Effect of Inert Particles on the Synthesis of Carbon Nanotubes in a Gas-Solid Fluidized Bed Reactor

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Abstract: The effects of the gas flow rate (2,000 ∼ 4,000 sccm), catalyst amount (10 ∼ 50 g), and static bed height (H_S) of the inert particles (0 ∼ 0.10 m) on the physical properties (tube diameter, I_D/I_G ratio, carbon yield, and volume expansion) of multi-walled carbon nanotubes (MWCNTs) in a gas-solid fluidized bed (0.056 m-ID × 1.0 m-high) reactor were determined. Agglomerated MWCNTs were synthesized by pyrolysis of acetylene on Fe/Mo/Al_2O_3 catalyst in a gas-solid fluidized bed reactor. The physical properties of the MWCNTs were determined by HR-TEM, SEM, and Raman spectroscopy. The MWCNTs synthesized at 873 K had an outer diameter of a few tens of nanometers. The MWCNTs produced from the inert medium fluidized bed reactor were entangled sub-aggregates with an average diameter of 15 ∼ 20 nm. Although carbon nanotubes (CNTs) could not be synthesized well at a very low gas velocity, they could be synthesized well when inert medium particles were added into the reactor, and the average CNT diameter varied with respect to the gas velocity. Volume expansion of the synthesized CNTs after completion of the reaction decreased with increasing H_S. However, the carbon yield of acetylene was not significantly changed with increasing H_S. Volume expansion of the CNT agglomerates and the carbon yield of acetylene decreased with increasing catalyst amount.

Keywords: carbon nanotube, catalyst, scanning electron microscopy, Raman spectroscopy, particle size

Introduction

Carbon nanotubes (CNTs) are a form of carbon allotrope that was first recognized as a by-product in fullerene production [1]. Much research has been conducted to determine the CNT characteristics because of their excellent structural, electrical, mechanical, electromechanical, and chemical properties [2,3]. Several techniques have been developed to synthesize CNTs, including electric arc discharge, laser evaporation, and catalytic chemical vapor deposition (CCVD) through the decomposition of hydrocarbons. Commonly, the CNTs that are grown at high density in a line where a catalyst is placed on a silicon wafer or glass substrate in a horizontal quartz reactor are synthesized well by the chemical vapor deposition (CVD) method [4]. However, whereas such a horizontal CVD reactor can produce only a limited amount of CNT, ca. 2 kg/day can be produced in a fluidized bed reactor [5-7].

With conventional gas-solid fluidization, it is extremely difficult to fluidize ultra-fines because inter-particle attraction forces the particles to adhere tightly to each other in all directions, an effect which may play a significant role in the synthesis of CNTs in a fluidized bed reactor. This adherent force brings the carbon from the carbon source into contact with the catalyst [8]. In a fluidized bed reactor, a large quantity of a high-surface-area precursor powder is in good contact with the reactant gas by fluidizing fine powders compared to the catalyst amount on a small boat in the horizontal CVD reactor, which enables the production of large quantities of CNTs [9]. For large-scale production of CNTs, a fluidized bed reactor can be utilized as an alternative to avoid obstruction of...
Table 1. Literature Summary of Synthesis of CNTs by Catalytic Chemical Vapor Deposition (CCVD) in a Fluidized-bed Reactor

<table>
<thead>
<tr>
<th>Investigator</th>
<th>Reaction conditions</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Venegoni and coworkers [15]</td>
<td>nd × 28, C₂H₄, Fe/SiO₂, 1023</td>
<td>MWCNT (10 ~ 20 nm) was synthesized. At higher temperature, deposition yields decrease, due to catalyst particles sintering.</td>
</tr>
<tr>
<td>Wang and coworkers [8]</td>
<td>1000 × 250, C₂H₂, C₃H₆, Fe/SiO₂/Al₂O₃, 923</td>
<td>Provides 70 ~ 80 % MWCNTs with a high production rate of 50 kg/day.</td>
</tr>
<tr>
<td>Mauron and coworkers [9]</td>
<td>1000 × 53, C₂H₄, Fe/Al₂O₃, 773–1123</td>
<td>For temperatures of 773 ~ 973 K, MWCNT was synthesized; for temperatures of 973 ~ 1123 K, SWNT was synthesized.</td>
</tr>
<tr>
<td>Perez-Cabero and coworkers [10]</td>
<td>1200 × 22, C₂H₄, Fe/SiO₂, 973</td>
<td>Catalyst become more active in acetylene decomposition at higher iron contents</td>
</tr>
<tr>
<td>Corrias and coworkers [21]</td>
<td>1000 × 53, C₂H₂, Fe/Al₂O₃, 923</td>
<td>Carbon yield often exceed 95; nanotubes selectivity is close to 100 %</td>
</tr>
<tr>
<td>Son and coworkers [11]</td>
<td>1000 × 50, C₂H₂, Fe/SiO₂/Al₂O₃, 873</td>
<td>The MWCNTs produced are agglomerated and entangled with each other from the fluidized bed reactor.</td>
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</tbody>
</table>

