The Effect of Mechanochemical Treatment of Supported Catalyst on the Growth of Carbon Nanotubes

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As an pretreatment, a $Fe(NO_3)_3 \cdot 9H_2O$-$Al(OH)_3$ mixture was ground by a high energy mill and used as a supported catalyst for the growth of carbon nanotubes by a thermal CVD. The crystal structure of the catalyst disordered by the grinding influenced significantly the synthesis of carbon nanotubes in a thermal CVD.

Key Words : Carbon nanotubes, Mechanochemical treatment, CVD

Introduction

Since the first observation of carbon nanotubes in 1991,[1] the studies on carbon nanotubes due to distinct electric and mechanical properties[2,3] have been probably the most active field in carbon science. Prior to industrial applications,[4,5] many researchers have studied about the growth of high performance carbon nanotubes. The methods for growing carbon nanotubes are arc discharge, laser ablation and chemical vapor deposition (CVD) method, etc.[6-8] CVD method using the decomposition of carbon source on the transition metal catalyst such as Ni, Co, Fe and their compounds is lately representative growth method. As compared with other methods, the advantage of CVD method is that the carbon nanotubes can grow at the relative low temperature with various raw materials and products. The varieties of products by raw materials mean that the key to high quality of the production is the characteristics control of their catalysts used as raw materials. It might be very important, especially, for the preparation of supported transition metal catalysts to improve reaction properties in the growth of carbon nanotubes by CVD.[9,10]

The main purpose of this study is to prepare high quality of carbon nanotubes by modifying original properties of supported transition metal catalysts. Mixed grinding on the pretreatment of catalyst by high energy mill using a mixer mill is suggested as a modification step to initiate the mechanochemical effect which decreases the particle sizes and changes properties of catalytic surfaces.[11,12] From this study, we have found that mixed grinding on the supported transition metal catalysts had a strong influence on the growth of carbon nanotubes by thermal CVD.

Experimental Section

Prior to the synthesis of carbon nanotubes, the supported metal catalysts were prepared by the following procedure. The raw materials for the preparation of supported catalyst were $Fe(NO_3)_3 \cdot 9H_2O$ (99.99%) and $Al(OH)_3$ (99.9%) purchased from Kojundo Chemical Laboratory Co., Inc., Japan. 6 mmol of $Fe(NO_3)_3 \cdot 9H_2O$ was dissolved in 200 mL of ethanol for 30 min. Then, 1 g of $Al(OH)_3$ was added to the solution and well-dispersed for 6 hrs with a strong stirring. Finally, the $Al(OH)_3$-dispersed solution was dried for 24 hrs at 80 ^oC and powder samples were obtained. Next, the powder samples were treated by two different methods. One is a mixing by an agate mortar for 20 min, keeping the crystal structures of original species, so called unground catalyst. The other is a mixed grinding of unground catalyst under dry condition by mixer mill (MM200, Retsch), resulting in a change of crystal structure, so called ground catalyst. The grinding jar and ball were made from tungsten carbide and alumina, respectively. The weight ratio of powder sample and grinding ball was 1 : 18. The specified milling times were 30, 60, 120 min and the vibration speed of grinding jar was a frequency of 30 Hz. Then, the unground and 120 min ground catalysts were used for the growth of carbon nanotubes by using a thermal CVD process in which C_2H_2 gas was used as a carbon source at atmospheric pressure. The prepared catalysts were moved into the quartz tube and placed in the center of the furnace, which a uniform heating zone was maintained. First, the furnace was heated to the reaction temperature ranging from 700 to 800 ^oC under Ar gas to prevent the oxidation of catalyst. Once the furnace was heated up to the reaction temperature, H_2 gas was purged with the flow rate of 0-100 sccm to reduce the surface of catalyst for 10 min. Subsequently, 10 sccm of C_2H_2 gas with 0-100 sccm of H_2 gas was flowed for 1 hrs. After the reaction was finished, the furnace was cooled down the room temperature under Ar gas.

The catalysts treated by two different methods were analyzed by X-ray diffractometer (XRD, Rigaku D/MAX III B) and scanning electron microscope (SEM, Phillips XL 30S FEG). Microstructural analyses of carbon nanotubes obtained by thermal CVD was carried out by transmission electron microscope (TEM, EM 912 Omega) and SEM.

