

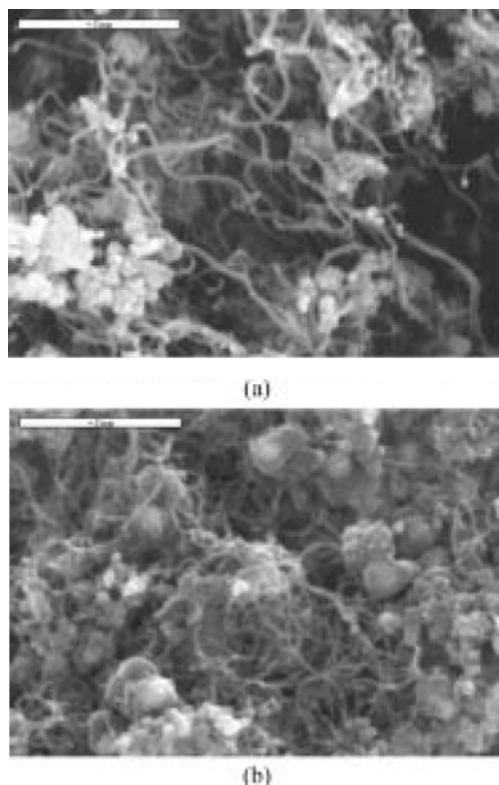


Fig. 1. SEM images of the CNTs grown over 20Fe : 20Ni : 60Al<sub>2</sub>O<sub>3</sub> catalyst for 1 h at 600 °C under 10/100 sccm of C<sub>2</sub>H<sub>2</sub>/H<sub>2</sub> flow after activating for (a) 5 min and (b) 1 h.

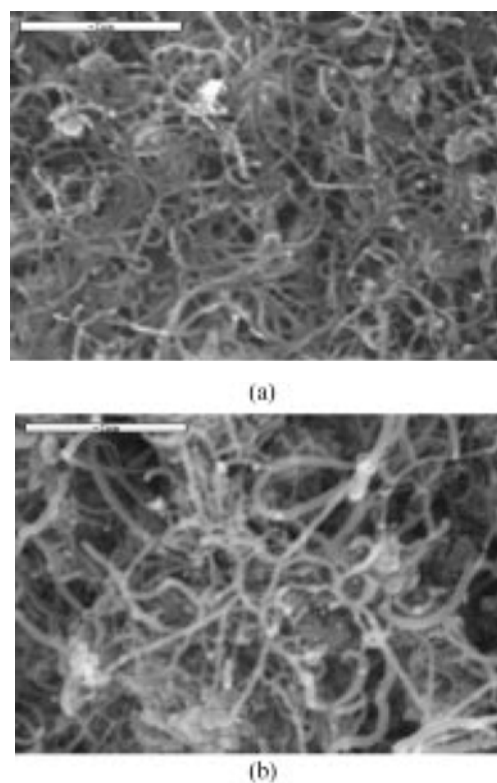
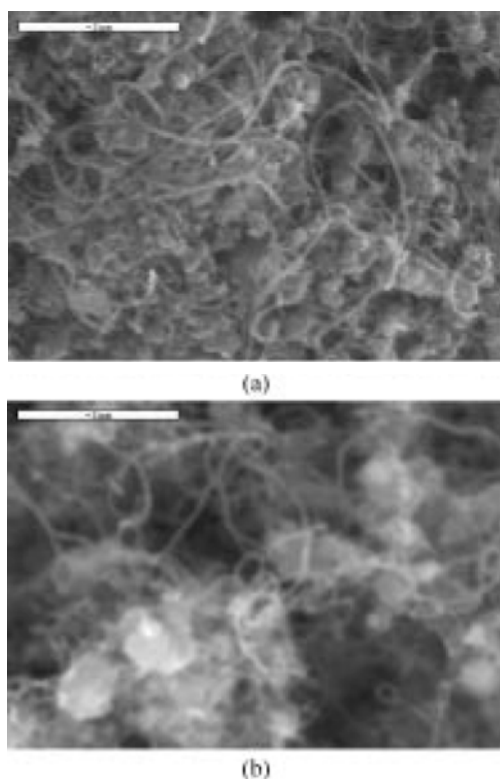


Fig. 2. SEM images of the CNTs grown over 1 h activated 30Fe : 10Ni : 60Al<sub>2</sub>O<sub>3</sub> catalyst for 1 h under 10/100 sccm of C<sub>2</sub>H<sub>2</sub>/H<sub>2</sub> flow at (a) 600 and (b) 700 °C.

