

Catalytic Mechanism for Growth of Carbon Nanotubes under CO-H₂ Gas Mixture

Uoo-Chang Chung,^{*} Yong-Hwan Kim, Deok-Bo Lee,[‡] Yeon-Uk Jeong,[§]
Won-Sub Chung,^{*} Young-Rae Cho, and Ik-Min Park

^{*}Industrial Liaison Innovation Cluster, Pusan National University, Busan 609-735, Korea
School of Material Science and Engineering, Pusan National University, Busan 609-735, Korea
^{*}E-mail: wschung1@pusan.ac.kr

[‡]Reliability Analysis Research Center, Hanyang University, Seoul 133-791, Korea

[§]Dept. of Inorganic Materials Engineering, Kyungpook National University, Daegu 702-701, Korea

Received May 25, 2004

In order to investigate the catalytic mechanism for the growth of carbon nanotubes (CNTs), a comprehensive study was conducted using carbon materials synthesized at 680 °C with a gas mixture of CO-H₂ after reduction at 800 °C by H₂ gas from iron oxide, and metal Pt. The resulting material was observed by scanning electron microscopy (SEM) and X-ray diffraction patterns (XRD) after a variety of reaction times. The carbon materials synthesized by metal Pt were little affected by reaction time and the sintered particles did not form CNTs. X-ray analysis revealed that metal Fe was completely converted to iron carbide (Fe₃C) without Fe peaks in the early stage. After 5 min, iron carbide (Fe₃C) and carbon (C) phases were observed at the beginning of CNTs growth. It was found that the intensity of the carbon(C) peak gradually increased with the continuous growth of CNTs as reaction time increases. It was also found that the catalyst of growth of CNTs was metal carbide.

Key Words : Metal, Metal carbide, Catalyst, Synthesis, Carbon nanotubes (CNTs)

Introduction

Carbon nanotubes (CNTs) have been the subject of comprehensive research due to their unique mechanical and electronic properties. Carbon nano-materials have been used in many technological applications such as electromagnetic interference, efficient field emitters, nano-probes, quantum wires, reinforcing components for composite materials, and methane and hydrogen storages.¹⁻⁴ Several methods have been used to synthesize CNTs; these include arc discharge (AD), laser vaporization (LV), chemical vapor deposition (CVD), and vapor phase growth (VPG) by hydrocarbon and CO.⁵⁻⁷

In the previous study, the nickel oxide and iron oxide act as catalyst particles for the growth of CNTs.^{8,9} Baker reported that CNTs are grown by diffusion of the carbon precursors through the catalyst particles and nucleation of the CNTs on the particle surface.¹⁰ A few research results have reported that catalysts of the growth of CNTs are mainly transition metals such as Fe, Ni, and Co, and several models have been suggested to explain the growth of CNTs prepared by the thermal CVD method.¹¹

However, it has not yet been identified, and the detailed mechanisms involving iron oxide use are still not well understood.

Therefore, to clarify the growth mechanism of CNTs, the vapor phase growth (VPG) method was used with iron oxide and Pt using CO-H₂ gas mixture. The shape and crystal structure of the synthesized carbon materials were evaluated by SEM, TEM, and XRD techniques.

Experimental Section

The samples were reduced and synthesized using a horizontal tube furnace. Figure 1 details the experimental apparatus. The major equipment consists of SiC electric tube furnace 6 cm in diameter and 100 cm in length, and a gas flow control system. In addition, the experimental apparatus includes a gas mixing chamber, an alumina boat, and thermocouples. Both iron oxide and metal Pt samples were used in a comparison study of the growth behavior and mechanism of CNTs. The iron oxide is hematite ore (Fe₂O₃) imported from Australia. It was crushed by ball mill and passed through a sieve shaker to obtain a desired size distribution. The particle diameters of samples were 45-65 μm and 2-3 μm for iron oxide and metal Pt respectively. The amount of total Fe, FeO, SiO₂, Al₂O₃ and other elements in the samples were chemically analyzed. The chemical compositions and physical properties of iron oxide are shown in Table I.

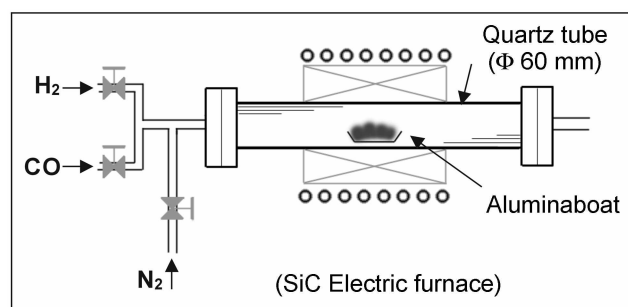


Figure 1. Schematic diagram of tubular reactor system.