Results and Discussion

X-ray diffraction patterns of unground catalyst and 30, 60, 120 min ground catalysts of a $Fe(NO_3)_3 \cdot 9H_2O$-$Al(OH)_3$ sample have been observed. In this paper, the x-ray diffraction patterns of the unground and 120 min ground catalyst were shown in Figure 1. As the grinding time increases, diffraction intensity of $Al(OH)_3$ decreases. From this experimental result, the diffraction intensity of $Al(OH)_3$ decreased sharply as compared with that of the unground catalyst during the early stage of grinding up to 30 min. In the 120 min ground catalyst, the x-ray diffraction peaks of $Al(OH)_3$ almost disappeared. This indicates that $Al(OH)_3$ is completely in disorder after 120 min grinding. It can be readily deduced that the crystal structure of unground catalyst transfers to a disordered state with grinding.

Figure 2 shows the SEM images of unground and 120 min ground catalyst of $Fe(NO_3)_3 \cdot 9H_2O$-$Al(OH)_3$ sample. Figure 2(a) reveals the shape of a $Fe(NO_3)_3 \cdot 9H_2O$-$Al(OH)_3$ sample for unground catalyst and the original crystal structure of a sample was presented. However, Figure 2(b), as the image of 120 min ground catalyst, shows the existence of smaller particles than those of Figure 2(a). It is thought that fine particles are resulted from fracturing the original sample though grinding.

Based on the analysis for unground and 120 min ground catalysts, the growth of carbon nanotubes was performed by a thermal CVD process. Through repeated experiments, the optimal condition was as follows; the reaction temperature was 700 °C, and the flow rates of H_2 and C_2H_2 gases were 50 sccm and 10 sccm, respectively. First, the yield of products was observed soon after the reaction was finished. The yield of products was defined as the weight ratio of product and catalyst. The yield of products prepared on 120 min ground catalyst was twice higher than that of unground catalyst.

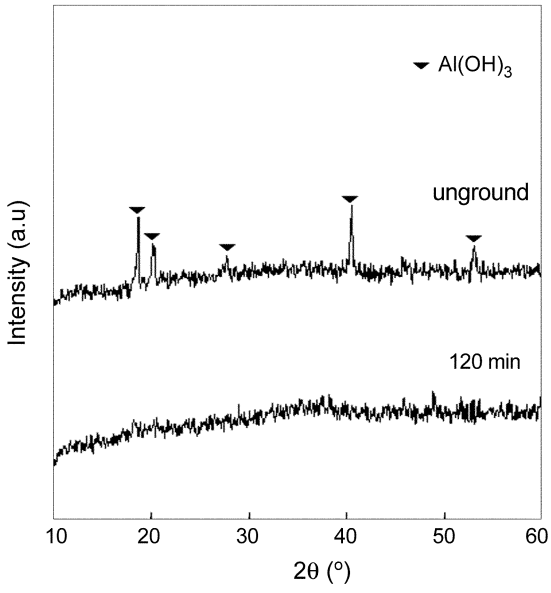

Figure 1. X-ray diffraction patterns for unground and 120 min ground catalyst of $Fe(NO_3)_3$ $9H_2O$-$Al(OH)_3$.

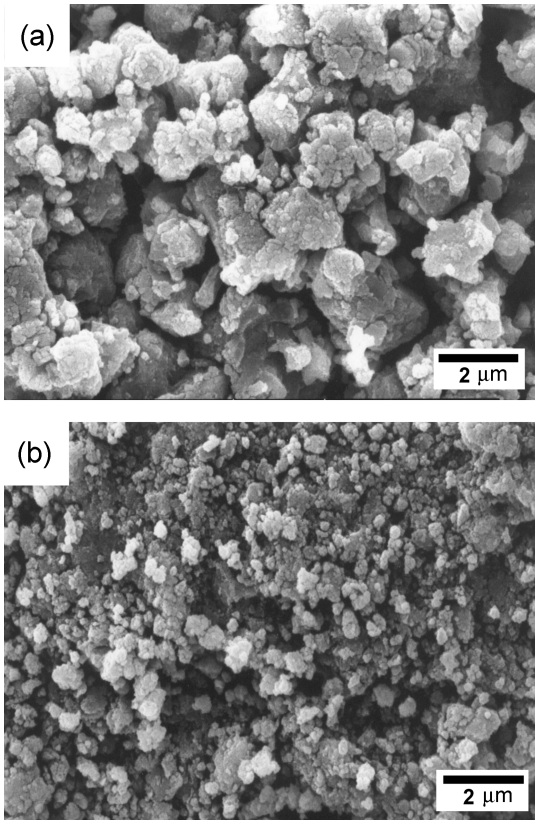

Figure 2. SEM images of powder samples; (a) unground catalyst, and (b) 120 min ground mixture.