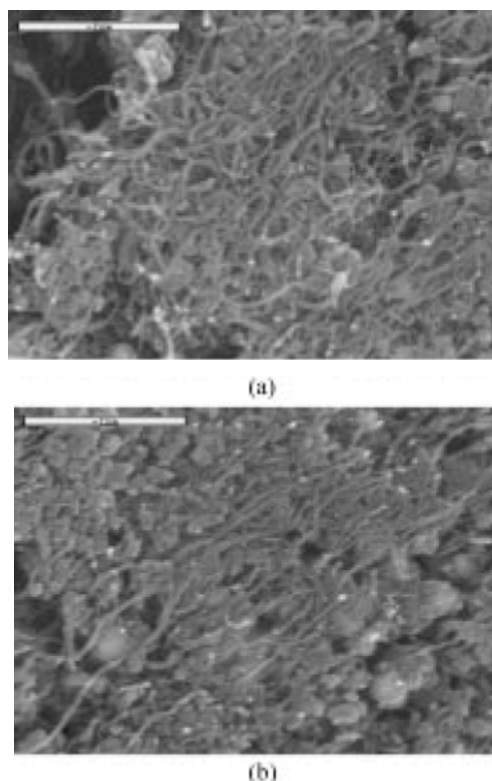


**Fig. 3.** SEM images of the CNTs grown over 1 h activated 30Fe : 10Ni : 60Al<sub>2</sub>O<sub>3</sub> catalyst at 600 °C under 10/100 sccm of C<sub>2</sub>H<sub>2</sub>/H<sub>2</sub> flow for (a) 0.5 h and (b) 1.5 h.

bably due to the coalescence of the metal particles that prefers the adsorption of carbonaceous species, leading to the deactivation of the metal surfaces. Such a non-tubular carbon species deposition was reported [Peigney et al., 1998] in the case of the CNTs growth over Fe-Al<sub>2</sub>O<sub>3</sub> catalysts using CH<sub>4</sub>/H<sub>2</sub> mixture during an increment of temperature from 900 to 1,000 °C. A complete cessation of the CNTs growth was also observed in the growth over Fe-Ni catalysts at about 725 °C using CO/H<sub>2</sub> mixture [Park et al., 1997].

Fig. 3(a) and (b) show SEM images of the CNTs grown over the same catalyst for 0.5 and 1.5 h, respectively. From the figures as well as Fig. 2(a), it may be seen that the growth density and length of CNTs highly increases with increasing the reaction time from 0.5 to 1 h and then markedly decreases at 1.5 h compared to that of 1 h. The decrease of CNT density at 1.5 h is unable to be clearly explained at this point. However, the above observations indicate that the reaction temperature and time have remarkable effect on the growth of CNTs, and the best growth temperature and time are 600 °C and 1 h, respectively.

Shown in Fig. 4(a) and (b) are SEM images of the CNTs grown over 30Fe : 10Ni : 60Al<sub>2</sub>O<sub>3</sub> catalyst at 600 °C and 1 h under 20/100 and 30/100 sccm of C<sub>2</sub>H<sub>2</sub>/H<sub>2</sub> flow rates, respectively. The tube density decreases with increasing C<sub>2</sub>H<sub>2</sub>/H<sub>2</sub> flow rate. Compared with the SEM image of the CNTs grown over the same catalyst under 10/100 sccm C<sub>2</sub>H<sub>2</sub>/H<sub>2</sub> flow [Fig. 2(a)], the growth density of CNTs also shows the same decreasing trend. It has been reported that the flow rate is one of the important factors in the CVD method for the growth of CNTs [Jiao et al., 1996]. The morphology of CNTs largely varies with changing the flow rate as well as the partial pressure



