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A Study on the Morphology of Carbon Nanomaterials Prepared by Thermal Chemical Vapor Deposition on Mechanochemically Treated Catalysts

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Carbon nanotubes (CNTs) have been grown by the thermal chemical vapor deposition (CVD) process in which C_2H_2 gas was deposited on the $Fe(NO_3)_3$-$Al(OH)_3$ mixture pretreated by mechanochemical treatment with a high energy mixer mill. As the duration time of grinding for the $Fe(NO_3)_3$-$Al(OH)_3$ mixture by the mixer mill increased, amorphous $Al(OH)_3$ and smaller Fe particles agglomerated into spheres. With unground and ground mixtures of $Fe(NO_3)_3$-$Al(OH)_3$, CNTs were grown at 700°C. As a result, CNTs grown on ground mixtures have a more uniform diameter and morphology than those on unground mixtures. The characterization of $Fe(NO_3)_3$-$Al(OH)_3$ mixture and as-grown CNTs was carried out by XRD, SEM and TEM.

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1. Introduction

Carbon nanotubes (CNTs) have been attractive for their distinct physical and chemical properties.[1,2] Many methods including arc discharge, laser ablation and chemical vapor deposition (CVD) have been used for the growth of CNTs.[3,4] Recently, the CVD process using plasma or a heat source has been developed as an effective method suitable for the mass production of high-quality CNTs. Unlike other methods, a catalyst in the CVD process due to direct contribution to the graphitization of decomposed carbon is extremely important.[5] Nanosized transition metal particles such as Ni, Co and Fe with various types of soluble salts are dispersed on the support with a larger surface area by the impregnation method. In this case, the dispersion state of metal particles on the support directly affects the growth of CNTs in a high-temperature reaction. The rigidity of the catalyst may be maintained through heat treatment, while the formation of insufficient dispersion leads to a large amount of low-grade CNTs. In this study, we introduced the mechanical grinding process using a high-energy mixer mill to maintain the rigidity of the catalyst and control the active site of the catalyst. Such long time grinding may cause a mechanochemical effect in the growth of CNTs using the CVD process.[6,7] The main purpose of this study is to investigate the change of morphologies by mechanochemical treatment of the $Fe(NO_3)_3$-$Al(OH)_3$ mixture as a catalyst in the growth of CNTs in the thermal CVD process.

2. Experimental

2.1 *Preparation of supported catalyst for the growth of CNTs*

For this study, $Fe(NO_3)_3 \cdot 9H_2O$ and $Al(OH)_3$ were used as catalytic precursor and support, respectively. Ten grams of $Al(OH)_3$ was dispersed in ethanol for 3 hr and 6 mmol of $Fe(NO_3)_3 \cdot 9H_2O$ was dissolved for 24 hr with strong stirring. The suspension was dried at 80°C and powder was obtained after 48 hr. The dried powder was well mixed by the following two methods. The first method is grinding with an agate mortar and pestle for 20 min, while keeping the powders' crystal structures, resulting in the so called 'unground mixture.' The other method is grinding under a dry condition by a mixer mill (MM200, Retsch), which causes the change of the powders' crystal structures, resulting in the so called 'ground mixture.' One gram of the mixture was put in a tungsten carbide grinding jar of 20 ml inner volume with two tungsten carbide balls of 9 mm diameter. The grinding was carried out at approximately 1800 rpm. The duration of grinding was 15–120 min.

2.2 *Growth of CNTs by thermal CVD*

CNTs were grown by the thermal CVD process on the unground and ground mixtures with C_2H_2 as a carbon source. Bulk mixtures of 100 mg put in alumina crucibles were loaded into a quartz tube with an inner diameter of 45 mm and a length of 1000 mm and placed at the center of a furnace, where a uniform heating zone was maintained. H_2 gas flow of 100 sccm was introduced for 20 min to reduce the surface of Fe particles used as a catalyst active site and then H_2 flow of 100 sccm and C_2H_2 flow of 10 sccm were simultaneously introduced for 30 min to prepare the CNTs. The overall process of reduction and growth was carried out at 700°C. Morphological and structural characteris-

tics of the mixtures used for the catalysts were examined by SEM and XRD, respectively. The grown CNTs were characterized by SEM and TEM.