Second, the products were characterized with the electron microscope observation. Figure 3 shows the SEM images of products prepared on two catalysts by a thermal CVD. Figures 3(a) and 3(b) show the products prepared on unground and 120 min ground catalysts, respectively. As can be seen from Figure 3(a), a few of carbon nanotubes appeared and most of products were observed as the carbon nanorods. On the other hand, most of products prepared on 120 min ground catalyst were carbon nanotubes. Diameters of carbon nanotubes and carbon nanorods prepared on unground and ground catalysts of a $Fe(NO_3)_3 \cdot 9H_2O$-$Al(OH)_3$ were ranged from 10 to 40 nm and from 150 to 200 nm, respectively. TEM observation was also performed to analyze the shape of products. Figure 4 shows the TEM image of product prepared on 120 min ground catalyst. It was observed that lots of carbon nanotubes were synthesized on catalysts and metal particles were existed as tips on the top of carbon nanotubes. A similar morphological aspect was observed for unground catalyst. Also, diameters of carbon nanotubes by TEM observation were ranged from 10 to 40 nm as they were very similar to those of SEM observation. From these results, the yield and quality of carbon nanotubes prepared on 120 min ground catalyst were higher than those of unground catalyst. Consequently, the mechanochemical treatment of a $Fe(NO_3)_3 \cdot 9H_2O$-$Al(OH)_3$ sample by a high energy mill affects significantly the characteristics of carbon nanotubes synthesized by a thermal CVD.

The reason why the mechanochemical treatment on the

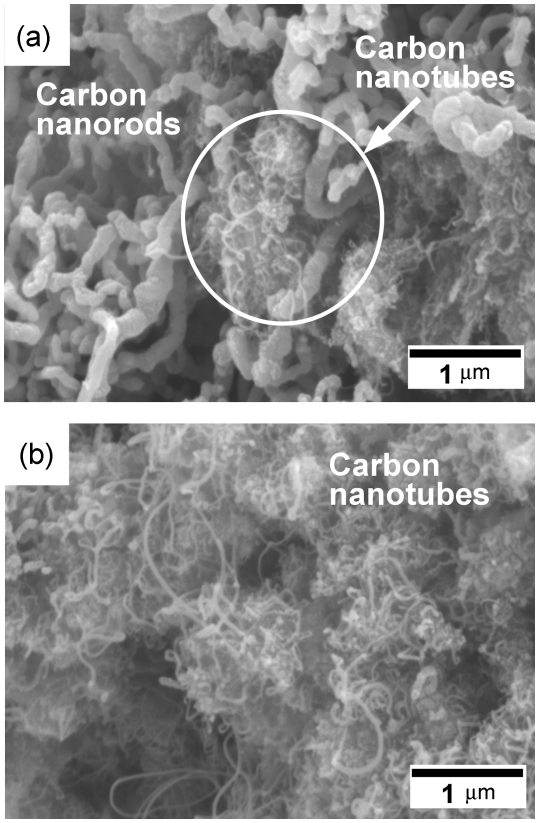

Figure 3. SEM images of grown products at 700 °C with C_2H_2 gas; (a) unground catalyst, and (b) 120 min ground catalyst.

sample influences the growth of carbon nanotubes is the increase of activation sites and a homogeneous mixing of the supported transition metal catalyst by a mixed grinding. It means that unground catalyst has the incomplete combination between transition metal and support. Considering our experiment results, mechanochemical treatment can be used as a very important step in the preparation of supported catalyst.

Summary

The effect of mechanochemical treatment of a $Fe(NO_3)_3 \cdot 9H_2O$-$Al(OH)_3$ sample by a mixer mill on the growth of carbon nanotubes by a thermal CVD was studied with the aid of XRD, SEM and TEM. The disordered state of $Al(OH)_3$ in a sample was attained at about 120 min grinding of supported catalyst. The quality and yield of carbon nanotubes prepared on 120 min ground catalyst are higher than those of unground catalyst. It was confirmed that mechanochemical treatment of supported transition metal catalyst offers a new possibility as a novel process of supported catalyst for improving the growth of carbon nanotubes

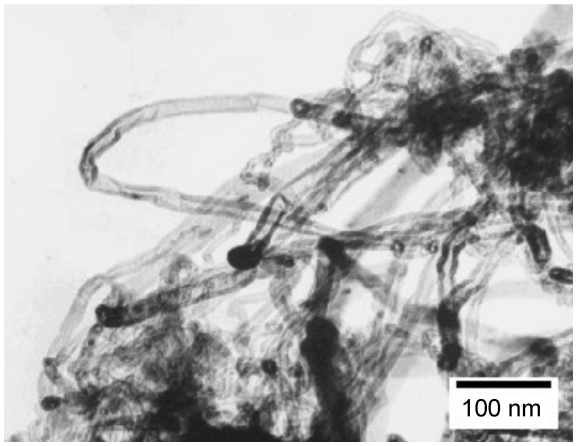

Figure 4. TEM image of carbon nanotubes grown on 120 min ground catalyst.

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