Catalyst-Induced Carbon Nanofiber Assembly

Seongyop Lim*, Seong-Ho Yoon, and Isao Mochida
Institute for Materials Chemistry and Engineering, Kyushu University, Kasuga, Fukuoka 816-8580, Japan
Corresponding author e-mail address: lim9@asem.kyushu-u.ac.jp

INTRODUCTION

Recently, the authors succeeded in selective synthesis of thin carbon nanofiber (CNF) with 7 ~ 40 nm diameters from ethylene at a high yield over carbon black supported NiFe catalysts (NiFe-CB, hereafter) [1]. Ni-CB catalyst produced a mixture of thick fibers (around 100 nm diameter) and thin fibers (around 10 nm diameter), whereas NiFe(9:1)-CB and NiFe(8:2)-CB provided selectively thin fibers of 10 ~ 40 nm diameter with herringbone texture. The diameter of fiber generally depends on the dimension of catalyst particles [2, 3], which can be determined not only by dispersion of precursors and catalysts on CB but also segregation/sintering through reduction of catalyst in hydrogen and synthesis of CNF [1,4]. Such a dispersion or segregation of catalyst particles on CB was found to be significantly affected by the composition of metals [1].

This study investigated the structure of CNFs from ethylene over CB-supported catalysts in detail through examination of catalyst particles after synthesis to elucidate the formation of CNF.

EXPERIMENTAL

The amount of catalyst on CB is simply calculated from the feed of catalyst precursors. For example, to prepare a 5% Ni-Fe (8:2)/carbon black catalyst, nickel (1.981 g nickel nitrate hexahydrate) and iron nitrates (0.723 g iron nitrate nonahydrate) corresponding to 0.5g pure metal contents (the composition of Ni/Fe=4/1 w/w) were dissolved in 50 ml ethanol, and then carbon black 10 g after drying in an oven at 105^{o}C was added to the nitrate solution. The resulting slurry was sonicated for 1 h, then being left overnight. Ethanol was evaporated from the slurry under vacuum, and then the resulting solid was dried in an oven at 105^{o}C overnight. The dried lump was ground to powder to be used as the catalysts for CNF synthesis.

CNFs were prepared in a quartz flow reactor (10 cm (D) × 45 cm (L)) heated by a conventional horizontal tube furnace. The gas flows to the reactor were precisely monitored and regulated by MKS mass flow controllers. Powdered catalyst grains (110 ~ 130 mg) were placed in an alumina boat at the center of the reactor tube in the furnace. After reduction in a 20%(v/v) H_2/He mixture for 2 h at 753 K, helium was flushed for 30 min before introduction of C_2H_4/H_2 mixture over the catalyst. The total flow rate was 200 ml/min through the whole process. The total amount of carbon deposited during the time on

stream was determined gravimetrically after cooling the product to ambient temperature.

The structure and morphology of the CNFs were observed under a scanning electron microscope (JSM-6320F, JEOL) and a high resolution transmission electron microscope (JEM-2010F, JEOL).

RESULTS AND DISCUSSION

Figure 1 shows SEM photograph of CNF produced over Ni alone and Ni-Fe (8:2) on CB at 753 K for 1 h from an ethylene/hydrogen mixture (4:1). Two kinds of CNFs over Ni alone supported on CB were observed in the product. One (Part A of Fig. 1 Ni) was relatively thick CNF of average 150 nm and the other (Part B of Fig. 1 Ni) appeared as grains at low magnification. Over Ni-Fe (8:2) supported on CB, a majority of the fibers showed diameter around 20 nm and their selectivity appeared as high as 95%, although a few thick fibers were observed in the photograph (part A in Fig. 1 NiFe(8:2)) The fibers were not straight, but entangled, exhibiting many nodes along their axes. These results reflect importance of catalyst composition to control the diameter of CNF.

