Three-Dimensional Analysis of Carbon Nanofibers by Cross-sectional TEM Observations

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Cross-sectional TEM images of carbon nanofibers formed through methane decomposition over Ni/SiO_2 catalysts were observed by using an ultramicrotome. The TEM images indicated that carbon nanofibers have regular hexagonal prism structures.

Carbonaceous materials with a nanoscale fibrous structure is generally called carbon nanofibers, which are the key material in the future nanotechnology due to their attractive properties. Carbon nanofibers can be produced through the catalytic decomposition of carbon-containing gases, such as hydrocarbons and carbon monoxide. Nickel, cobalt and iron metals are frequently used as catalysts, and the properties of carbon nanofibers are influenced by the types of carbon-containing gases or catalysts.[1] The utilization of carbon nanofibers has been proposed in the various fields (e.g., electronic devices,[2] templates,[3] and catalysts[4]). If the property of carbon nanofibers is different, the performance in their application must be different. Carbon nanofibers have a lot of characteristic properties, and their morphology is one of important properties. Until now, the morphology of carbon nanofibers has been investigated by using a transmission electron microscope (TEM). In conventional TEM studies, we can obtain their two-dimensional morphology such as straight, bent, twisted or helical, because they lie in the matrix with their axis perpendicular to the electron beam; however, the three-dimensional structure (i.e., cylinder or polygonal prism) is also important. To understand the information in the three-dimensional morphology of carbon nanofibers, it was deduced on the basis of the careful analysis of their two-dimensional images. Rodriguez et al. synthesized a variety shape of carbon nanofibers by choosing the appropriate reaction conditions, and proposed their three-dimensional structure on the basis of TEM images.[5]

It is considered that the combination between the conventional TEM images and the cross-sectional images of carbon nanofibers would give the direct information of the three-dimensional structures. As far as we know, the cross-sectional TEM images of carbon nanofibers have not been measured. Thus, in the present study, we use an ultramicrotome to obtain the sliced sample of carbon nanofibers. Since an ultramicrotome can make an extreme thin sample, we could see the cross-sectional images of carbon nanofibers.

Ni/SiO_2 catalysts for producing the carbon nanofibers were prepared by the impregnation of SiO_2 with aqueous solutions containing $Ni(NO_3)_2$, followed by drying in air at 353 K and calcination in air at 873 K. The carbon nanofibers were formed through methane decomposition at 803 K over the catalysts, which had been previously reduced with H_2 at 773 K.[6] Cross-sectional specimens for TEM observation were prepared by embedding carbon nanofibers in an acrylic resin (LR White Resin; London Resin Company Ltd.). After the matrix was polymerized by heating at 333 K for 24 h, the resulting samples were cut in 57-nm thick sections on an ultramicrotome. TEM images were obtained using JEOL JEM-2010F and JEM-3000F instruments operated at 200 kV.

Typical TEM images of unsliced nanofibers are shown in Figure 1. The nanofibers are bent, and Ni catalysts are present at their tips. The diameters of carbon nanofibers range from a few tens to one hundred nanometers. A typical faceted Ni metal particle at a fiber tip is shown in Figure 1b. The diameter of the nanofiber is almost the same as the size of the Ni particle. As described above, information about the three dimensional structure of the fibers cannot be obtained from such observations.

Therefore, TEM images of sectioned nanofibers are observed to examine the three-dimensional structure. As we see from Figure 2, the cross section appeared to be regular hexagonal, indicating that nanofibers are regular hexagonal prism. This result suggests that the cross-sectional image of carbon nanofibers gives the effective information on the three-dimensional structures. Since these carbon nanofibers are produced from Ni catalysts, the shapes of carbon nanofibers would be determined by those of Ni catalysts. The growth mechanism of carbon nanofibers was investigated in detail,[7] and new suggestions about carbon nanofiber growth have been reported, recently.[8] Typical growth mechanism of carbon nanofibers is as follows. Carbon and hydrogen atoms are formed through the decomposition of carbon-containing gases on the surface of a Ni metal particle. Hydrogen atoms are released into gas phase as hydrogen

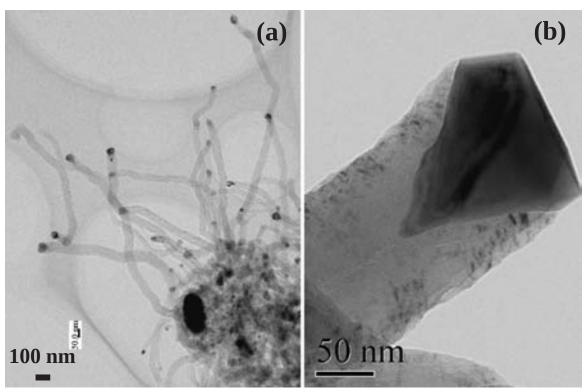

Figure 1. TEM images of carbon nanofibers formed by methane decomposition over Ni/SiO_2 catalysts at 823 K.

