

Synthesis of Carbon Nanotubes from Catalytic Decomposition of C₂H₂ through Pd/Al₂O₃ Catalysts

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CNTs have been synthesized by catalytic C₂H₂ decomposition through Pd/Al₂O₃ at low temperature. The CNTs were grown to a length of about 10 μm and diameter 150–200 nm with multiwalled structure. Pd catalysts have two major roles; one is the active catalyst for C₂H₂ decomposition, the other is a nucleation site of CNT's growth.

Key Words : Carbon nanotubes, C₂H₂, Pd/Al₂O₃, CVD, Decomposition

Introduction

Recently, carbon nanotubes (CNTs) have attracted a great deal of attention with nano materials consisting of particles with diameter less than 100 nm as an essential component of nanotechnology.^{1,2} Since CNTs were first observed in 1991,³ CNTs have been studied for many applications, such as electronics, mechanics, display and energy, and hydrogen storage because of their particular mechanical and electronic properties.

CNTs can be produced by arc discharge,⁴ laser-ablation,⁵ or by plasma-enhanced chemical vapor deposition (PECVD),⁶ or thermal chemical vapor deposition.⁷ A technique of synthesis by catalytic decomposition of hydrocarbons was recently reported in which hydrocarbons are decomposed directly into hydrogen and carbon. CNTs were synthesized by decomposition of C₂H₂ using Fe-Mo catalysts at 950 °C.⁸ Additionally, Youngdan Li *et al.* reported the production of hydrogen and nanocarbon by decomposition of methane on a nickel-based catalyst.⁹ In that method, it was difficult to have high productivity at low temperature and to separate metal particles from CNTs. In addition, iron, nickel, and cobalt were usually used as the nucleation site of CNT's growth.

Generally catalytic decomposition of hydrocarbons is the method for producing a pure hydrogen stream from natural gas.¹⁰ Hydrocarbons are cracked directly into hydrogen and carbon. Catalysts used in that experiment promote the complete decomposition of hydrocarbons and improve the energy efficiency of the process.¹¹ Most catalysts for decomposition of hydrocarbons were noble metals. Among the noble metal catalysts, supported palladium has been recognized as the most active catalyst for methane combustion with thermal stability.^{12,13}

In this paper we use CNT synthesis from catalytic decomposition of C₂H₂ through Pd/Al₂O₃ catalyst.

Experimental Procedures

Preparation of the catalyst. Pd(NO₃)₂·6H₂O was dissolved in distilled water and alumina granuals (3 mm dia.) added to the aqueous solution of a palladium nitrate.

The loaded supports were dewatered and dried at 120 °C for 6 hr. The supported catalysts were calcined at 400 °C for 3 hr with flowing O₂ gas in order to eliminate impurities adsorbed on supported catalysts and finally the sample of catalyst precursor was obtained.

Preparation of carbon nanotubes. Figure 1. shows a schematic diagram of the experimetal system. The reactor consists of a 30 mm o.d × 70 cm long quartz tube. The reactor was heated by an electrical tube furnace and was controlled to ± 1 °C by the temperature controller. To eliminate oxygen in C₂H₂ gases, the adsorbent was put on the front of quartz tube. The catalyst bed supported on stainless steel gauze was placed in the center of the furnace. In order to eliminate all chemisorbed water, catalysts were reduced in flowing H₂ (50 mL/min) for 1 hr at 650 °C.

The flow rate of gases was controlled by mass flow controllers (MFCs). Then C₂H₂ gas was introduced to the quartz tube with a flow rate of 30 sccm for 20 min at 650 °C and 950 °C. Then the reactor was cooled to room temperature with flowing Argon gas.

The CNTs were examined by scanning electron microscope (SEM) (Hitachi S-4300), thermal analyzer (Rheometric Scientific STA1500), transmission electron microscopy (TEM) (JEOL JEM3010) and Raman spectrometer (Renishaw micro raman).