Table 1. Chemical compositions and physical properties of iron oxide

Chemical compositions (wt%)	Fe	SiO ₂	Al ₂ O ₃	Mn	TiO ₂	S	P
	62.3	4.45	2.71	0.08	0.12	0.02	0.07
Physical properties	True density (g/cm ³): 4.45						
	Particle size : 45-63 μm						

Before charging samples, N₂ gas with a flow rate of 1 F.L. L/min at 800 °C was circulated through the reactor for 10 min, and the reduction of iron oxide was carried out in a H₂ gas atmosphere with a flow rate of 1.2 L/min for 15 min at 800 °C. The gas mixture, for the synthesis of metal Fe after reduction and metal Pt, was composed of 75% H₂ and 25% CO gases. The total gas flow rate was maintained at 1.2 L/min. Synthesis was conducted at 680 °C with reactions times varying between 2 and 150 min. Samples of metal Pt were directly synthesized without a reduction procedure. The shapes and crystal structures of the synthesized carbon materials were analyzed using SEM, TEM and XRD

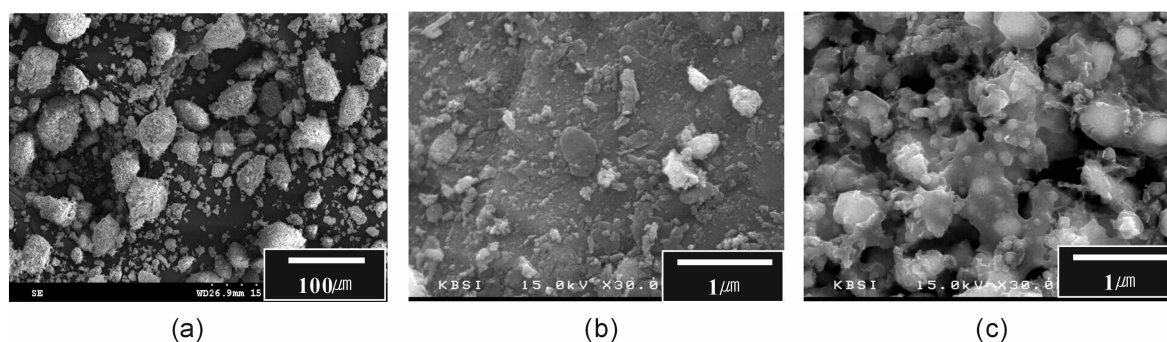
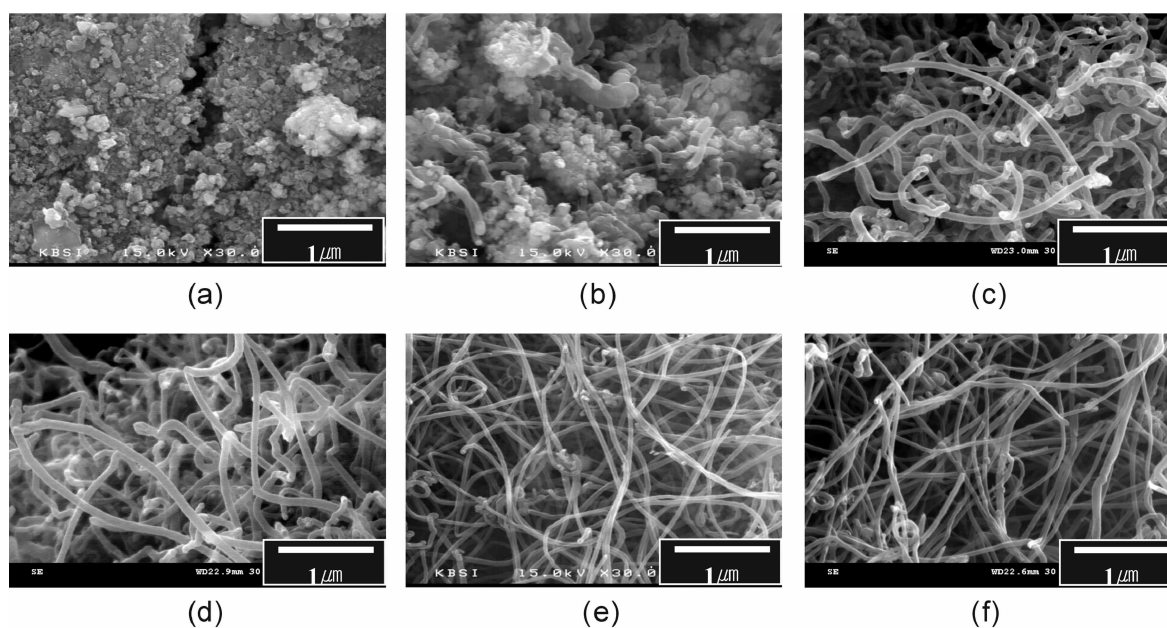
Table 2. Experimental conditions for reduction and synthesis