3. Results and Discussion

Figure 1 shows the XRD patterns of unground and ground mixtures of $Fe(NO_3)_3 \cdot 9H_2O$ and $Al(OH)_3$ for various grinding times. As can be seen from this figure, the peaks of Fe_2O_3 and $Al(OH)_3$ decrease with an increase of grinding time. Peak intensities of Fe_2O_3 and $Al(OH)_3$ decreased sharply as compared with those of the unground mixture during the early stage of grinding at 30 min. For the ground mixture at 120 min, the XRD pattern of $Al(OH)_3$ hardly has any distinct diffraction peaks except for the strong peaks of Fe. It is certain that the $Al(OH)_3$ phase of the mixture transformed to be come amorphous at 120 min grinding. The peaks of the Fe phase still remained, but were broadened, showing that the size of Fe particles becomes small. It is concluded that the crystal structure of the unground mixture changes to a disordered state as the grinding time increases.

SEM images of unground and 120 min ground mixtures of $Fe(NO_3)_3$-$Al(OH)_3$ for various grinding times areshown in Fig. 2. It was observed in the unground mixture (Fig. 2(a)) that nanometer-scale particles agglomerated into particles of 2~5 μm size. Fe particles were strongly mixed-ground to smaller particles by a high-energy mixer mill and dispersed on $Al(OH)_3$. In the beginning stages of grinding, small broken particles, which consist of Fe particles and $Al(OH)_3$, were observed. As the grinding time increased, these small particles agglomerated to spherical shapes with diameters of 100~200 nm as shown in Fig 2(b). On observing by XRD patterns and SEM images, it was established that small Fe granules were rigidly mounted on the amorphous $Al(OH)_3$ surface. After this characterization, the unground and 120 min ground mixtures were used for the growth of CNTs at

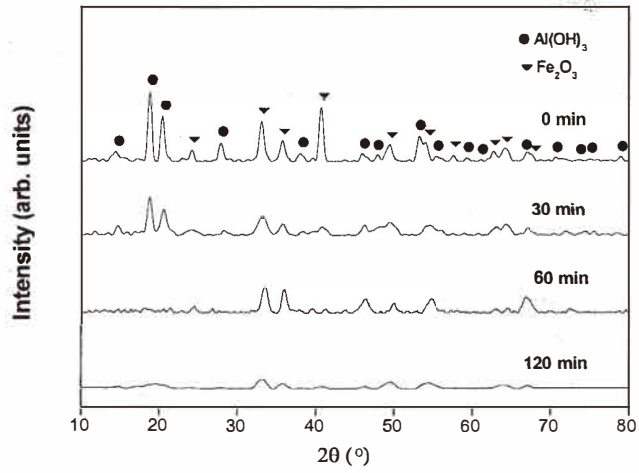

Fig. 1. X-ray diffraction patterns of the $Fe(NO_3)_3$-$Al(OH)_3$ mixture for various grinding times.

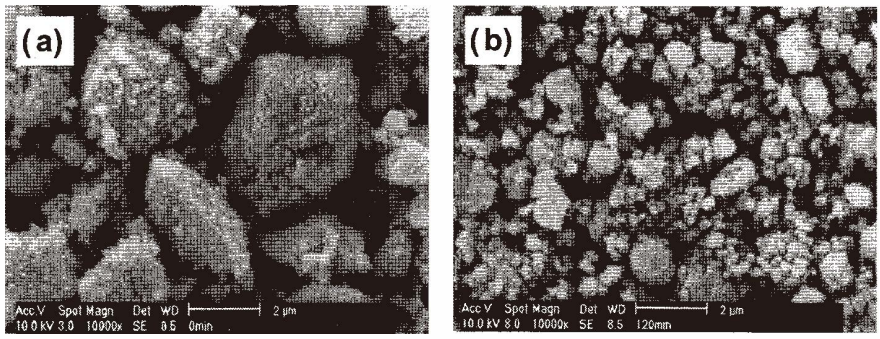

Fig. 2. SEM images of (a) unground mixture and (b) 120 min ground mixture of $Fe(NO_3)_3$ and $Al(OH)_3$