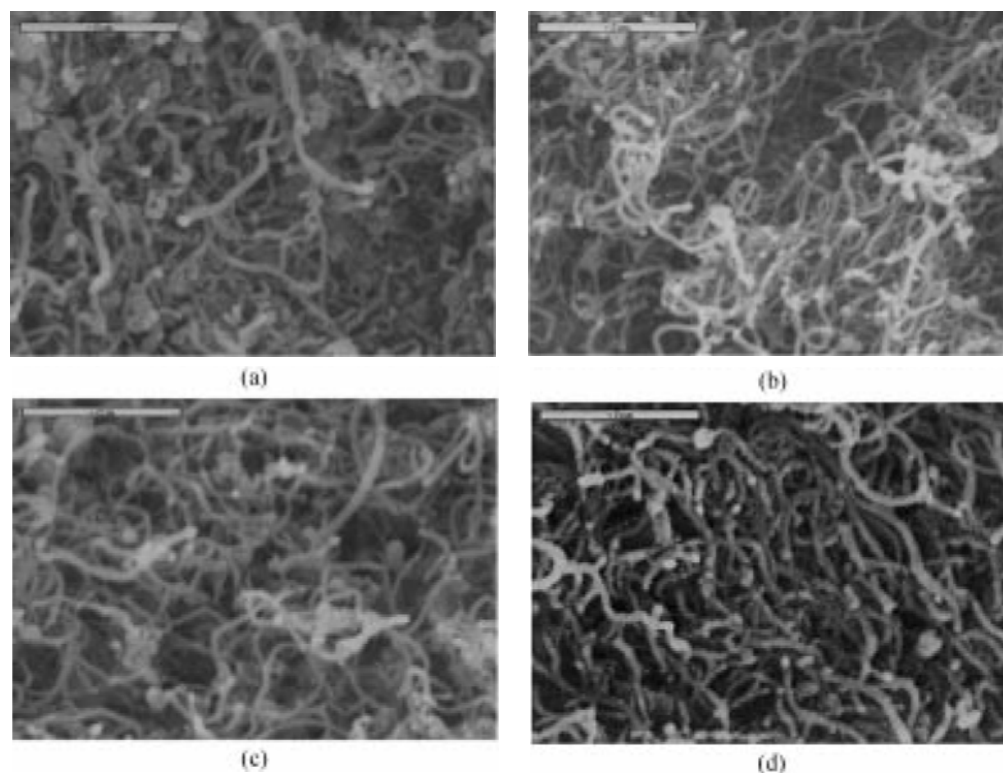
**Fig. 4.** SEM images of the CNTs grown over 1 h activated 30Fe : 10Ni : 60Al<sub>2</sub>O<sub>3</sub> catalyst for 1 h at 600 °C under (a) 20/100 and (b) 30/100 sccm of C<sub>2</sub>H<sub>2</sub>/H<sub>2</sub> flow.

of the reactants. At a given flow rate, the diameter of the CNTs increases with increasing the carbon source gas concentration [Choi et al., 2000]. In the present case, the increase of C<sub>2</sub>H<sub>2</sub> flow rate increased the total flow rate as well as C<sub>2</sub>H<sub>2</sub> concentration in the reactor since H<sub>2</sub> flow rate remained 100 sccm throughout the experiments. The observed SEM pictures revealed that the quantity of straight tubes with uniform diameter gradually increases with increasing the flow rate. But no remarkable change was observed in CNTs diameter although the C<sub>2</sub>H<sub>2</sub> concentration increased.

Consequently, the optimum growth condition of CNTs was identified to be a catalyst activation period of 1 h, reaction time of 1 h, growth temperature of 600 °C and C<sub>2</sub>H<sub>2</sub>/H<sub>2</sub> flow rate of 10/100 sccm. At this optimum condition, CNTs were thoroughly grown over other catalysts to compare the catalytic activity with each other. In order to obtain more clear information for the effect of growth time on the density of CNTs, besides this optimum condition, CNTs were thoroughly grown over all the catalysts (except 15Fe : 15Ni : 70Al<sub>2</sub>O<sub>3</sub> catalyst) after 1 h activation for 5 min, 0.5 and 1.5 h, respectively. The carbon yield (%) is compiled in Table 1 as a function of reaction time. The carbon yield was calculated by dividing the increased weight of the catalyst before and after the CNTs growth by the catalyst weight before the growth. From Table 1, it can be seen that for all the catalysts, the carbon yield (%) gradually increased with increasing reaction time except for the 10Fe : 30Ni : 60Al<sub>2</sub>O<sub>3</sub> catalyst at 1.5 h. The cause of the decrease in carbon yield (%) at 1.5 h over that of 1 h for 10Fe : 30Ni : 60Al<sub>2</sub>O<sub>3</sub> catalyst will be described later. The carbon yields (%) for the bimetallic catalysts are markedly higher than those for the single metal catalysts.