nd: Not defined

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Figure 1. Schematic diagram of the experimental setup.

Figure 1. Schematic diagram of the experimental setup.

When CNTs are synthesized in fluidized beds, the final volume of the carbon product is increased by a few times (up to a few dozen) relative to the size of the original catalyst. Therefore, the amount of initial catalyst in the beds must be restricted to a very small quantity. However, when the static bed height, H_s, is smaller than the inside diameter of the reactor, i.e., a shallow bed, fluidization performance is generally poor unless the supplied gas velocity is sufficiently higher than the minimum fluidization velocity (U_{mf}). To avoid this problem, inert particles with high thermal resistance can be added to increase the static bed height (H_b). Generally, a fluidized bed dryer with inert particles can be used for slurry drying of the fine particles. This method is a very attractive alternative to the other drying technologies in improving the overall heat and mass transfer coefficients with uniform fluidization [12,13]. More-effective catalysts for CNT growth are iron (Fe), cobalt (Co), and nickel (Ni); their activity for CNT crystallinity follows the order: Fe > Ni > Co. The CNT growth rate indicates that the performance of these catalysts is in the following order: Ni > Co > Fe [14].

Therefore, in this study, the effects of the gas flow rate (2,000 to 4,000 sccm), catalyst amount (10 ~ 50 g), and H_s (0 ~ 0.10 m) on the physical characteristics (tube diameter, I_D/I_G, carbon yield, and volume expansion) of MWCNTs in a gas-solid fluidized bed reactor (0.056 m-ID × 1.0 m-high) were determined.

**Experimental**

A schematic diagram of the experimental setup is shown in Figure 1. The main column was made of a stainless-steel pipe (0.05 m-ID × 1.0 m-high). At the bot-
Table 2. Physical Properties of the Catalyst and Inert Medium Particles

<table>
<thead>
<tr>
<th></th>
<th>Fe-catalyst (Al2O3)</th>
<th>Inert medium particle (Al2O3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean particle diameter</td>
<td>114.3 µm</td>
<td>63 µm</td>
</tr>
<tr>
<td>Effective particle density</td>
<td>2,883 kg/m³</td>
<td>3,980 kg/m³</td>
</tr>
<tr>
<td>Bulk density</td>
<td>1,580 kg/m³</td>
<td>1,594 kg/m³</td>
</tr>
<tr>
<td>Minimum fluidization velocity</td>
<td>0.014 m/s</td>
<td>0.017 m/s</td>
</tr>
</tbody>
</table>

Figure 2. Temperature variation inside the reactor (H₂: 0.1 m; total volumetric flow rate: 3,000 sccm; N₂/H₂/C₂H₂ gas ratio: 1/4/1; reaction time: 2 h; reaction temperature: 873 K).

The mean particle diameters of both the Fe/Mo/Al₂O₃ catalysts and alumina as the inert particles were 114.3 and 63 µm, respectively. The experimental conditions were fixed at a reaction temperature of 873 K, reaction time of 2 h, gas ratio of N₂ : H₂ : C₂H₂ at 1 : 4 : 1, and volumetric acetylene flow rate of 500 sccm, with a variable total volumetric flow rate. The total volumetric gas flow rate at the standard conditions, catalyst amount, and H₂ of the inert particles ranged from 2,000 to 4,000 sccm, 10 to 50 g, and 0 to 0.1 m, respectively.

