Prospective Growth Region for Chemical Vapor Deposition Synthesis of Carbon Nanotube on C-H-O Ternary Diagram

Takashi Tomie[1], Shuhei Inoue[2, *], Masamichi Kohno[3], and Yukihiko Matsumura[2]

1) Department of Mechanical Science Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashi-Hiroshima 739-8524 Japan
2) Energy and Environmental Engineering Division, Faculty of Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashi-Hiroshima 739-8524 Japan
3) Department of Mechanical Engineering, Kyushu University, 744 Moto-oka, Nishi-ku, Fukuoka 819-0395, Japan

Abstract Chemical vapor deposition has become a standard process for synthesizing carbon nanotubes. Since the successful use of chemical vapor deposition for the first time, much effort has been expended into exploring various carbon sources that can be used to synthesize carbon nanotubes, such as methane, ethane, and ethanol. However, whole perspectives for suitable carbon sources have not been clear. In this study, we performed experiments in order to determine that the appropriate C-H-O components ratio in raw materials can be used to synthesize carbon nanotubes.

* Corresponding author. Fax: +81-82-424-5923.

E-mail: shu18@hiroshima-u.ac.jp (S. Inoue)

We also examined a variety of raw materials in our newly developed round-trip-type vacuum furnace in order to determine whether they could be used to synthesize a carbon nanotube. We used Raman spectroscopy to identify the developed carbon nanotube, and we plotted the component ratios of effective and ineffective materials on a C-H-O ternary diagram; in this diagram, the growth region became highly apparent. It should be noted that for the growth of the carbon nanotube, this region should satisfy the equation $O < C < (H + O)$ in molar ratio. Furthermore, it was observed that adjusting the component ratios by mixing raw materials did not cause an inconsistency in the growth region.

Keywords: nanotubes, chemical vapor deposition

1. Introduction

Considering the massive-scale synthesis of carbon nanotubes (CNTs) [1], chemical vapor deposition (CVD) has become a standard process for synthesizing CNTs, because it is an economical and a fast process. In recent years, a HiPco [2] process was used to synthesize single-walled carbon nanotubes (SWCNTs) [3] on a commercial scale for the first time. Further, alcohol catalytic CVD [4] was successfully used to synthesize pure SWCNTs without any post treatments, which often lead to decrease in the crystallinity of SWCNTs. Finally, a super growth process [5] was used to synthesize a huge amount of SWCNTs as compared with other large-scale production processes. In most of these processes, oxygen and hydrogen atoms were included originally or added later; these atoms were expected to have important roles such that they helped in the removal of amorphous carbon from catalysts and prevented SWCNTs from containing metal particles. However, whole perspectives for suitable carbon source or ideal balance among carbon, hydrogen, and oxygen have not been reported. Therefore, we performed experiments from the point of view of determining the appropriate C-H-O components ratio in raw materials could be used to synthesize CNTs by CVD processes. In this study, we employed a C-H-O ternary diagram, which was known as the Bachmann diagram [6] for diamond synthesis, to clearly understand the most important relationship among the components of each raw material. We synthesized SWCNTs in a newly developed round-trip-type vacuum furnace and identified it by Raman spectroscopy. Consequently, in this diagram, the growth region became highly apparent. It should be noted that for the growth of the SWCNT, its growth region should satisfy the equation O < C < (H + O) in molar ratio.

2. Experimental

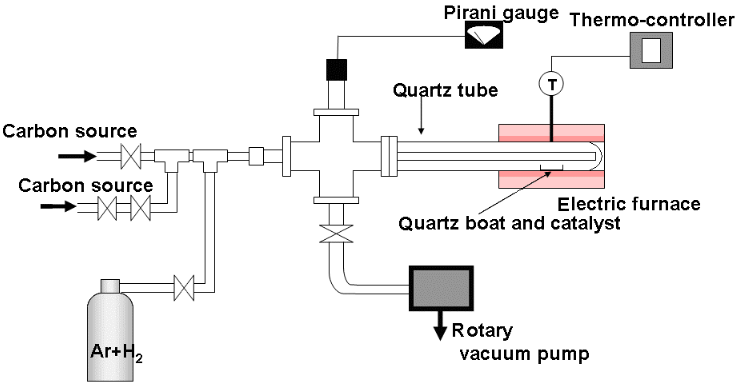


Fig. 1 Schematic of experimental apparatus. Because this apparatus employs the round-trip-type, the source gas is supplied from the inner tube, and then arrives at the catalysts in the outer tube.