**Table 1.** Carbon yield (%) as a function of reaction time over different supported catalysts under a flow of 10/100 sccm  $C_2H_2/H_2$  mixture at 600 °C

Catalyst	Gas medium	Temp. (°C)	Carbon yield (%)			
			5 min	30 min	60 min	90 min
40Ni : 60Al <sub>2</sub> O <sub>3</sub>	C <sub>2</sub> H <sub>2</sub> /H <sub>2</sub>	600	3.09	6.86	11.34	22.83
40Fe : 60Al <sub>2</sub> O <sub>3</sub>	C <sub>2</sub> H <sub>2</sub> /H <sub>2</sub>	600	4.48	8.69	16.11	26.55
20Fe : 20Ni : 60Al <sub>2</sub> O <sub>3</sub>	C <sub>2</sub> H <sub>2</sub> /H <sub>2</sub>	600	10.74	34.48	60.26	74.85
30Fe : 10Ni : 60Al <sub>2</sub> O <sub>3</sub>	C <sub>2</sub> H <sub>2</sub> /H <sub>2</sub>	600	14.21	46.89	94.19	134.65
10Fe : 30Ni : 60Al <sub>2</sub> O <sub>3</sub>	C <sub>2</sub> H <sub>2</sub> /H <sub>2</sub>	600	7.55	20.49	39.39	37.18

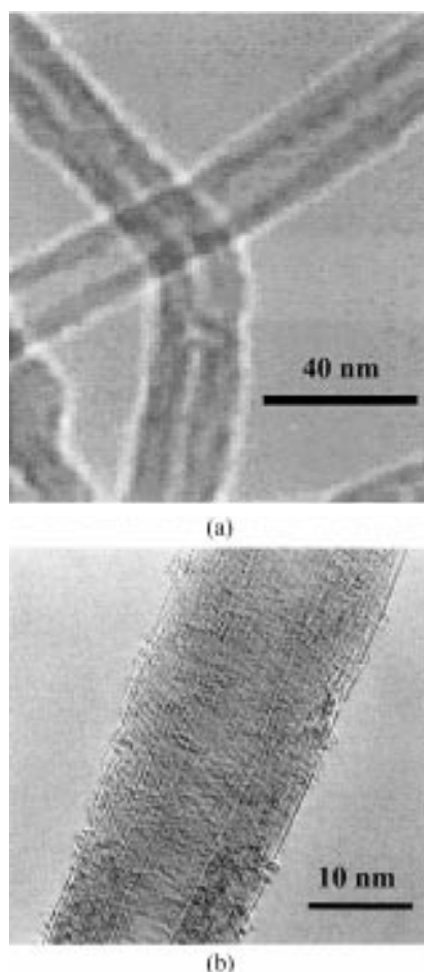
**Fig. 5.** SEM images of the CNTs grown for 1 h at 600 °C under 10/100 sccm of  $C_2H_2/H_2$  flow after 1 h catalyst activation over (a) 40Fe : 60Al<sub>2</sub>O<sub>3</sub>, (b) 15Fe : 15Ni : 70Al<sub>2</sub>O<sub>3</sub>, (c) 10Fe : 30Ni : 60Al<sub>2</sub>O<sub>3</sub> and (d) 40Ni : 60Al<sub>2</sub>O<sub>3</sub> catalysts.

Among the investigated catalysts, the catalytic activity of the 40Ni : 60Al<sub>2</sub>O<sub>3</sub> catalyst is the poorest, whereas that of 30Fe : 10Ni : 60Al<sub>2</sub>O<sub>3</sub> catalyst is the best.