700°C by a thermal CVD process. As the temperature increased, Fe particles rigidly stuck to porous $\gamma \geq Al_2O_3$ with a large surface area which is the transformed type from $Al(OH)_3$ due to the increase of the process temperature.

Figure 3 shows the SEM photographs of CNTs grown on the mixtures of Fe $(NO_3)_3$-$Al(OH)_3$. As shown in the unground mixture in Fig. 3(a), two morphological types of carbon nanomaterials are evident. One is the carbon filaments with diameter of 100–200 nm and length of 1~2 μm. The other is CNTs with an outer diameter of 20–50 nm and length of 1~10 μm. The heterogeneous character of the grown morphologies means that the size of the catalyst active site is poorly controlled. As an alternative, heat treatment for the unground mixture is carried out at 450°C for 2 hr. Figure 3(b) presents the images of CNTs grown on a heat-treated unground mixture. Most of the carbon products take the shapes of CNTs with a diameter of 20~50 nm, while a few products are estimated as well-graphitized carbon filaments with a diameter greater than 100 nm. In addition to this, the ground mixture prepared by a mechanical milling process is tested. Figure 3(c) presents the images of CNTs grown on a 120 min ground mixture. Unlike growth on the unground mixtures, CNTs having a uniform diameter of 30~50 nm are grown. CNTs on an unground mixture have a linear shape, while those on a ground mixture have several chains of threads with a high packing density. Though the scanning of surface morphologies by SEM observation is convenient, TEM observation is required for more precise observation of internal structures. Figure 4 shows the TEM images of CNTs for various grinding times of the $Fe(NO_3)_3$-$Al(OH)_3$ mixture. From these, morphologies of carbon nanomaterials observed in SEM images are observed as well. In an unground mixture, CNTs have a diameter of 20~40 nm and carbon filaments have a diameter of 40~80 nm (Fig. 4(a)). In the beginning at 30 min of grinding, carbon filaments with a more uniform diameter still remained (Fig. 4(b)). After that, at 60 min grinding, the amount of carbon filaments is sharply reduced (Fig. 4(c)). As shown in Fig. 4(d), the overall morphology of carbon products on the 120 min ground mixture reveal chains of threads similar to the SEM observation. Linear types of CNTs in the beginning of grinding changed into entangled types as the duration of grinding on mixture increased. The reason why the morphologies