CNTs were catalytically synthesized by pyrolysis of source gases on bi-metallic catalysts in a newly developed vacuum furnace. The catalysts were prepared according to the following recipe [7, 8]: in brief, iron acetate and cobalt acetate or iron acetate and molybdenum acetate were dissolved in ethanol (40 mL) and mixed with USY-type zeolite or aluminum oxide powder (1 g). The amounts of Fe-Co and Fe-Mo were 2.5 wt % each. The solution was dispersed in an ultrasonic wave bath for 60 min and dried for 24 h at 80 ºC. Then, the catalysts were ground in a mortar and placed in the designated area in the reactor. The temperature of the reactor was controlled from room temperature to the target temperature (700 ºC or 800 ºC) in 30 min. During this heating process, the reactor was filled with a mixture of hydrogen and argon gases (5% hydrogen, 95% argon, 0.001% contaminants) at 400 Pa; hydrogen was expected to reduce the catalyst. When the reactor attained the target temperature, the gas was evacuated and the source gases were supplied for 10 or 30 min. The pressure of the source gases is listed in Table 1, along with the source species. Our newly developed vacuum furnace is shown in Fig. 1. Unlike the furnace used previously [9], the furnace used in this study was a round-trip–type furnace, and the source gases were supplied through the inner quartz tube and led to the outer quartz tube where the catalyst was placed. This type of vacuum furnace is superior to the one used previously in terms of a decrease in the number of connections required. The raw samples were analyzed by Raman spectroscopy (514.5 nm) in order to identify the growth of the CNT. All the source gases used in this study are listed in Table 1, and Fig. 2 shows their composition in the C-H-O ternary diagram.

The way of plotting on this diagram is same as above-mentioned Bachmann diagram. Unlike their paper we expressed the component ratios of C, H, and O ($N_C + N_H + N_O = 1$) in Tables, but we also used the ratio of two elements when we plotted in the ternary diagram. For instance, in case of methanol (CH_3OH), the ratio of O : H is 1 : 4 that means H is rich. Here, the first line is drawn from the top (expressed C) to the bottom 80 on the OH line as shown in Fig. 3. Secondly, the ratio of C : H is 1 : 4 that means H is rich. Here, the second line is drawn from the top (expressed O) to the bottom 20, which is closer to H on the CH line as shown in Fig. 3.

3. Results and discussions

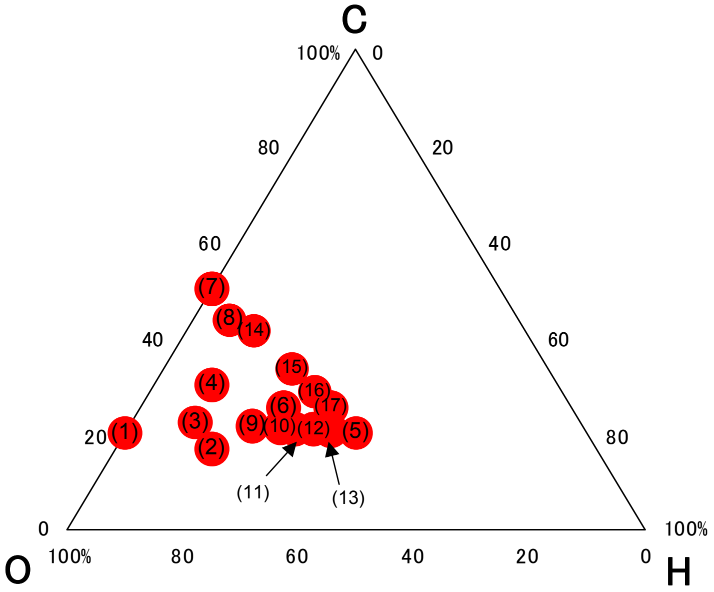


Fig. 2 The C-H-O ternary diagram. The source gases used in this study are shown in this diagram.

Raman spectroscopy was used to identify the growth of the CNT, and the G/D ratio was used to simply express its purity; this ratio was plotted on the C-H-O ternary diagram. Because the number of data is finite, Fig. 4 is drawn by using triangle-meshed interpolation of all the experimental data. In this study, the following two types of support materials were used: USY zeolite and aluminum oxide. A low-purity CNT was synthesized on a C-H line by using the USY zeolite. As shown in Figs. 4(a) and 4(b), a small amount of oxygen drastically improves the G/D ratio. On the other hand, as shown in Figs. 4(c) and 4 (d), the level of purity of the CNT decreases when aluminum oxide is used as the support material. These results suggest that zeolite is congenial to materials that contain a small amount of oxygen, as is the case with alcohol and aluminum oxide. Furthermore, it is observed that the high-purity region expanded more when the reaction temperature is 800 ºC than when it is 700 ºC.