Fig. 5(a), (b), (c), and (d) show SEM images of the CNTs grown for 1 h over 40Fe : 60Al<sub>2</sub>O<sub>3</sub>, 15Fe : 15Ni : 70Al<sub>2</sub>O<sub>3</sub>, 10Fe : 30Ni : 60Al<sub>2</sub>O<sub>3</sub> and 40Ni : 60Al<sub>2</sub>O<sub>3</sub> catalysts, respectively. It can be seen that CNTs are grown over all the catalyst surfaces. Comparing the findings regarding the density of CNTs grown for 1 h, as presented in Figs. 1, 2 and 5, it seems that the highest density CNTs were grown over 30Fe : 10Ni : 60Al<sub>2</sub>O<sub>3</sub> catalyst [Fig. 2(a)]. This indicates that the growth density of CNTs as seen in the SEM photographs can be fairly well correlated with the carbon yield (%) as the highest carbon yield (%) was obtained over the 30Fe : 10Ni : 60Al<sub>2</sub>O<sub>3</sub> catalyst (Table 1).

A close look at the SEM photographs revealed that the diameters of CNTs grown over different catalysts are different. In order to understand their diameters, we attempt to determine it for the CNTs grown over some catalysts by TEM and HRTEM. Fig. 6(a)

shows the TEM image of some CNTs grown over 30Fe : 10Ni : 60Al<sub>2</sub>O<sub>3</sub> catalyst at 600 °C [Fig. 2(a)]. The hollow appearance represents the fibrous nature of the grown CNTs and the average diameter of the tubes is about 30 nm. Fig. 6(b) shows the high resolution transmission electron microscopy (HRTEM, JEOL 2000EX) image of a CNT grown over 20Fe : 20Ni : 60Al<sub>2</sub>O<sub>3</sub> catalyst at 600 °C [Fig. 1(b)]. The tube consists of twenty-one graphite layers with a hollow. The interlayer spacing between the graphite platelets is 0.34 nm and the diameter of the tube is 20 nm that coincides with the diameter estimated from the SEM image [Fig. 1(b)]. In order to obtain more information on the density and diameter of CNTs grown over 20Fe : 20Ni : 60Al<sub>2</sub>O<sub>3</sub> catalyst, the specific surface areas of the 1 h activated catalyst before and after the growth of CNTs were measured by the Brunauer-Emmett-Teller (BET) method using N<sub>2</sub> adsorption at liquid nitrogen temperature [Peigney et al., 1997; Hong et al., 2000]. The measured surface areas of the catalyst before and after the growth of CNTs are 191.5 and 290.4 m<sup>2</sup>/g, respectively. The increase in surface area about 98.9 m<sup>2</sup>/g clearly indicates the

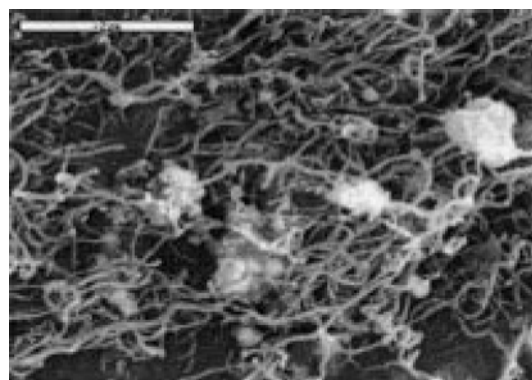


**Fig. 6.** (a) TEM images of CNTs grown over 30Fe : 10Ni : 60Al<sub>2</sub>O<sub>3</sub> catalyst and (b) HRTEM image of a CNT grown over 20Fe : 20Ni : 60Al<sub>2</sub>O<sub>3</sub> catalyst for 1 h at 600 °C under 10/100 sccm of C<sub>2</sub>H<sub>2</sub>/H<sub>2</sub> flow after activating for 1 h.

growth of CNTs. The measured value corresponds to the surface area of the grown CNTs and the calculated diameter of CNTs is 17.9 nm. It also indicates that it is possible to estimate almost true diameter of CNTs from SEM photographs. By following this idea, we estimated the diameters of CNTs grown over 40Fe : 60Al<sub>2</sub>O<sub>3</sub>, 10Fe : 30Ni : 60Al<sub>2</sub>O<sub>3</sub> and 40Ni : 60Al<sub>2</sub>O<sub>3</sub> catalysts. The diameters of CNTs determined from TEM, HRTEM, surface area measurement and estimated from SEM images are summarized in Table 2.

