A Study on the Morphology of Carbon Nanomaterials prepared by Thermal CVD on the Mechanochemical Treated Catalysts

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

1. Introduction

Carbon nanotubes (CNTs) have been attractive for distinct physical and chemical properties[1]. Many methods including arc discharge, laser ablation and chemical vapor deposition (CVD) have been used for the growth of CNTs[2,3]. Recently, CVD process using plasma or heat source have been known for effective method suitable for mass production of high qualified CNTs. Unlike other methods, catalyst in CVD process due to direct contribution to the graphization of decomposed carbon is greatly important[4]. Nano-sized transition metal particles such as Ni, Co and Fe with the types of soluble salts are dispersed on the support with a high surface area by impregnation method. In this case, the dispersion state of metal particles on support directly effects to the growth of CNTs in high temperature reaction. The rigidity of catalyst may be maintained through heat treatment, while insufficient dispersion causes to mass-produce low grade CNTs. In this study, we introduced the mechanical grinding process using a high energy mill to maintain the rigidity of catalyst and control active site of catalyst. Such a long time grinding may cause mechanochemical effect in the growth of CNTs using the CVD process[5]. The main purpose of this study is to investigate the change of morphologies by mechanochemical treatment to Fe-$Al(OH)_3$ mixture as catalyst on the growth of CNTs in 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. 10g of $Al(OH)_3$ was dispersed in ethanol for 3 hr and 6 mmol of $Fe(NO_3)_3 \cdot 9H_2O$ is dissolved for 24 hrs with a strong stirring. The suspension state of solution was dried at 80℃ and powder mixtures were obtained after 48 hrs. Dried powder mixtures were well mixed by following two different methods. One is only a mixing of mixture by an agate mortar and pestle for 20 min, keeping their crystal structures, so called 'unground mixture'. The other is a mixed grinding with the ground mixture under dry condition by a mixer mill (MM200, Retsch), which causes the change of their crystal structures, so called 'ground mixture'. 1 g of the mixtures were put in an tungsten carbide grinding jar of 20 *ml* inner volume with 2 tungsten carbide balls of 9 mm-diameter. The mixture grinding was done at approximately 1800 rpm. The duration of grinding was 15~120 min.

2.2 The growth of CNTs by thermal CVD

CNTs were prepared by thermal CVD process on the unground and ground mixtures with C_2H_2 as a carbon source. 100 mg of bulk mixtures put in alumina crucibles was loaded into the quartz tube with an inner diameter of 45 mm and a length of 1000 mm and placed at the center of the furnace, where a uniform heating zone was maintained. 100 sccm of H_2 gas flowed for 20 min to reduce the surface of Fe particles used as a catalyst active site and then 100 sccm of H_2 and 10 sccm of C_2H_2 were simultaneously flowed for 30 min to prepared CNTs. The overall process of the reduction and growth was carried out at 700℃. Morphology and crystallinity of the mixtures used for the catalysts were checked by SEM and XRD, respectively. The grown CNTs were characterized by SEM and TEM.

3. Results and Discussion

Fig. 1 shows the XRD patterns of unground and ground mixture 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 and $Al(OH)_3$ decrease with an increase of grinding time. Peak intensities of Fe 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 x-ray diffraction pattern of $Al(OH)_3$ scarcely has any distinct diffraction peaks except the strong peaks of Fe. It is certain that $Al(OH)_3$ phase of the mixture transformed to be amorphous at 120 min grinding. The peaks of Fe phase still remained, but were broadened, showing that the size of Fe particles becomes small. It is concluded that the crystal structure of unground mixture changes to a disordered state as the grinding time increases.

SEM images of unground and ground mixtures of Fe-$Al(OH)_3$ for various grinding times were observed. It was observed in unground mixture that nanomater-scale particles were agglomerated into several micrometer scales of masses. Fe particles were strongly mixed-ground to more smaller particles by a high energy mixer mill and dispersed on $Al(OH)_3$. In beginning stages of grinding, small broken particles, which consist of the mixture of Fe and $Al(OH)_3$, were observed. As the grinding time increased, the shape of small particles was closed to sphere with the diameter of 100~200 nm and agglomerated. As observed by XRD patterns and SEM images, it was expected that small Fe granules were rigidly mounted on amorphous $Al(OH)_3$ surface. After this characterization, the unground and 120 min ground mixtures were used for the growth of CNTs at 700℃ by thermal CVD process. As the temperature increases, Fe particles are rigidly stuck to porous γ-Al_2O_3 with high surface area which is the transformed type from $Al(OH)_3$ due to the raise of the process temperature.