Variables	Conditions
Reaction temperature and time	Reduction : 800 °C, 15 min Synthesis : 680 °C, 2-150 min
Gas flow rate and ratio	Reactor cleaning → N ₂ (1.0 L/min) Reduction → H ₂ (1.2 L/min) Synthesis → CO-H ₂ (1.2 L/min) H ₂ /CO = 3
Sample charging weight	0.25 g

techniques. The experimental conditions are summarized in Table 2.

Results and Discussion

Surface morphologies of samples. Figure 2 shows the SEM morphologies of the iron oxides before and after reduction in the H₂ gas atmosphere for 15 min at 800 °C. The particle size before reduction was in the range of 30 to 60

**Figure 2.** Surface morphologies of iron oxides (a) and (b) before, and (c) after reduction for 15 min at 800 °C.**Figure 3.** SEM morphologies of iron oxides after synthesis at 680 °C with a ratio of H₂/CO = 3 at various reaction times of (a) 2 min, (b) 5 min, (c) 10 min, (d) 30 min, (e) 70 min, and (f) 150 min, respectively.

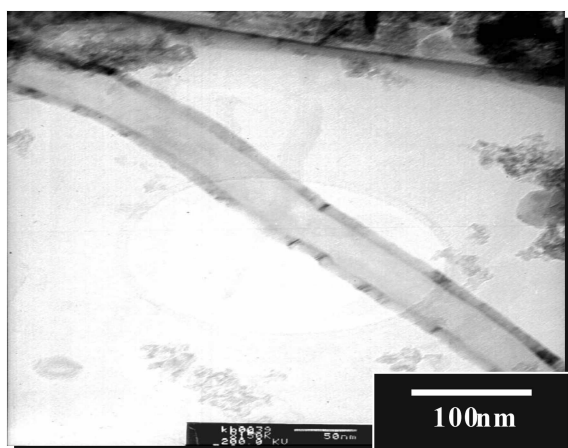


Figure 4. TEM morphologies of carbon nanotubes after synthesis for 70 min at 680 °C with a ratio of $H_2/CO = 3$.

μm , and a dense surface was observed, as shown in Figures 2a and 2b, respectively. After reduction the surface transformed into a porous sponge-iron, as shown in Figure 2c. Increasing the specific surface area by reduction was hypothesized to facilitate the synthesis of CNTs because of the high possibility of forming site for CNTs growth.

Figure 3 shows the SEM morphologies of iron oxides after synthesis under $CO-H_2$ gas mixture, in a ratio of $Y_{H_2}/Y_{CO} = 3$, with reaction time of 2 to 150 min at 680 °C. A crack formed in the surface of sample after 2 min of synthesis (Figure 3a), and particles were degraded by the carburization.¹² After 5 min (Figure 3b), CNTs were partly formed, but their shapes were not clear. The shapes of the carbon material synthesized for 10 and 30 min (Figures 3c and 3d) were a zigzag pattern, and the formation of CNTs was clear. The continuous growth of CNTs was observed over a period of 70 min (Figure 3e). The shapes were thinner and more obvious than before.

As shown in Figure 3f, the growth of CNTs slowed (synthesis time, 150 min) and CNTs had nearly the same in shape as those in Figure 3e (70 min). The retardation on the growth of CNTs after 70 min could have resulted from a difficulty in diffusion of carbon through the surface of the dense iron carbide that thickened during the longer time periods and the generation of methane (CH_4) resulting from the reaction between carbon (C) and hydrogen (H_2) gas ($C + 2H_2 \rightarrow CH_4$).