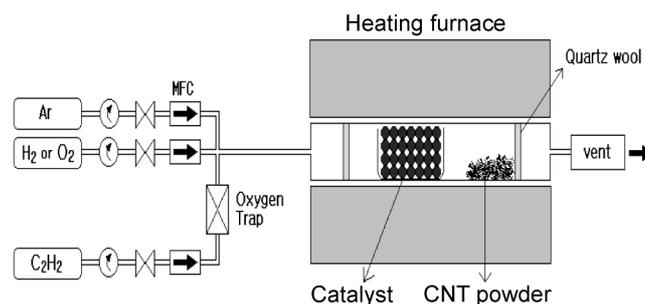
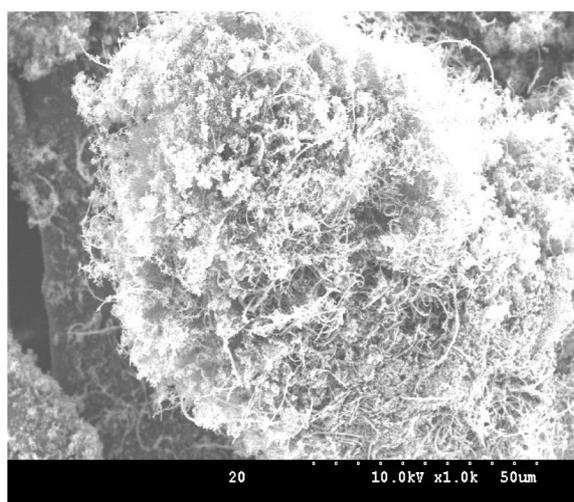
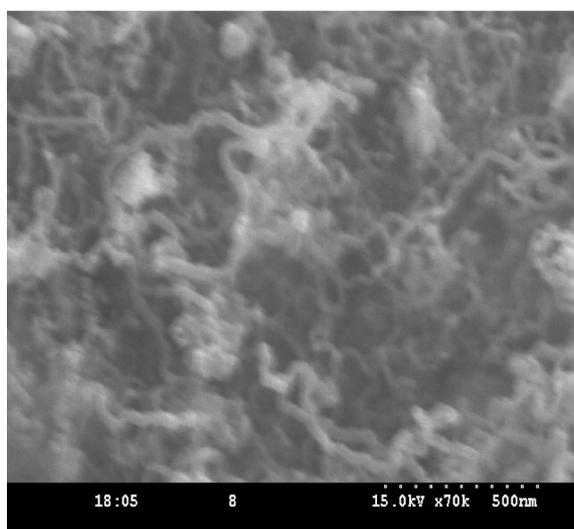


Figure 1. Experimental setup used for synthesis of CNTs.

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(A)



(B)

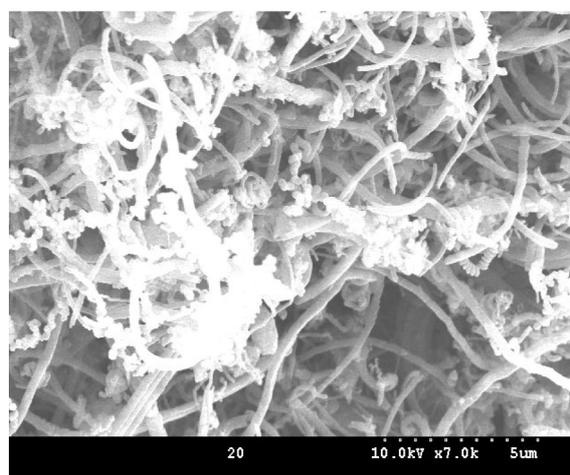
Figure 2. SEM image of CNTs on Pd/Al₂O₃ catalysts grown by decomposition of C₂H₂ at 650 °C, (b) Magnified view of CNTs which are in the range dia. 15-25 nm.