From Table 2, it can be seen that the narrowest diameter CNTs were grown over 20Fe : 20Ni : 60Al<sub>2</sub>O<sub>3</sub> catalyst. The diameters of the CNTs grown over bimetal catalysts are thoroughly narrower than those grown over single metal catalysts. This clearly indicates that both the density and diameter of CNTs can be controlled by using bimetallic catalysts.

In most of the cases, the density of CNTs grown for 1.5 h was



**Fig. 7.** SEM images of the CNTs grown for 1.5 h at 600 °C under 10/100 sccm of C<sub>2</sub>H<sub>2</sub>/H<sub>2</sub> flow after 1 h activation over 10Fe : 30Ni : 60Al<sub>2</sub>O<sub>3</sub> catalyst.

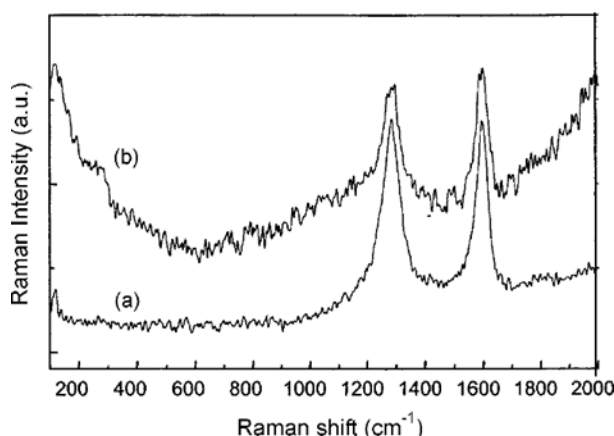
markedly lower than that for 1 h. In case of single metal catalysts, the effect of longer reaction time on CNT density was much severer. However, the addition of iron with nickel and vice versa (30Fe : 10Ni, 20Fe : 20Ni and 10Fe : 30Ni) created dramatically different behavior of the CNT growth. In case of 10Fe : 30Ni : 60Al<sub>2</sub>O<sub>3</sub> catalyst, the growth density (Fig. 7) is comparable with that for 1 h growth time [Fig. 5(c)] although the diameter of the CNTs grown for 1.5 h is narrower than that for 1 h, reaching 20 nm. The appearance of such narrow tubes with similar tube density is responsible for decreasing the carbon yield (%) of this catalyst during increasing the growth time from 1 h to 1.5 h (Table 1).

The decrease of CNT density and diameter at 1.5 h reaction time indicates that there might be some other factors that have important impacts on the growth of nanotubes. The most probable effect might be hydrogen etching during the growth. Recently, the authors [Choi et al., 2000] have investigated the hydrogen etching effect on the diameter and length of CNTs grown over nickel thin films under CH<sub>4</sub>/H<sub>2</sub> mixture when increasing the reaction time. The nanotube diameter decreased almost in a linear fashion with the time, for example, from 70 nm to 20 nm when the growth time was extended from 50 to 100 min. For lower hydrogen concentrations, however, the etching effect significantly decreased. In the present case, high hydrogen concentration probably imparted a severe etching effect. Therefore, this etching behavior indicates that smaller diameters of CNTs can be synthesized by controlling reaction time under appreciable hydrogen flow.

Fig. 8(a) and (b) show FT-Raman spectra of the CNTs grown over 10Fe : 30Ni : 60Al<sub>2</sub>O<sub>3</sub> catalyst for 1 h and 1.5 h [Fig. 5(c) and 7], respectively, with the excitation wavelength of 1,064 nm (Nd : YAG laser). The spectra clearly show two strong peaks. Both the peaks (E<sub>g</sub> mode) at 1,593 cm<sup>-1</sup> [Fig. 8(a)] and 1,597 cm<sup>-1</sup> [Fig. 8(b)] are due to the formation of graphitized CNTs [Rao et al., 1997]. The peak at around 1,284 cm<sup>-1</sup> (A<sub>g</sub> mode) indicates the presence of amorphous carbonaceous particles on the CNT walls [Choi et

**Table 2.** Diameter (d) of CNTs grown over different catalysts at 600 °C under 10/100 sccm of C<sub>2</sub>H<sub>2</sub>/H<sub>2</sub> flow for 1 h (A is representing Al<sub>2</sub>O<sub>3</sub>)