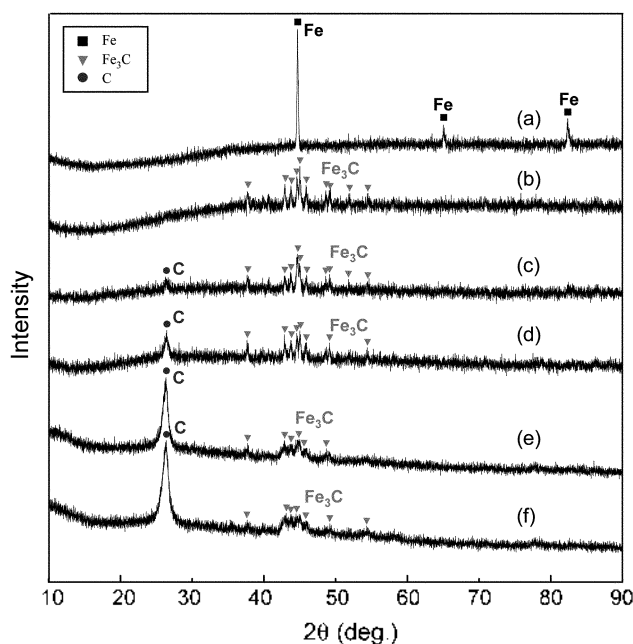


Figure 6. X-ray diffraction patterns of iron oxides (a) after reduction for 15 min at 800 °C and after synthesis at 680 °C in times of (b) 2 min, (c) 5 min, (d) 10 min, (e) 70 min, and (f) 150 min, respectively.

Figure 4 shows the TEM morphology of synthesized CNTs under the optimal conditions: for 70 min at 680 °C. Linear multi-wall CNTs of 30-50 nm in diameter were observed.

Figure 5 shows the SEM morphologies of metal Pt before and after synthesis. The particle size before the experiment was about 2-3 μm (Figure 5a), and they directly synthesized without reduction procedure. As shown in Figures 5b and 5c, the sintered particles did not form CNTs.

X-ray observation. The reduced and synthesized samples were examined with XRD and their diffraction patterns are shown in Figures 6 and 7. After reduction, as shown in Figure 6(a), the iron oxides were completely converted to Fe. The phases of samples synthesized for 2 min (Figure 6b) were completely converted to Fe_3C . After 5 min (Figure 6c), the Fe_3C and C phases were observed, and C peak had formed at the beginning of CNTs growth. As synthesis time increased, as shown in Figures (6d) to (6f), the intensity of the carbon (C) peak gradually increased due to the continuous growth of CNTs. After 70 min, reaction time had

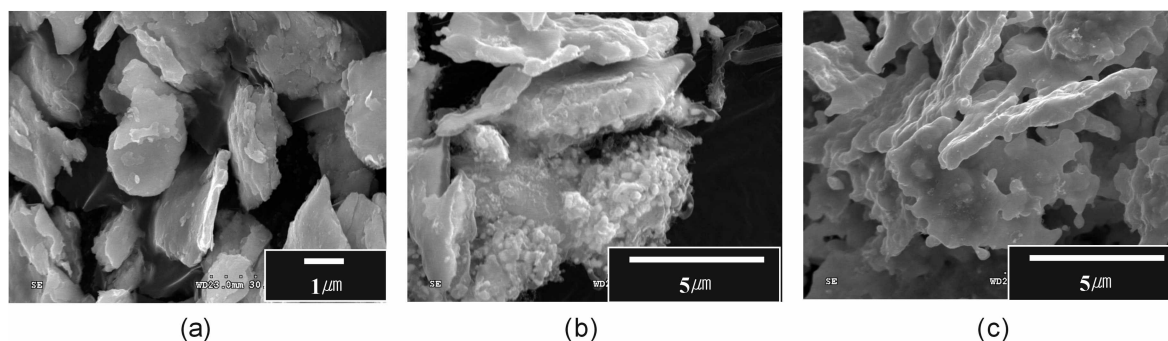


Figure 5. SEM morphologies of Pt (a) before and (b, c) after synthesis.