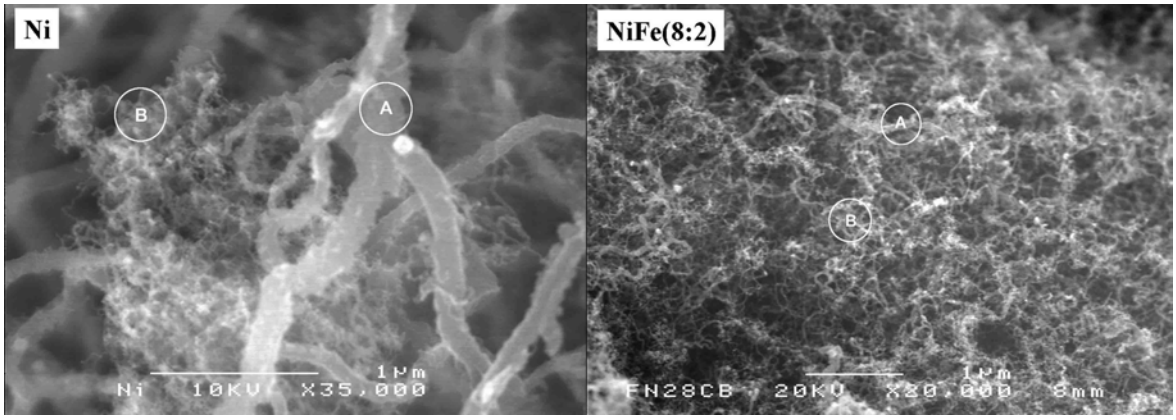

Figure 1. SEM images of CNFs from C_2H_4/H_2 (4:1) at 753 K on the 5% Ni alone and 5% Ni-Fe (8:2) supported on MCB#3050B

Such a correlation between the catalyst composition and the structure/diameter of fiber was examined under TEM. Figure 2 shows TEM images of CNF over Ni supported on CB.

The thick fiber of about 200 nm diameter in Figure 2A corresponds to part A in Figure 1 Ni. High magnification of such a thick fiber (Figure 2B) was found to be assembled or entangled by very fine fibers of 7 ~ 25 nm diameters. The thick fiber looked like a straw rope. The thin fiber as a component of the thick fiber was found to have a herringbone texture.

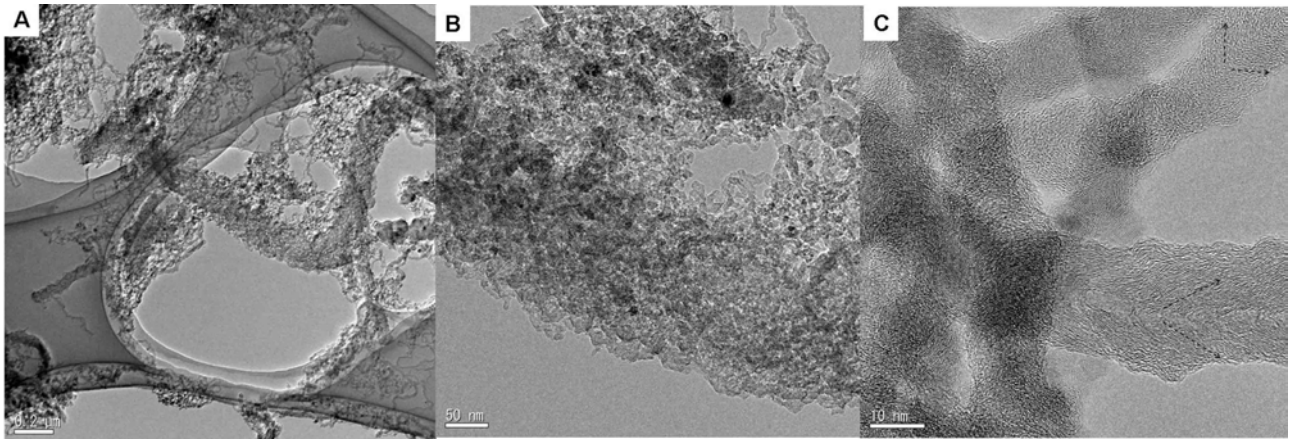

Figure 2. TEM images of CNF over 5% Ni supported on CB at 480^{o}C.