Table 2 lists the carbon sources that were effective in the previous studies. Here, these effective carbon sources are plotted together with those deemed effective in the present study onto a C-H-O ternary diagram shown in Fig. 5, with a circle (•); the ineffective carbon sources used in the previous studies are plotted together with those deemed ineffective onto a C-H-O ternary diagram, with a cross (×). From these diagrams, one tendency among the C, H, and O ratios can be observed. As shown in Fig. 5, the growth region should satisfy the equation $O < C < (H + O)$ in molar ratio for the synthesis of the CNT. In this equation, because the materials shown in the top half of the ternary diagram ($C > (H + O)$) are normally solid, this region is excluded from the effective region. Further, in this figure, the carbon sources whose G/D ratio is greater than 1 are considered being effective carbon sources. However, this definition is not so strict that some carbon sources especially close to

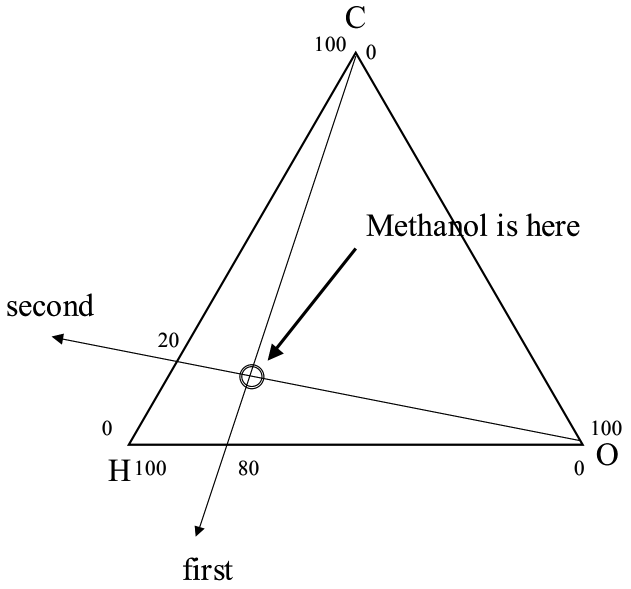
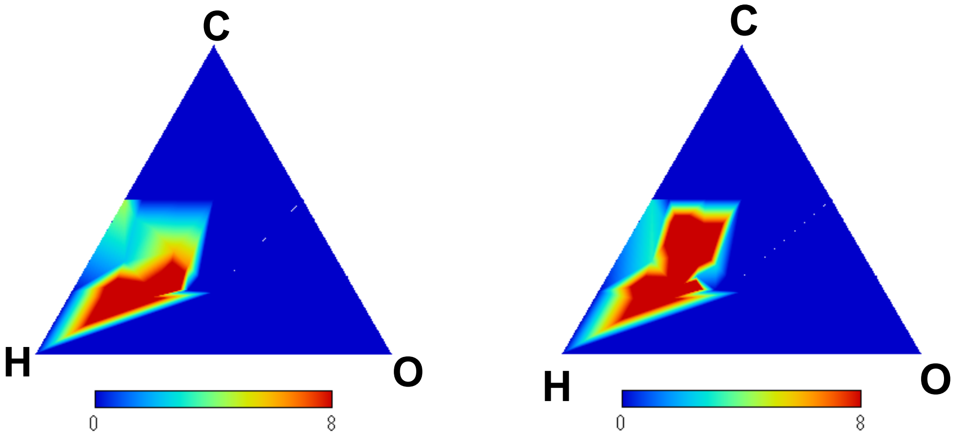


Fig. 3 The way of plotting on C-H-O ternary diagram. We expressed the molar ratio, but the way of plotting is same as Bachmann diagram.

