Effect of H_2 on Formation Behavior of Carbon Nanotubes

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The effect of H_2 gas on the carbon nanotubes (CNTs) synthesis with CO-H_2 gas mixture was investigated using mass measurements and scanning electron microscopy (SEM). The maximum weight and yield of the synthesized carbon were obtained when the mixture ratio of H_2 : CO was 3 : 7 and 9 : 1, respectively. In case of 100% carbon monoxide (CO) without hydrogen (H_2) addition, the weight of carbon increased, but CNTs were not observed. The CNTs began to be made when the contents of H_2 reaches at least 10%, their structures became more distinct with an increase of H_2 addition, and then the shapes of CNTs were more thin and straight. When the contents of H_2 was 80% (H_2 : CO = 8 : 2), the shapes and growth of CNTs showed an optimal condition. On the other hand, when the contents of H_2 was higher than the critical value, the shapes of CNTs became worse due to transition into inactive surface of catalyst. It was considered that the inactive surface of catalyst resulted from decrease of carbon (C) and H_2 concentration by facilitation of methane (CH_4) gasification reaction ($C + 2H_2 \rightarrow CH_4$) between C and H_2 gases. It was also found that H2 addition had an influence considerably on the shape and structure of CNTs.

Key Words : H_2, Carbon nanotubes, Synthesized carbon, Catalyst, Gasification reaction

Introduction

A great deal of interest has been generated in the carbon nanotubes (CNTs) due to their unique properties.[1,2] Extensive research on the solid carbon formed from decomposition of gaseous phase has been performed due to their various types of shapes and structures.[3,4] Since the discovery of CNTs by Ijima,[5] attention has been focused on the control of shapes and structures in their applications such as efficient field emitters, nano-probes, quantum wire, reinforcing components for composite materials, and methane and hydrogen storages.[6-10]

The deposition of carbon from gaseous phase results in a few different morphologies. The form of the deposited carbon is very important in the practical application.[11] It has been reported that H_2 could play a role in the growth of CNTs and the carbon deposition from carbon monoxide.[12,13] Nolan[14] investigated the dependance of H_2 on Ni catalyst in the growth of nanotubes, and it was agreed with results obtained by Chen *et al.*[15] In the previous study, acetylene, CH_4, and C_6H_6 are used as a carbon source[16,17] but the synthesis of CNTs using CO-H_2 gas mixture is still not known well.

The purpose of this research is to investigate the shapes and structures of CNTs with H_2 addition in CO using a cheap iron oxide catalyst, and to provide optimal condition for CNTs synthesis, and to examine possibility of economical efficiency and mass production.

Experimental Section

The major equipment for a reduction and synthesis of samples consists of SiC electric tube furnace and a gas flow control system including a gas mixing chamber, an alumina boat, and thermocouples. The detailed experimental apparatus has been described in our previous work.[18] The total Fe content of iron oxide used as catalyst for synthesis of CNTs was approximately 60%. The size distribution of particles was measured using an optical microscope, and the average particle size was found to be 45-65 μm. The iron oxides were sieved using a sieve shaker to obtain a homogeneous size distribution after crushing by ball mill. Before charging samples, N_2 gas with a flow rate of 1.0 L/min at 800 °C was provided into the reactor for 10 min, and the reduction of iron oxide carried out under H_2 gas atmosphere a with flow rate of 1.2 L/min for 15 min at 800 °C. The gas mixture, used for CNTs synthesis of metal Fe after reduction, was composed of H_2 and CO gases. The images of the synthesized carbon materials were taken using SEM technique. The experimental conditions are shown in Table 1.

Results and Discussion

Optimal reduction condition of catalyst. The preliminary

Table 1. Experimental conditions for reduction and synthesis

Variables	Conditions
Reaction temperature and time	Reduction : 800 °C, 15 min Synthesis : 680 °C, 70 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 (1.0 L/min) H_2/CO = 0-9 → CO (0.3 L/min) H_2 (0.1-2.0 L/min)
Sample charging weight	0.25 g

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experiment was performed to decide optimal reduction condition of catalyst before CNTs synthesis. Figure 1 shows reduction degree of catalyst after reducing under H_2 gas atmosphere with a flow rate of 1.2 L/min for 15 min in the range of 450 to 900 °C. The change in the sample weight was measured and the reduction degree was calculated from Eqs. (1) and (2).

$$RD\,(\%) = \Delta W/[(W_i - d_o)\cdot(1 - F_{gan.})] \times 100 \quad (1)$$

$$\Delta W = W_i - W_f \quad (2)$$

where RD (%) is the reduction degree, W_i is the sample weight (g) before reduction, W_f is the sample weight (g) after reduction, d_o is a mass fraction (–) of oxygen in the iron oxide, and $F_{gan.}$ is the mass fraction (–) of gangue in the iron oxide.