Figure 3 shows the catalyst particles after synthesis of CNF over Ni alone supported on CB at 480^{o}C. In a high magnification (Figures 3A and B), a major of big catalyst particles of more than 60 nm diameter were found to consist of very small particles as shown in Figure 3B. This polycrystalline particle provided no clear spot at the electron diffraction. The assembly of thin CNFs as seen in Figure 2 appeared to correspond to such a polycrystalline particle.

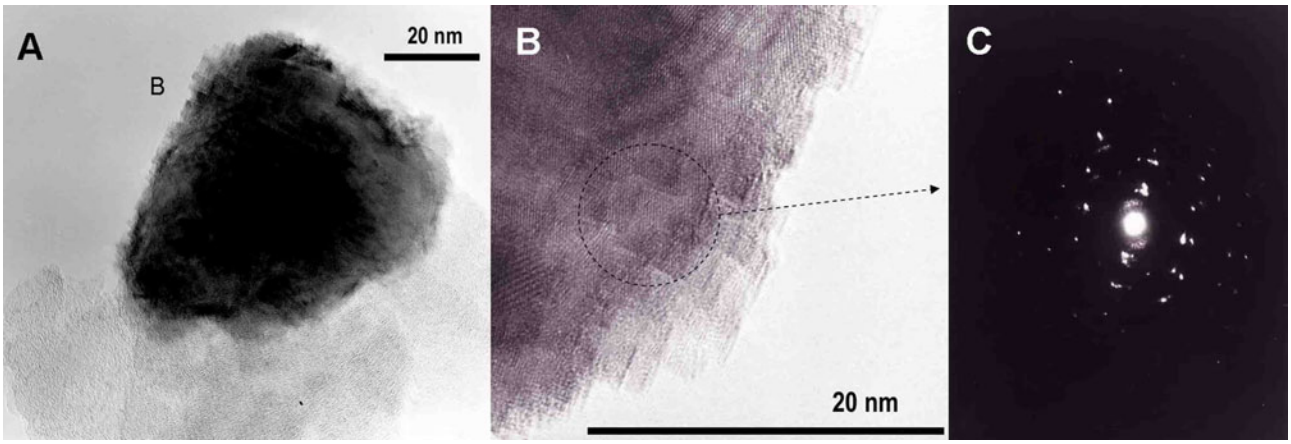

Figure 3. TEM images and electron diffraction at a selected area of Ni alone supported on CB after synthesis of CNF at 480^{o}C.

On the other hand, a major of fibers produced over NiFe (8:2) supported on CB showed an independent herringbone texture with ca. 20 nm diameter as shown in Figure 4A. Compared to Ni alone as shown in Figure 3, the particle of NiFe (8:2) after synthesis of CNF showed smooth surface to be formed as a single crystal (see Figure 4B), which can be confirmed in the electron diffraction as shown in Figure 4C. The formation of such a particle appeared to be ascribed to small addition of iron as a bimetallic catalyst with nickel.