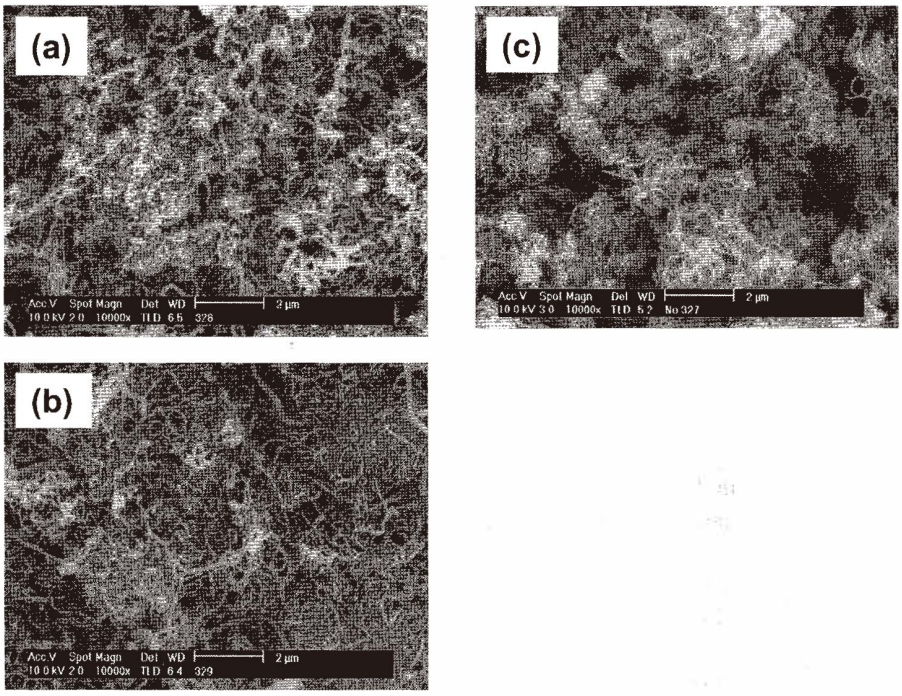

Fig. 3. SEM images of CNTs grown on (a) original unground mixture, (b) heat-treated unground mixture and (c) 120 min ground mixture.

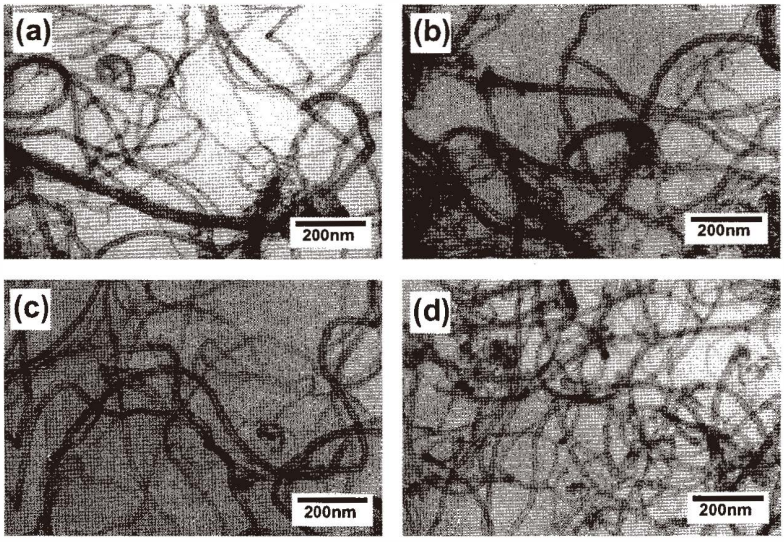

Fig. 4. TEM images of CNTs grown on (a) unground mixture, (b) 30 min ground mixture, (c) 60 min ground mixture and (d) 120 min ground mixture.

of CNTs are affected so signifcantly by the grinding time is that strong grinding by the mixer mill has changed the initial conditions of the catalyst, which had no rigidity or homogeneity intoa stable state with good packing density due to rigid support for the catalytic precursors. As a result, it is considered that the mechanochemical treatment of the $Fe(NO_3)_3$-$Al(OH)_3$ mixture used as the supporting catalyst gives rise to the growth formation of CNTs.

4. Conclusions

CNTs have been grown on the $Fe(NO_3)_3$-$Al(OH)_3$ mixture, mechanochemically treated by a high-energy mixer mill, through the thermal CVD process. The conclusions are as given below:

1. As the duration of grinding on the $Fe(NO_3)_3$-$Al(OH)_3$ mixture increases, amorphous $Al(OH)_3$ is obtained and increasinglysmaller Fe particles are agglomerated to spherical shapes.
2. Carbon products grown on a ground mixture are CNTs with the comparatively uniform diameter of 20~50 nm, while those on an unground mixture also exhibit carbon filaments with diameter of 100~200 nm.
3. CNTs grown on unground mixtures mainly take a linear shape, while those on ground mixtures take an entangled thread-type shape.
4. It is expected that well dispersion achieved by the mechanochemical treatment will induce rigidity in the catalyst and control the growth direction.

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