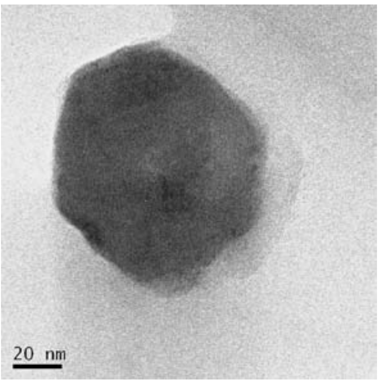

Figure 2. TEM images of cross sections of a carbon nanofiber.

molecules, while carbon atoms diffuse through the bulk of the Ni particle and graphitize as nanofibers. In addition, in some case, surface diffusion of carbon atoms is also important, and it could be the rate-determining steps for carbon nanofiber growth. On the basis of this mechanism, it is likely that the shape of nanofiber depends on that of faceted Ni metal particle at a fiber tip. Thus, the sections of Ni catalysts at the tips of carbon nanofibers would be hexagonal.

However, in as-prepared Ni/SiO_2 catalysts, it is impossible that Ni particles on SiO_2 have the hexagonal sections. Therefore, during the methane decomposition, Ni particles must change their shapes. Figure 3 shows TEM images of Ni/SiO_2 catalysts before and just after contact with methane at 773 K. Specimens for these TEM observations were not cut in sections. Before methane decomposition, Ni metal particles supported on SiO_2 did not have specific shapes (Figure 3a). In contrast, faceted Ni metal particle, which was appeared to be hexagonal shapes, was formed just after the contact with methane, and nanofibers were not yet formed (Figure 3b), indicating that the reconstruction of Ni metal particles would take place by contacting with methane before the growth of nanofibers. These results agree with the mechanism of carbon nanofiber growth proposed by Yang and Chen.[9] In addition, in the case of carbon nanotube growth, in situ HRTEM shows that the Ni nanoclusters undergo dynamic morphological transformations during growth of nanotubes.[10]

The structural change of Ni metal particles on the carbon matrix was reported using in situ TEM measurements with heating.[11] According to this investigation, quasi-liquefied Ni metal particles were confirmed at 873 K, although the melting point for Ni metal (1728 K) is significantly higher. The reason for the quasi-liquefaction would be the formation of NiC_x species through the supersaturation of carbon atoms into Ni. These NiC_x species have lower melting point than Ni metal; therefore, the quasi-liquefaction would be observed at 873 K. In the case of methane decomposition, as soon as methane molecules decompose on the surface of Ni metal particles, formed carbon atoms are dissolved in the bulk of Ni metal. It is considered that this dissolution of carbon atoms in Ni metal particle induce the reconstruction. Consequently, they are quasi-liquefied and transformed into the shape with hexagonal section, and these particles grow hexagonal column-shaped nanofibers.

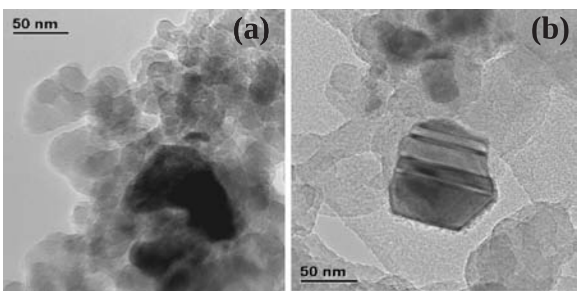

Figure 3. TEM images of Ni/SiO_2 catalysts (a) before and (b) just after contact with methane.

However, XRD patterns of Ni/SiO_2 catalysts after the contact of methane did not show the diffraction lines due to NiC_x species.[12] It was recognized that NiC_x species formed during methane decomposition were metastable.[13] NiC_x species easily decompose into Ni metal and carbons at room temperature; therefore, they were not confirmed in XRD measurements.

In summary, cross-sectional TEM measurement indicated that carbon nanofibers prepared by methane decomposition over Ni/SiO_2 catalysts had regular hexagonal sections. The shape of nanofiber depends on that of faceted Ni metal particle at a fiber tip, in other words, Ni metal particles with hexagonal cross section formed hexagonal column-shaped nanofibers. There results strongly support the suggestion on the three-dimensional morphology of carbon nanofibers suspected by the conventional TEM observations.

References and Notes

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