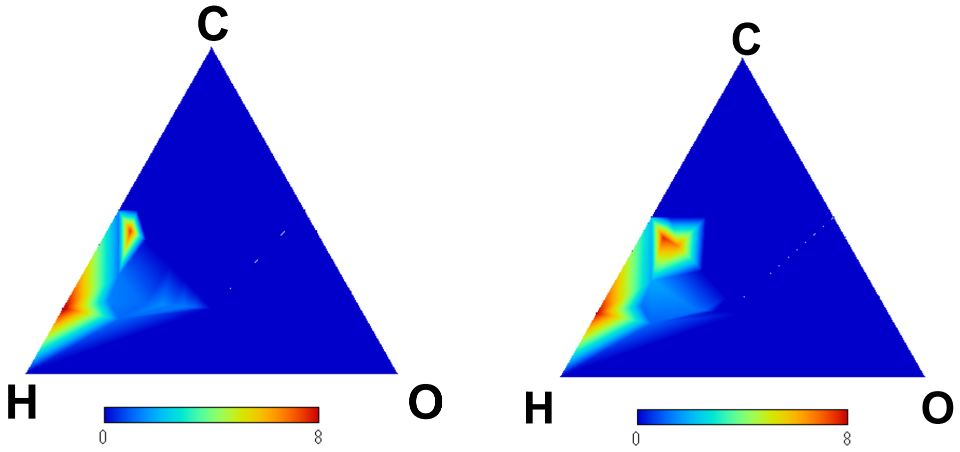
the threshold might contradict. In addition, although we could not confirm the radial breathing mode for some samples, all of them seemed to include an SWCNT, because the G-band appeared around 1590 cm-1. Therefore, it is appropriate to consider that the effective region shown in Fig. 5 is identical to the region of SWCNT growth. Furthermore, it was found that adjusting the component ratios in the C-H-O ternary diagram by mixing raw materials did not cause an inconsistency. For instance, methane and ethane/hydrogen mixture (C2H6 : H2 = 1 : 1) have the same ratio, and both of them can be used to synthesize CNTs.

4. Conclusion

In this study, we synthesized a CNT in our newly developed round-trip-type vacuum furnace using several kinds of raw material. Further, employing the C-H-O ternary diagram results in deriving the tendency for the growth region of the CNT in the CVD processes. Results of this study confirmed that a certain level of affinity existed between catalyst supporters and carbon sources;



(a) Zeolite, Fe-Co 700 °C (b) Zeolite, Fe-Co 800 °C



(c) Aluminum oxide, Fe-Mo 700 °C (d) Aluminum oxide, Fe-Mo 800 °C

Fig. 4 The G/D ratio of synthesized CNTs measured by Raman spectroscopy with 514.5 nm wavelength. Each data corresponding to Fig. 2 is plotted on the C-H-O ternary diagram. Because the number of data is finite, these figures are drawn by interpolating among data.

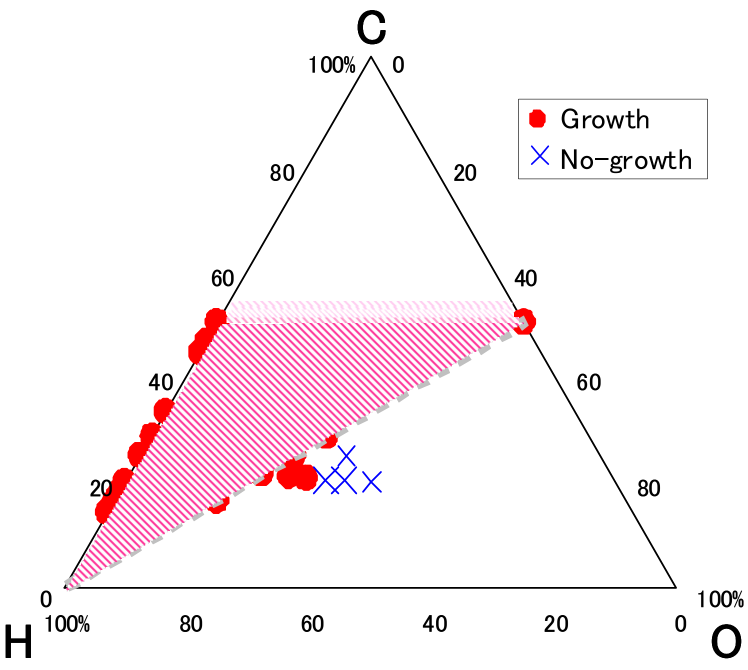


Fig. 5 The growth region of CNTs in CVD processes. The effective raw materials are shown with a circle (•) and the ineffective one is shown with a cross (×) in the C-H-O ternary diagram. Consequently, the growth region became clear in this diagram.

however, there was no contradiction for the synthesis in mixing raw materials to adjust the position on the C-H-O ternary diagram. It should be noted that to synthesize a CNT the equation O < C < (H + O) should be satisfied in molar ratio. In addition, the influence of C-H-O component on the diameter was found; however, its tendency has not been cleared yet.

Acknowledgment

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