The experimental procedure was as follows. A mixture of catalyst and inert particles was loaded inside the reactor above the gas distributor; N₂ and H₂ gases were supplied at the desired flow rates until the reaction temperature was achieved. Then, a mixture of acetylene, hydrogen, and nitrogen was added to the reactor. When the reaction time had elapsed, the supply of acetylene and hydrogen was stopped, the power supply to the furnace was turned off, and the reactor was purged with nitrogen until the temperature of the reactor reached room temperature. Then, the reactor was dismantled and the products were collected. Hydrogen was constantly supplied until the reaction temperature was reached, because H₂ activates the catalyst by reduction [15]. The collected carbon materials were analyzed by FE-TEM (JEM 2100F), FE-SEM (JSM-7000F), and FT-Raman spectroscopy (FRA 106/S).

The temperature profiles at two points in the bed are shown in Figure 2: 0.05 m above the gas distributor and under the gas distributor, which was maintained at 873 K during the reaction period.

The SEM and X-ray mapping images of Al and Fe ingredients by EDS of the Fe/Mo/Al₂O₃ catalyst and the SEM image of the inert particles are shown in Figure 3. Dispersion of the deposited metallic particles on the catalyst support (alumina) was characterized using the EDX mapping technique. The Fe ingredient acting as the active site was well distributed over the catalyst support of Al₂O₃ (Figures 3b and 3c). Figure 3(d) shows the SEM image of inert Al₂O₃ particles with irregular shapes and a wide size range of 20 to 100 µm. Successful CNT syntheses started when the fluidizing gas velocity exceeded Uₘ₉ with good heat and mass transfers. The Uₘ₉ values of the Fe-catalyst and the inert particles were 0.014 and 0.017 m/s, respectively. Therefore, the total gas flow rate for this experiment was determined to be within the range from 2,000 (U₉ = 0.031 m/s) to 4,000 (U₉ = 0.062 m/s) sccm at 873 K.

Results and Discussion

The SEM and TEM images of the CNTs synthesized...
Figure 3. (a) SEM image of Fe-catalyst, (b) X-ray mapping image of Fe elements, (c) X-ray mapping image of Al elements, (d) SEM image of inert medium particles (Al₂O₃), and (e) EDX spectrum of Fe-catalyst.

Figure 4. (a) SEM and (b) TEM images of CNTs synthesized with inert particles (H₂: 0.1 m; catalyst amount: 30 g; total volumetric flow rate: 3,000 sccm; N₂/H₂/C₂H₂ gas ratio: 1/4/1; reaction time: 2 h; reaction temperature: 873 K).

The CNTs were synthesized with inert particles, H₂ of 0.1 m, catalyst of 30 g, a reaction time of 120 min, a reaction temperature of 873 K, a volumetric flow ratio of N₂/H₂/C₂H₂ set at 1/4/1, and a total volumetric flow rate of 3,000 sccm. As can be seen in Figure 4(b), MWCNTs with a tube diameter of 15 ∼ 20 nm were synthesized. When the CVD synthesis method was employed, synthesis of pure CNTs without amorphous carbon was impossible; in particular, when acetylene was used as a carbon source, considerable amounts of carbon nanofibers were also produced at 823 ∼ 973 K [16,17].

Figure 5 shows a conceptual scheme based on the schematic mechanism of a model for CNT agglomerate formation suggested by Yu and coworkers [18]. When the catalyst reacts with decomposed carbon at higher temperatures, the catalyst particles break due to CNT growth at the active site and then the CNT agglomerate volume gradually expands. The general result after reaction completion is shown in Figure 5, where CNTs are entangled with each other to form a huge lump. This lump is called the CNT agglomerate, where CNTs near the surface grow. However, the CNT product of the present experiment using inert particles showed that CNTs near the sur-
face were laid down horizontally, as shown in Figure 4(a) and as shown conceptually in Figure 5(d). A relatively large amount of carbon particles was decomposed from the acetylene that was deposited on the particle surface. However, the ratio between the Raman intensity (I_D) of the amorphous carbon of the synthesized CNT product and the Raman intensity (I_G) of the crystalline structured carbon atom (I_D/I_G) obtained under identical conditions without inert particles was 1.42, while the same ratio (I_D/I_G) of the CNTs produced in the reaction with inert particles at a value of H_s of 0.1 m was 1.29. A comparison of these ratios indicates that the impure content was slightly lower when the inert particles were used. It was presumed from this result that the carbon source does not interfere with the surface of the CNT growth, even if the surface of the CNT agglomerate grows horizontally through physical contact with the inert particles, because it continuously permeates to the inside of the CNT agglomerates.