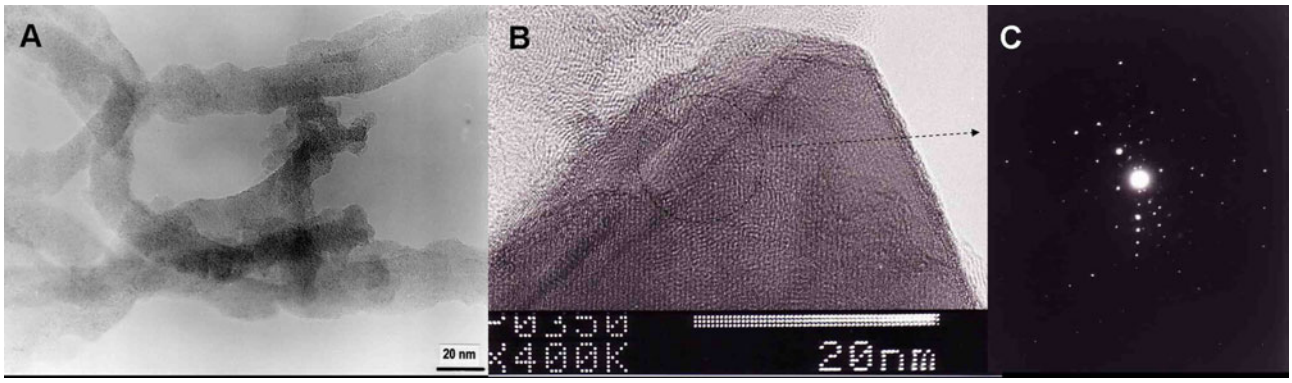

Figure 4. TEM images of CNF and catalyst particle, and the electron diffraction of the catalyst particle after synthesis using 5% Ni-Fe (8:2) supported on CB at 480^{o}C.

Nickel and its alloys with Fe have been recognized to be active for CNF growth through the steps of carbonate precipitation, thermal decomposition into oxides, reduction to metal or alloys, conditioning with carbon source and hydrogen, and CNF growth [5, 6]. Such steps induced the segregation of metal or alloys into nano particles which governs the growth of CNFs in terms of their yield, diameter, and structure [4]. Bimetallic combination of active and inactive metals can allow high dispersion of the active metal component. In addition, Ni-Fe alloys have been reported to be strong to sintering, being more finely dispersed on carbon surfaces than the individual metals as in a study on the catalyst dispersion in active carbon-supported iron alloys [7].

This study showed that the catalyst particles appeared to be finely dispersed or formed on CB. However, the sintering/segregation of particles through the overall steps until the formation of CNF probably occurred differently in single metallic and bimetallic particles supported on CB.

In terms of catalyst precursors impregnated on the support, Ni alone and Ni-Fe (8:2) must be finely dispersed on CB, even if the Ni component may be more finely dispersed in Ni-Fe (8:2) than that in Ni alone. The reduction in hydrogen appeared caused a apparent difference, probably which Ni alone suffered more severe sintering than Ni-Fe (8:2), and even segregation of a Ni alone particle was less effective than that of a Ni-Fe (8:2) alone. Thus, a large size of the Ni alone particles was formed consisting of very small crystallites, whereas the particles of Ni-Fe (8:2) was formed as a single crystallite, which were larger than the small crystallite constructing Ni alone particles. As results, the fibers as shown Figures 2 and 4A were formed over such a particle of catalyst.

CONCLUSION

We showed thin fiber assembly induced by formation of catalyst. Based on exact understandings of the formation of such a fiber over catalyst, a new microstructure and a new nano-space are expected to be designed, synthesized and controlled for practical applications.

REFERENCES

[1] Lim S, Yoon S-H, Korai Y, Mochia I. Selective synthesis of thin carbon nanofibers: part I. over nickel-iron alloys supported on carbon black. Carbon 2004, in press.

[2] Rodriguez NM. A review of catalytically grown carbon nanofibers. J Mater Res 1993;8(12):3233-3250.

[3] De Jong KP, Geus JW. Carbon nanofibers: catalytic synthesis and applications. Catal Rev –Sci Eng 2000; 42(4): 481-510.

[4] Tanaka A, Yoon S-H, Korai Y, Mochida I. The segregation phenomena of non-supported Fe-Ni catalysts on the syntheses of CNFs. Extended abstracts, 29th Annual Japan Carbon Conference. Kansai University (Osaka, Japan): The Carbon Society of Japan, 2002; 364-365.

[5] Best RJ, Russell WW. Nickel, Copper and Some of their Alloys as Catalysts for Ethylene Hydrogenation. J Amer Chem Soc 1954; 76: 838-842.

[6] Sinfelt JH, Carter JL, Yates DJC. Catalytic Hydrogenolysis and Dehydrogenation over Copper-Nickel Alloys. J Catal 1972; 24: 283-296.

[7] Guerrero-Ruiz A, Sepulveda-Escribano A, Rodriguez-Ramos I. Carbon supported bimetallic catalysts containing iron. I. Preparation and characterization. Appl Catal A: Gen 1992;81:81-100.