In Figure 1, reduction degree gradually increased as reaction temperature increases, but it was little affected by temperature when reaction temperature is higher than 800 °C, and then, sample was reduced completely. Therefore, the experimental condition for reduction determined at 800 °C. The high reduction degree of catalyst before synthesis is an essential condition for high yield of CNTs because low reduction degree means the insufficiency of an active catalyst required to make CNTs.[19]

Effect of gas ratios in CO-H_2 gas mixture. The gas mixture, for CNTs synthesis of metal Fe after reduction, was composed of H_2 and CO gases. And then, total gas flow rate was kept at 1.0 L/min, they were synthesized at 680 °C with various gas ratios of H_2/CO = 0 to 9. As shown in Figure 2,

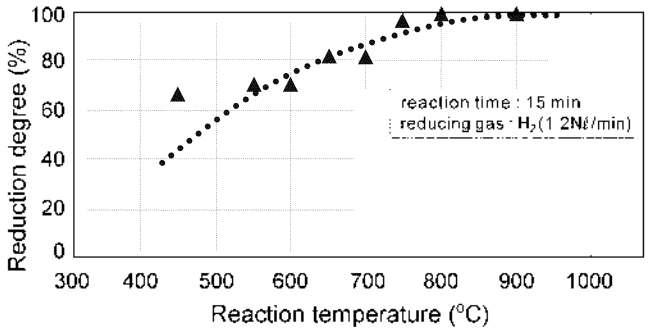

Figure 1. Effect of reaction temperature on reduction degree.

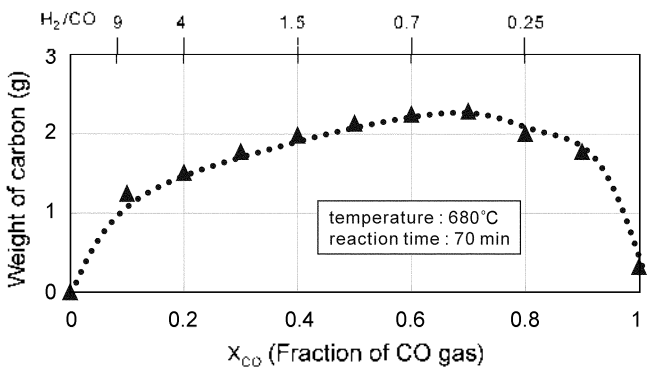

Figure 2. Effect of H_2 addition on synthesis of carbon nanotubes.

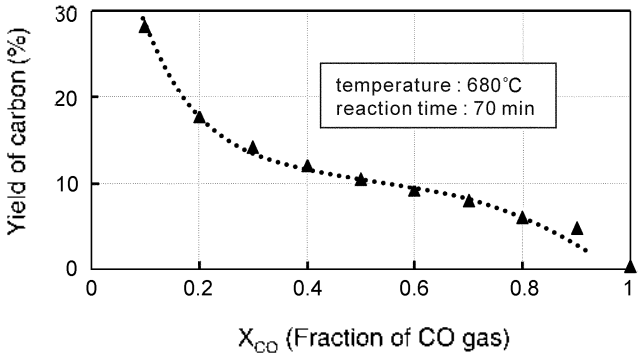

Figure 3. Effect of H_2 addition on synthesis yield of carbon nanotubes.

weight of the synthesized carbon solid was maximum at a gas ratio of H_2 : CO = 3 : 7, and weight of the synthesized carbon solid using 100% CO was very small as compared with H_2 addition. It was found that H_2 facilitated synthesis reaction of carbon.

Figure 3 shows yield of synthesized carbon at various gas ratios of CO-H_2 gas mixture. The yield was maximum value at a gas ratio of H_2 : CO = 9 : 1, and its value decreased with an increase of CO gas. The yield value was calculated by Eq. (3) as follows;

$$\text{yield}\,(\%) = \frac{\text{obtained carbon weight (g)}}{\text{supplied carbon weight (g)}} \times 100 \quad (3)$$

From these results, it was also found that H_2 gas was a major parameter in the synthesis of CNTs and carbon deposition reaction ($2CO \rightarrow C + CO_2$) by decomposition of CO gas.[20] Owing to conversion to active catalyst from inactive catalyst by H_2 addition, the formation of CNTs can be accelerated.[21,22]