Fig. 2 shows the SEM photographs of CNTs grown on the mixtures of Fe -$Al(OH)_3$. As shown in unground mixture in Fig. 2(a), two morphological types of carbon nanomaterials are revealed. One is the estimated carbon nanorods(CNRs) with the diameter of 200~400 nm and length of 1~2 μm. The other is CNTs with the outer diameter of 20~50 nm and the length of 1~10 μm. The heterogeneous aspect of the grown morphologies means that the size of catalyst active site is poorly controlled. As an alternative, heat treatment for unground mixture was carried out at 450 ℃ for 2 hrs. Fig. 2(b) presents the images of CNTs grown on heat-treated unground mixture. Most of carbon products takes the shapes of CNTs with the diameter of 20~50 nm, while a few products are estimated as well-graphitized carbon filaments with the diameters of above 100 nm. In addition to this, ground mixture prepared by mechanical milling process was tested as well. Fig. 2(c) presents the images of CNTs grown on 120 min ground mixture. Unlike unground mixtures, CNTs having uniform diameter of 30~50 nm were grown. CNTs on unground mixture had linear shapes comparatively, while those of ground mixture had several skeins of thread with a high packing density. Though the scanning of surface morphologies by SEM observation was convenient, TEM observation was required for the observation of more precise internal structures. Fig.3 shows the TEM images of CNTs under corresponding conditions in Fig. 2. CNTs grown on unground mixture (Fig. 3(a)) have the diameter of 30~40 nm, corresponding to the observation in Fig 2(a). (Fig. 3(b)), almost similar aspect compared with original unground mixture, was observed, but carbon filaments with the diameter of 100 nm and the length of several micrometers were often observed. However, CNTs grown on 120 min ground mixture in Fig. 3(c) revealed even more uniform diameter of 30~40 nm in all products. As shown in Fig. 2(c), CNTs seem to be agglomerated each other. Except for this, we have also investigated the growth of CNTs in other ground mixture conditions such as 15, 30 and 60 min. As a result, the diameter control of CNTs in ground mixtures by a mechanical milling process is more convenient than that in unground mixtures.

4. Conclusions

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

1. As the duration time of grinding on the Fe-$Al(OH)_3$ mixture increases, amorphous $Al(OH)_3$ is obtained and more smaller Fe particles agglomerated in sphere shapes.
2. Carbon products grown on ground mixtures are the CNTs with the comparatively uniform diameters of 20-50 nm, while that of unground mixtures also exhibit the CNTs with the diameters of 100~200 nm.
3. CNTs grown on unground mixtures take mainly linear types, while those of ground mixtures do entangled thread types.
4. It is expected that well-dispersion technique by the mechanochemical treatment will induce the rigid catalyst and control growth directions.

Acknowledgments

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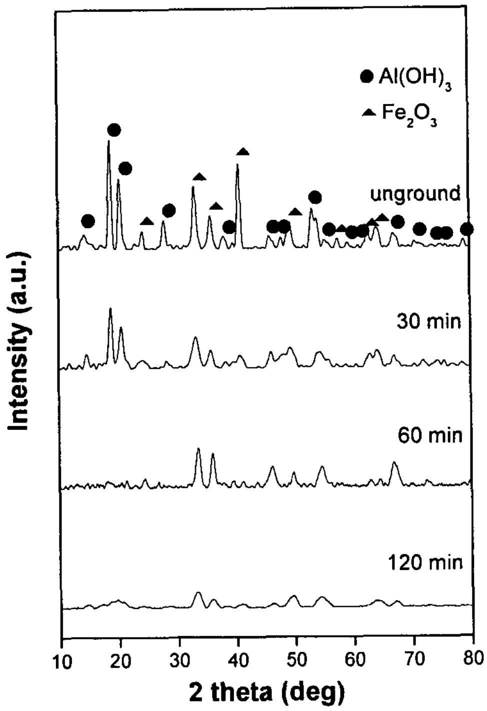
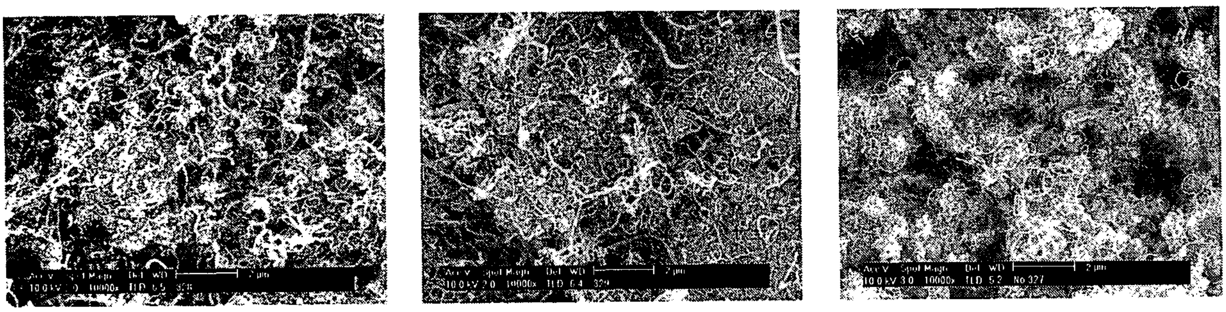
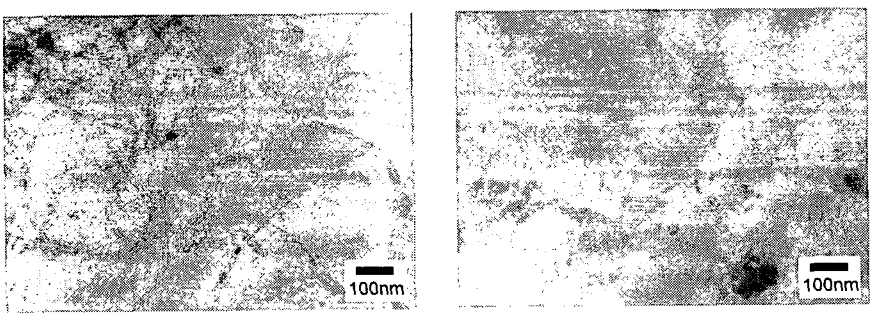


Fig. 1. X-ray diffraction patterns of the Fe-Al(OH)$_3$ mixtures for various grinding times.



(a) (b) (c)

Fig. 2. SEM images of CNTs grown on (a) original unground mixture, (b) heat-treated unground mixture and (c) 120 min ground mixture.



(a) (b)

Fig. 3. TEM images of CNTs grown on (a) unground mixture and (b) 120 min ground mixture.