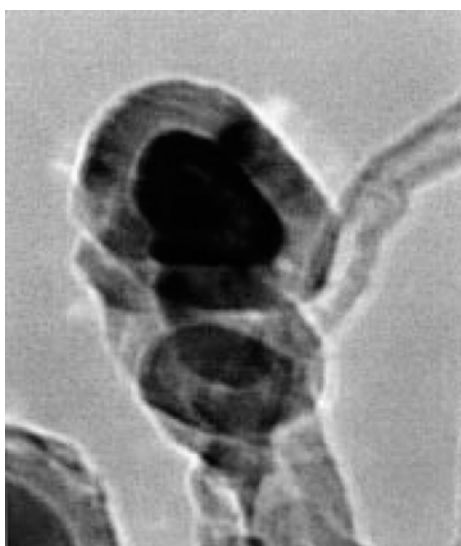
Catalyst:	40Ni : 60A	20Fe : 20Ni : 60A	30Fe : 10Ni : 60A	10Fe : 30Ni : 60A	40Fe : 60A
d (nm):	55-60	18-20	30	40-45	50-55



**Fig. 8.** FT-Raman spectra of the CNTs grown over 10Fe : 30Ni : 60Al<sub>2</sub>O<sub>3</sub> catalyst for (a) 1 h and (b) 1.5 h.

al., 2000]. It can be seen from Fig. 8 that the Raman scattering intensities of Eg mode peaks are not much changed with the growth time, whereas that of Ag mode are markedly decreased with increasing the growth time. These findings support that amorphous carbon particles adhering to the CNT walls were etched by hydrogen and resulted in the decrease of CNTs diameter as found in SEM images. In comparison with the FT-Raman spectra reported for single-wall nanotubes (SWNTs) [Rao et al., 1997] and multi-wall nanotubes (MWNTs) [Choi et al., 2000; Ando et al., 2000], the present observed result coincides with that of MWNTs because the Eg mode peak has no shoulder peaks, and no peak for radial breathing mode (RBM) appears at around 180 cm<sup>-1</sup>. The FT-Raman findings coincide with that observed by HRTEM image [Fig. 6(b)] that in the present study MWNTs was grown over the catalyst surfaces.

In each case of the SEM picture, it seems that metal particles are positioned at the tips of the nanotubes, as can be seen by the white spots in the SEM photographs. Fig. 9 shows the HRTEM image of



**Fig. 9.** HRTEM image of the metal tip of a CNT grown over 20Fe : 20Ni : 60Al<sub>2</sub>O<sub>3</sub> catalyst for 1 h at 600°C under 10/100 sccm of C<sub>2</sub>H<sub>2</sub>/H<sub>2</sub> flow after activating for 1 h.

the metal tip of a CNT grown over 20Fe : 20Ni : 60Al<sub>2</sub>O<sub>3</sub> catalyst. This shows that the growth of the CNTs followed the tip growth mode [Amelinckx et al., 1995], where the lengthening of CNTs occurred by lifting off the metal particles from the alumina support. The necessary carbon feedstock, of course, came from the catalytic decomposition of acetylene, which is dissolved in metals, oversaturated, diffused, and precipitated on the rear surfaces of metal particles generating the CNTs, as suggested in our previous report [Mo et al., 2000].

## CONCLUSION

Multi-wall carbon nanotubes were grown over Fe, Ni and Fe-Ni bimetallic catalysts supported on alumina using catalytic decomposition of acetylene at various controlled conditions. This work established how to control the growth density and diameter of CNTs by varying catalyst composition as well as by adjusting the catalyst activation time, reaction temperature and time, and gas flow rate of carbon source. For Fe-Ni bimetallic catalysts supported on alumina, the optimum growth condition of CNTs was identified to be a catalyst activation period of 1 h, reaction time of 1 h, growth temperature of 600 °C and C<sub>2</sub>H<sub>2</sub>/H<sub>2</sub> flow rate of 10/100 sccm. The diameters of the CNTs grown over bimetal catalysts are thoroughly narrower than those grown over single supported metal catalysts, indicating that both the density and diameter of CNTs can be controlled by using bimetal catalysts. It was considered that the diameter and density of CNTs decreased with the increase of the growth time mainly due to hydrogen etching and the growth of CNTs followed the tip growth mode.

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