Figure 4 shows SEM morphologies of CNTs after synthesis at various gas ratios. In case of 100% CO without H_2 addition (H_2 : CO = 0 : 1), as shown in Figure 4(a), CNTs were not observed. It is considered that carbon is not grown to CNTs due to existence of inactive catalyst by insufficiency of H_2 gas, they are precipitated to the amorphous carbon.[23] The CNTs were formed with 10% H_2 addition (H_2 : CO = 1 : 9), and their shapes and structures were more distinct as H_2 gas increases. Especially, when the mixture ratio of H_2 : CO was higher than 6 : 4, the amorphous carbon was completely disappeared, and then, the shapes of CNTs were more thin and straight. When the contents of H_2 gas was 80% (H_2 : CO = 8 : 2), the shapes and growth of CNTs showed the optimal condition. On the other hand, when the contents of H_2 were higher than the critical value (over 80% H_2), the shapes of CNTs became worse due to transition into inactive surface of catalyst. It was considered that an inactive surface of catalyst was resulted from decrease of C and H_2 concentration by methane (CH_4) gasification reaction ($C + 2H_2 \rightarrow CH_4$) between C and H_2 gases. It was also found that H_2 played a major role in the growth of CNTs.

Effect of H_2 flow rate. To investigate the effect of a flow

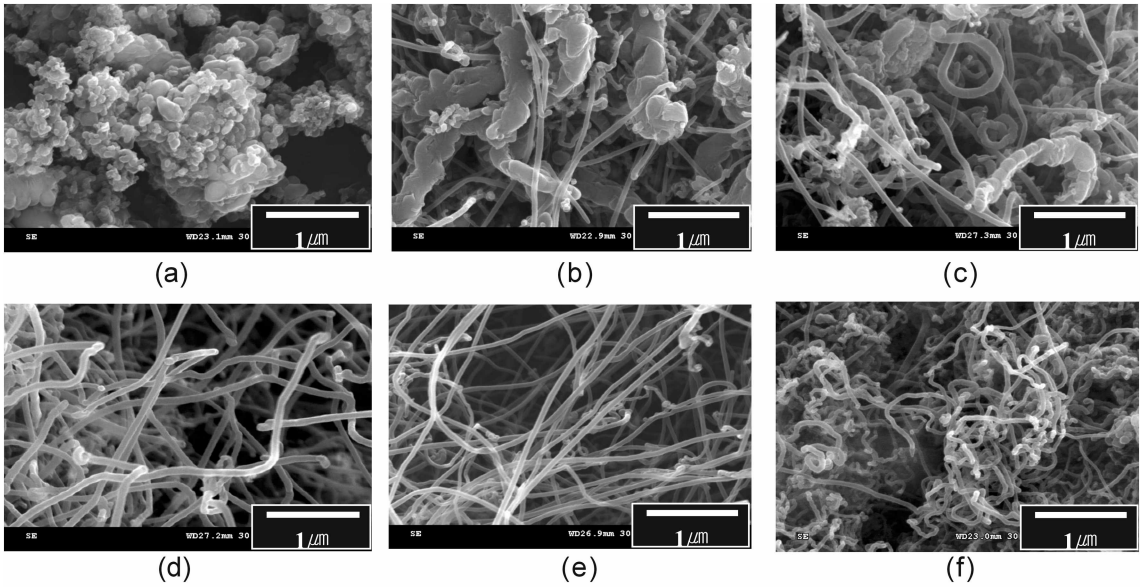

Figure 4. SEM morphologies of catalyst after synthesis at 680 °C with various gas ratios of H_2 : CO; (a) 0 : 1, (b) 1 : 9, (c) 5 : 5, (d) 6 : 4, (e) 8 : 2, and (f) 9 : 1, respectively.

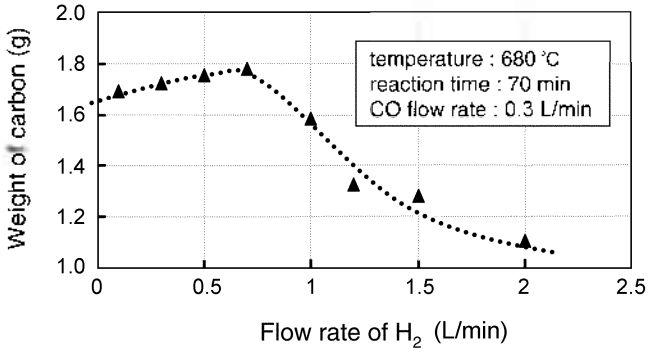

Figure 5. Effect of H_2 gas flow rate on synthesis of carbon nanotubes.