Low- and high-resolution SEM images of the CNTs synthesized with and without inert particles are shown in Figure 6. The SEM image of the CNT agglomerate synthesized without inert particles, shown in Figure 6(a), presents a very irregular and rough surface. However, the SEM image of the CNT agglomerate synthesized with the inert particles, shown in Figure 6(c), presents a surface that is fairly regular and smooth. Figure 6(d) shows the SEM image of the surface of Figure 6(c) where the grown CNTs can be seen to be lying down, presumably due to bumping with inert particles of relatively higher density.

Figures 7(a), (b), and (c) show the SEM image of the product, and the TEM image of the carbon particles and carbon fibers which are synthesized massively without growing CNT, respectively [11]; carbon impurities are lumped together over a size range of a few mm to a few
Figure 7. (a) Photograph, (b) SEM image, and (c) TEM image of the product formed without inert particles and (d) photograph, (e) SEM image, and (f) TEM image of the product formed with inert particles (volumetric flow rate: 2,000 sccm; reaction temperature: 873 K; reaction time: 120 min).

Table 3. Carbon Yield of Carbon Source, Volume Expansion, and CNT Diameter at Different Volumetric Flow Rates with Inert Particles (Reaction Temperature: 873 K; Catalyst Amount = 30 g; Hs = 0.1 m; Reaction Time: 120 min; N2/H2/C2H2 Gas Ratio = 1/4/1).

<table>
<thead>
<tr>
<th>Flow rate (sccm)</th>
<th>2,000</th>
<th>3,000</th>
<th>4,000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon yield (%)</td>
<td>19.1</td>
<td>31.6</td>
<td>26.6</td>
</tr>
<tr>
<td>Volume expansion (%)</td>
<td>379.1</td>
<td>846.0</td>
<td>912.5</td>
</tr>
<tr>
<td>CNT diameter (nm)</td>
<td>50.4</td>
<td>15.4</td>
<td>16.9</td>
</tr>
<tr>
<td>ID/IG [-]</td>
<td>1.57</td>
<td>1.48</td>
<td>1.52</td>
</tr>
</tbody>
</table>

*) Carbon yield = \( \frac{\text{mass of final product} - \text{mass of initial catalyst}}{\text{mass of total carbon source fed}} \)

**) Volume expansion = \( \frac{\text{final CNT vol. - initial catalyst vol.}}{\text{initial catalyst vol.}} \)

cm, Figures 7(d), (e), and (f) show the actual image of the CNT products and SEM and TEM images of the product, respectively, with 312.8 g (Hs = 0.1 m) of inert particles at a volumetric flow rate of 2,000 sccm. As can be seen in Figure 7(d), the white part consists of the inert particles that are mixed with the produced CNT agglomerate. The product at this time did not form lumps bigger than a few mm in size and the average diameter of the CNT agglomerates was 318 µm. As can be seen in Figure 7(e), CNTs with a diameter of 20 nm and carbon fibers with a diameter of 100 nm were synthesized simultaneously within the CNT agglomerate. When inert particles were not mixed, carbon materials formed early on the catalyst that was entangled with other carbon materials, resulting in the formation of large lumps; a higher gas velocity (above \( U_{mf} \)) was required to separate the agglomerates entangled by CNT growth. However, when the inert particles were mixed, the direct contact frequency among the catalyst particles decreased and the movement of the inert particles may have torn them up, resulting in the production of uniform, small-sized CNT agglomerates.