Results and Discussion

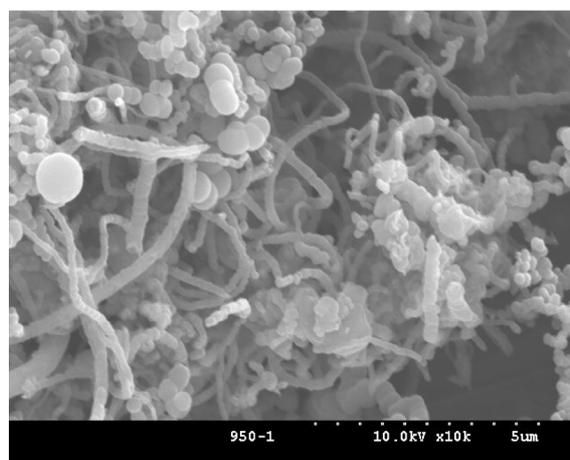
CNTs were synthesized on Pd/Al₂O₃ catalyst using C₂H₂ gas with flow rate of 30 sccm for 20 min at 650 °C. We found that CNTs had covered the entire heated section of the reactor as well as the Pd/Al₂O₃ catalyst.

We checked the surface morphology of catalysts, as shown in Figure 2. The CNTs were fibrous and grown in a random direction on palladium catalysts. The diameter of CNTs was about 15-25 nm.

Figure 3. is a SEM image of CNT powder deposited on the inner surface of the quartz tube by decomposition of C₂H₂ gas with flow rate of 30 sccm for 20 min through Pd/Al₂O₃ catalyst at (a) 650 °C and (b) 950 °C. CNT powder grown at 650 °C shows a length of 10 μm and dia. 150-200 nm with multiwalled structure, as shown in Figure 4. The diameter of CNT powder is larger than that of CNTs on Pd/Al₂O₃



(A)



(B)

Figure 3. SEM image of CNT powder grown by decomposition of C₂H₂ through Pd/Al₂O₃ catalyst at (a) 650 °C, (b) 950 °C.

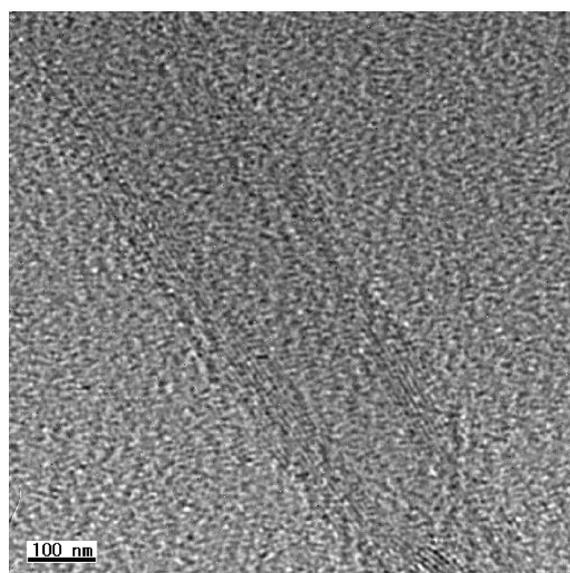


Figure 4. HRTEM image of CNT powder produced by decomposition of C₂H₂ through Pd/Al₂O₃ at 650 °C, which shows an inside hollow and multiwalled structure.

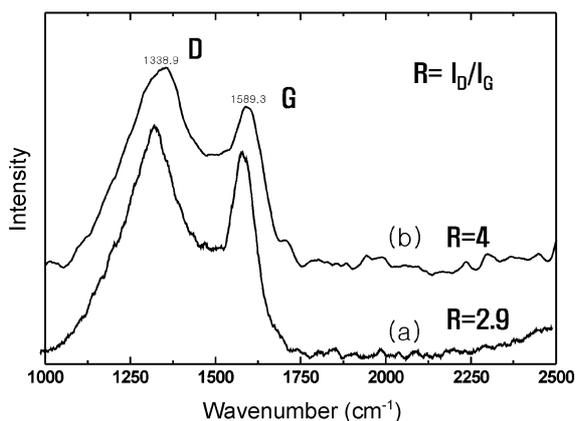


Figure 5. Raman spectrum of CNT powder produced by decomposition of C₂H₂ through Pd/Al₂O₃ catalyst at (a) 650 °C, (b) 950 °C.

catalyst. CNTs at 950 °C have more carbon defects (amorphous carbon, carbon fiber etc.,) than at 650 °C.