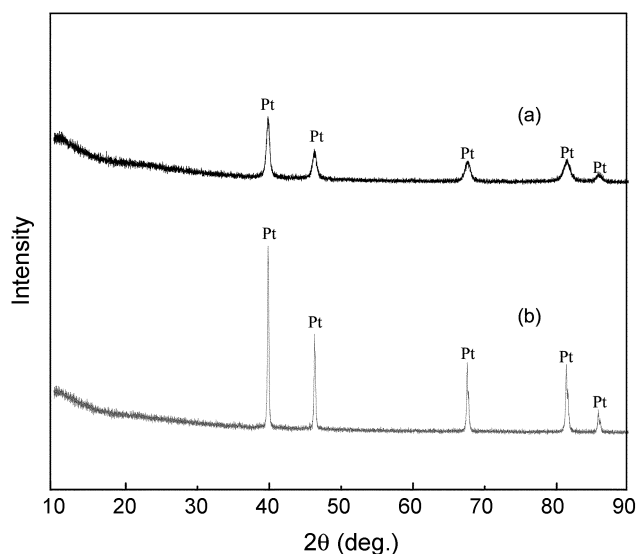


Figure 7. X-ray diffraction patterns of Pt (a) before synthesis, and (b) after synthesis for 70 min at 680 °C.

little effect on growth. It can be illustrated by the retardation of CNTs growth as mentioned in Figure 3. The Fe_3C peaks after 70 min were broad, it was estimated that amorphous carbon (C) on the Fe_3C surface could be coated, or Fe_3C was degraded to fine Fe_3C particles with the passage of time. It was found that CNTs were grown from Fe_3C .

Figure 7 shows the X-Ray diffraction patterns of metal Pt before and after synthesis. Without Fe_3C , Fe, and C phases, only the peak intensity of the sample was increased. Therefore, CNTs were not formed. It was found that the materials synthesized from metal Pt were amorphous, and this result was comparable with results observed in Figure 5.

These X-ray results agreed with the SEM and TEM analyses as shown in Figures 3 to 5. From SEM, TEM and X-ray results, it was also determined that a catalyst to the growth of CNTs was metal carbide.

Conclusions

Partial CNTs were observed in the carbon material

synthesized in the early stage of reaction. The formation of CNTs was clear after 10 min, and their shapes were a zigzag pattern. As synthesis time increased, the intensity of C peaks increased gradually along with the continuous growth of CNTs, but their peaks were little affected by reaction times longer than 70 min. The growth of CNTs with longer reaction time could be demonstrated by a repeated diffusion between Fe_3C formed by carbide reaction and carbon produced by carbon deposition reaction ($\text{CO} \rightarrow \text{C} + \text{CO}_2$). The shape of CNTs observed under optimal conditions, 70 min at 680 °C, was a lineal multi-wall CNTs 30-50 nm in diameter.

The Pt particles was sintered as synthesis time increased without formation of CNTs. The peak of metal Pt after 70 min of synthesis was the same as that before synthesis excluding an increase of peak intensity. It was found that the carbon materials synthesized from the metal Pt were amorphous. The X-ray results were comparable with the SEM analyses. The catalyst of CNTs growth was determined to be metal carbide, not metal.

References

1. Lee, B. O.; Woo, W. J.; Song, H. S. *J. Ind. Eng. Chem.* **2001**, *7*, 305.
2. Trans, S. J.; Verschuere, A. R. M.; Dekker, C. *Nature* **1998**, *393*, 49.
3. Saito, Y.; Hamaguchi, K.; Hata, K.; Uchida, K. *Nature* **1997**, *389*, 554.
4. Dai, H. J.; Hafner, J. H.; Rinzler, A. G.; Colbert, D. T.; Smalley, R. E. *Nature* **1996**, *384*, 147.
5. Iijima, S. *Nature* **1991**, *354*, 56.
6. Guo, T.; Nikolaev, P.; Thess, A.; Colbert, D. T.; Smalley, R. E. *Chem. Phys. Lett.* **1995**, *243*, 49.
7. Cassell, A. M. *et al. J. Phys. Chem.* **1999**, *103*, 6484.
8. Yuan, L.; Saito, K.; Pan, C.; Williams, E. A.; Gordon, A. S. *Chem. Phys. Lett.* **2001**, *340*, 237.
9. Yuan, L.; Saito, K.; Hu, W.; Chen, Z. *Chem. Phys. Lett.* **2001**, *346*, 23.
10. Baker, R. T. K. *Carbon* **1989**, *27*, 27.
11. Wang, Z. L.; Liu, Y.; Zhang, Z. *Handbook of Nanophase and Nanostructured Materials*; Kluwer Academic, Plenum Publishers: Tsinghua University Press: **2003**; Volume I, pp 111-115.
12. Hwang, H. S.; Chung, U. C. *Met. & Mater. Int.* **2004**, *10*, 77.