rate of H_2, the flow rate of CO was kept at 0.3 L/min, and metal catalysts were synthesized at 640 °C with various H_2 gas flow rates of 0.1 to 2.0 L/min. The images of the synthesized carbon materials were observed using SEM. As shown in Figure 5, the synthesized carbon weight increased with H_2 addition, and the value showed maximum in the H_2 gas with a flow rate of 0.7 L/min. When H_2 value was higher than 0.7 L/min, it decreased as H_2 contents increase. The synthesized weight was rapidly decreased in the H_2 gas with a flow rate of 2.0 L/min. Therefore, H_2 plays an important role in the growth and synthesis of CNTs. This result agreed with SEM analysis in Figure 4. From these results, to decide optimal content of H_2 addition is very important in the CNTs

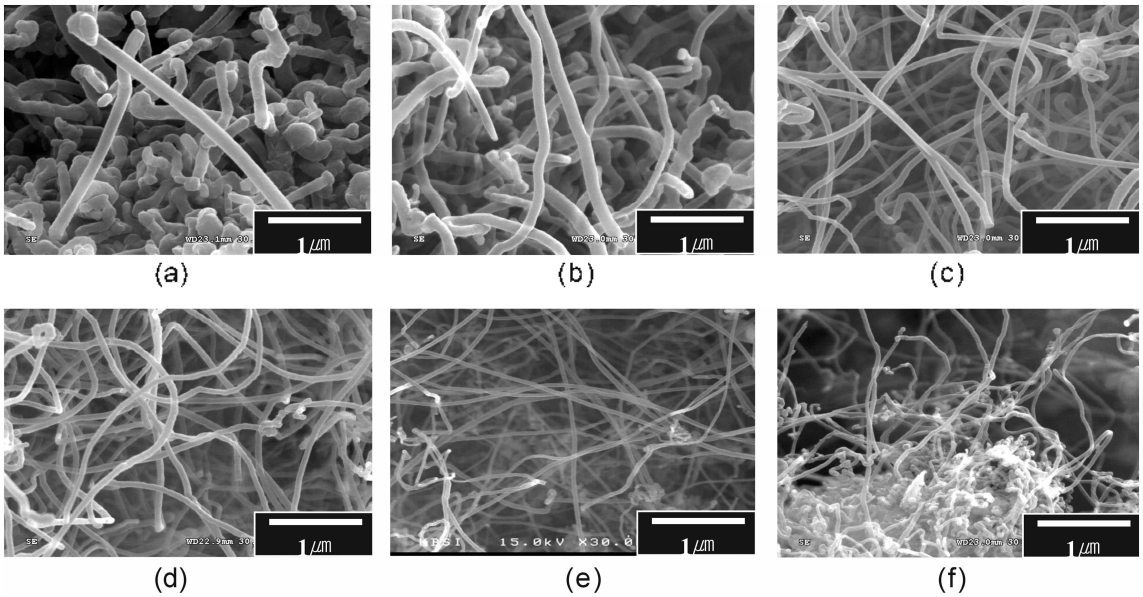

Figure 6. SEM morphologies of catalyst after synthesis at 680 °C with CO gas of 0.3 L/min at various flow rates of H_2; (a) 0.1 L/min, (b) 0.3 L/min, (c) 0.5 L/min, (d) 1.0 L/min, (e) 1.2 L/min, and (f) 1.5 L/min, respectively.

production because of consideration of the quality and economic efficiency by the excellent yield rate.

Figure 6 shows SEM images of metal catalyst after synthesis with various ratios of CO-H_2 gas mixture. As H_2 addition increases, the shapes of CNTs became a straight from spiral and more thin in the diameter. However, when H_2 contents were more than critical value (H_2; 1.5 L/min), the growth of CNTs was so repressed. It was also found that H_2 addition had an influence considerably on the shape and structure of CNTs.

Conclusions

The effect of H_2 addition on the CNTs synthesis was intensively investigated by SEM characterization. The weight of the synthesized carbon solid was maximum in a gas ratio of H_2 : CO = 3 : 7. The yield of synthesized carbon was maximum value at H_2 : CO = 9 : 1. In case of 100% CO gas without H_2 addition, CNTs were not observed. It is considered that carbons are not grown to CNTs due to existence of inactive catalyst by insufficiency of H_2 gas. finally these are precipitated to the amorphous carbon. The CNTs were formed with 10% H_2 addition. their shapes and structures were more thin and straight with an increase of H_2 gas. When the contents of H_2 gas was 80% (H_2 : CO = 8 : 2). the shapes and growth of CNTs showed the optimal condition. With an increase of H_2 contents. CNTs were obviously grown. and their shapes became a straight from spiral and more thin in the diameter. However, when H_2 contents were more than critical value, it acted as a barrier on the growth of CNTs.

From these results. to decide optimal content of H_2 addition is very important in the CNTs production because of consideration of the quality and economics efficiency by the excellent yield rate. It was also found that H_2 gas was a major factor in the shape and growth of CNTs.

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