Figure 5. shows the Raman spectrum of CNTs grown at (a) 650 °C and (b) 950 °C. The Raman-allowed (G) line at 1590 cm⁻¹ has been assigned to the stretching mode (E_{2g}) of graphite. The disorder-induced (D) line at 1337 cm⁻¹ indicates carbon defects.¹⁴

In the Raman spectra we confirmed that the CNTs had crystalline structure and some carbon defects. The ratio of the integrated intensity of the D line to the G line $R=I_D/I_G$ provides a sensitive characterization of the disorder in the sample.¹⁵ The peak intensity ratio, R at 650 °C and 950 °C, have 2.9, 4.0 respectively. The peak intensity ratio of the D to G bands increased with higher temperature, indicating that crystallinity of CNTs grown at 650 °C is higher than that of CNT at 950 °C. This result agrees with Figure 3. This suggests that as pyrolysis of C₂H₂ at 950 °C occurs not only on Pd/Al₂O₃, but also itself C₂H₂, the CNTs on catalysts and carbon defects are formed.

Figure 6. shows the TGA graph of synthesized CNTs. Measurement was carried out in air, at a temperature range from 25 °C to 900 °C and the heating rate was 5 °C per

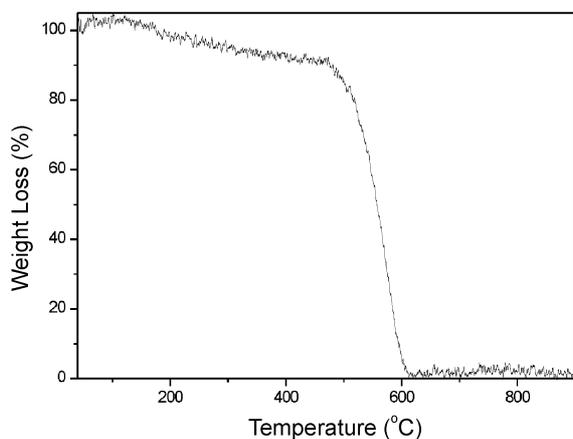
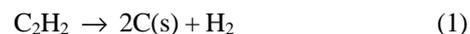


Figure 6. TGA data of weight loss for CNT powder grown at 650 °C. The CNTs start to gasify vertically at 470 °C.

minute. In this figure, the initial burning temperature was about 150 °C. Weightloss started at 150 °C. Weight of CNTs reduced slowly from 150 °C to 470 °C and vertically after 470 °C. The former area is a weight-loss of amorphous carbon and the latter is a weight-loss of CNTs. This result corresponds to the typical properties of CNTs, as previous reported.¹⁶ Weight-loss ended at 600 °C with a little metal.

We suggest that the C₂H₂ is thermally decomposed through Pd/Al₂O₃ at low temperature.



The catalysis reaction occurs on the surface of Pd/Al₂O₃. Solid carbons and hydrogens are formed through pyrolysis of C₂H₂. Solid carbons are adsorbed on Pd catalysts and dissolved into catalysts. Hence, CNTs are grown on the catalysts and are separated from the Pd catalyst.