The results of the synthesis experiment with the inert particles at different volumetric flow rates are shown in Table 3. In these cases, the volumetric flow rate of acetylene was fixed at 500 sccm. The carbon yield was 31.6 % at a total volumetric flow rate of 3,000 sccm, but was reduced by 40 % to only 19.1 % at 2,000 sccm, whereas it was 29.8 % at 4,000 sccm. These carbon yields might indicate that the particle fluidization was relatively lower at 2,000 sccm than at 3,000 or 4,000 sccm, and, thus, the frequency of contact among the catalysts and acetylene was decreased. In addition, the volume expansion increased upon increasing the total volumetric flow rate and this effect further improved the fluidization quality. The CNT diameter was a maximum of 50.4 nm at 2,000 sccm because the particle fluidization and the heat and mass transfer rates at 2,000 sccm were relatively lower than those at 3,000 and 4,000 sccm. Kang and coworkers [3] also reported that the nanotube diameter decreased and the length increased with increasing gas flow rate.
The physical properties (Raman spectra, carbon yield of acetylene, volume expansion, average size of agglomerate, and mean tube diameter) of the CNTs synthesized with different values of $H_S$ are shown in Figure 8. As can be seen in Figure 8(a), the $I_D/I_G$ ratios of the CNTs synthesized with various $H_S$ ranged from 1.29 to 1.53, which was not a significant increase. Although the carbon yield of acetylene was slightly decreased at a value of $H_S$ of 0.05 m, there was no relationship between the value of $H_S$ of the inert particles and the acetylene carbon yield. As can be seen in Figures 8(b) and (c), the volume expansion, mean tube diameter, and agglomerate size of the synthesized CNTs decreased with increasing $H_S$ as a result of attrition of the inert particles.

Raman spectra, carbon yields of acetylene, volume expansions, average agglomerate sizes and mean tube diameters of the CNTs synthesized with different amounts of catalyst are shown in Figure 9. As can be seen in Figure 9(a), the $I_D/I_G$ ratios of the CNTs synthesized with different catalyst amounts ranged from 1.26 to 1.46. The $I_D/I_G$ ratios of the synthesized CNTs did not significantly vary with increasing catalyst amount. As can be seen in Figure 9(b), the carbon yield of acetylene and volume expansion of the synthesized CNTs decreased with increasing catalyst amount. This result is contrary to a general notion that the conversion of the carbon source will increase with increasing catalyst amount. Chen and coworkers [19] reported that the increase of the catalyst amount slightly enhanced the methane conversion, but the carbon yield based on the catalyst amount decreased with increasing catalyst amount as a result of diffusion limitation on the catalyst's surface occurring in this reaction conditions. The test run (CNT-12) of Table 3 by Chen and coworkers [16] indicated that the methane conversion and carbon yield decreased with increasing catalyst amount for a constant methane flow rate at 100 cm$^3$/min. Lee and coworkers [14] reported that the growth rate of CNT was almost constant during growth for 30 min, but it decreased significantly after 40 min when the carbonaceous particles covered the surface of metal particles. These results might suggest that the carbon yield of the synthesized CNTs decreased with increasing catalyst amount because of catalytic deactivation. Further work is required to confirm the effect of the
The mean tube diameter of the synthesized CNTs might be related to the active catalyst size. Figure 9(c) indicates that there is no relationship between the catalyst amount and the mean tube diameter of the CNTs.

**Conclusions**

CNT agglomerates synthesized using inert particles were shown to have horizontally oriented structures and mean tube diameters ranging from 15 to 20 nm. In the absence of the inert particles, CNTs were not synthesized at a volumetric flow rate of 2,000 sccm, whereas under the corresponding conditions (\( U_g = 0.031 \text{ m/s} \) at 873 K and \( U_{m} = 0.017 \text{ m/s} \)) CNTs were synthesized effectively in the presence of inert particles in the fluidized beds. The size and volume expansion of the CNT agglomerates decreased with increasing HS of the inert particles. However, the intensity ratio of I_D/I_G did not change with increasing HS. The volume expansion of the CNT agglomerates and the carbon yield of acetylene decreased with increasing catalyst amount. Further work is, however, required to confirm the effect of the catalyst amount on the carbon yield. There was no relationship between the catalyst amount and the mean tube diameter of the CNTs.

**Nomenclature**

- \( d_p \) : mean particle diameter [\( \mu \text{m} \)]
- \( H_S \) : static bed height [m]
- \( I_D \) : intensity of D peak in Raman Spectra [-]
- \( I_G \) : intensity of G peak in Raman Spectra [-]
- \( U_g \) : superficial gas velocity [m/s]
- \( U_{mf} \) : minimum fluidization velocity [m/s]
- \( \rho_s \) : effective particle density [kg/m³]
- \( \rho_{bulk} \) : bulk density [kg/m³]

**Greek Letters**

- \( \rho_s \) : effective particle density [kg/m³]
- \( \rho_{bulk} \) : bulk density [kg/m³]

**References**