The heat of adsorption and data of C-H dissociation rate constant data at 550-850 °C on Pd catalysts are not known for the decomposition of C₂H₂ gases. However, Kesmodel *et al.* showed that chemisorbed acetylene at 300 K results in the formation of mainly ethynyl, C-CH₃ and a small amount of residual acetylene. Dehydrogenation begins at around 400-500 K, with formation of CH species.¹⁷ Naresh Shah *et al.* have reported hydrogen production from methane decomposition for Pd catalysts at 700 °C.¹⁸ Pd was active catalyst for methane decomposition. Even a small amount of Pd yielded substantial hydrogen at lower temperature.

We demonstrate that Pd catalysts have an efficiency for decomposition of C₂H₂ at low temperature.

Conclusions

CNTs have been synthesized by C₂H₂ decomposition through Pd/Al₂O₃ at 650 °C. The synthesized CNTs have a diameter in the range 150-200 nm with multiwalled structure. Finally, we suggest that Pd catalysts not only are active catalysts for C₂H₂ decomposition, but also nucleation sites of growth. When the temperature of decomposition is 950 °C, CNTs have more carbon defects than at 650 °C.

This approach can be easily applicable to massive production of CNTs at low temperature.

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References

- Lee, J. K.; Choi, S. M. *Bull. Korean Chem. Soc.* **2003**, *24*, 32.
- Jung, O. J.; Kim, S. H.; Cheong, K. H.; Li, W. S.; Saha, I. *Bull. Korean Chem. Soc.* **2003**, *24*, 49.
- Iijima, S. *Nature (London)* **1991**, *354*, 56.
- Guo, T.; Nikolaev, P.; Rinzler, A. G.; Tomanek, D.; Colbert, D. T.; Smalley, R. E. *J. Phys. Chem.* **1995**, *99*, 10694.
- Yudasaka, M.; Komatsu, T.; Ichihashi, T.; Iijima, S. *Chem. Phys. Lett.* **1997**, *278*, 102.
- Ren, Z. F.; Huang, Z. P.; Xu, J. W.; Wang, J. H.; Bush, P.; Siegel, M. P.; Provencio, P. N. *Science* **1998**, *282*, 11057.

7. Ivanov, V.; Fonseca, A.; Nagy, J. B.; Lucas, A.; Lambin, P.; Bernaerts, D.; Zhang, X. B. *Carbon* **1995**, 33, 1727.
 8. Lyu, S. C.; Liu, B. C.; Lee, T. J.; Liu, Z. Y.; Yang, C. W.; Park, C. Y.; Lee, C. J. *Chem. Commun.* **2003**, 6, 734.
 9. Li, Y.; Chen, J.; Qin, Y.; Chan, L. *Energy & Fuels American Chemical Society* **2000**, 14, 1188.
 10. Ryu, C. K.; Wong, M.; Ryu, I. S.; Kang, S. K. *Catalysis Today* **1999**, 47, 141.
 11. Hoyos, L. J.; Paliard, H.; Primet, M. *Appl. Catal.* **1992**, A81, 227.
 12. Steinberg, M.; Cheng, M. *J. Hydrogen Energy* **1984**, 14, 797.
 13. Tuinstra, F.; Koenig, J. L. *J. Chem. Phys.* **1970**, 53, 1126.
 14. Chen, X. H.; Chen, C. S.; Chen, Q.; Cheng, F. Q.; Zhang, G.; Chen, Z. *Z. Mater. Lett.* **2002**, 57, 734.
 15. Al-Jishi, R.; Dresselhaus, G. *Phys. Rev.* **1982**, B26, 4514.
 16. Shi, S. J.; Lian, Y. F.; Liao, F. H.; Zhou, X. H.; Gu, Z. N.; Zhang, Y.; Iijima, S. *Solid State Commun.* **1999**, 300, 2555.
 17. Kesmodel, L. L.; Waddill, G. D.; Gates, J. A. *Surf. Sci.* **1984**, 138, 464.
 18. Shah, N.; Panjala, D.; Huffman, G. P. *Energy & Fuels American Chemical Society* **2001**, 15, 1528.
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