

Preparation and Characterizations of CNFs with very different Surface Area

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Introduction

Carbon nanofibers (CNFs) have been recognized as unique forms of carbon materials [1-4]. The diversity of CNFs can be induced by the control of the alignments of laminated c-plane layers along the fiber axis, which provided typically three types of CNFs such as platelet (alignment perpendicularly against the fiber axis), tubular (alignment parallel along the axis), and herringbone (alignment angled to the axis) CNF [4].

Recently, we found out that some physical properties such as surface area and crystallinity, strongly depends on the preparation conditions of CNF in CVD method. Nevertheless the diameter of CNF sustains almost the same, resultant CNF that was from the different compositions of catalyst showed the much different surface areas and other physical properties.

In this work, the present authors summarized the effects of the catalyst compositions and the structural difference of resultant CNFs. We also conjectured the growing mechanism of CNFs by the reverse gas chromatography. The optimization of synthetic conditions such as catalyst composition, reaction temperature, carbon sources and their ratios can afford the maximum surface area of over 500 m²/g of CNF without further activation.

Experimental

Two compositions of Cu-Ni catalysts were prepared by the precipitation and burning methods. The non-supported Cu-Ni catalysts of Cu-Ni (2/8) and Cu-Ni (2/8) were prepared by the precipitation of the copper and nickel carbonates from the copper nitrate and nickel nitrate solution using ammonium bicarbonate as described in detail by Best and Russell [5]. The other Cu-Ni catalysts of Cu-Ni (2/8) and Cu-Ni (2/8) were prepared by supporting Cu-Ni on conductive carbon black (#3050, Mitsubishi Chemical Co. Ltd) and subsequent burning of carbon black in the air atmosphere. CNFs were prepared by the thermal pyrolysis of ethylene and hydrogen mixed gases over copper-nickel catalysts at 580 °C using a conventional horizontal tube furnace. Resultant CNFs were characterized by FE-SEM, HR-TEM, STM, XRD and BET.

Results and Discussion

Table 1 shows results of preparations.

CNFs from the Cu-Ni (2/8) showed higher surface areas than those from Cu-Ni (8/2). CNFs from the Cu-Ni (2/8) also showed much higher yields than those from Cu-Ni (8/2). Among catalysts, Cu-Ni (2/8) prepared by the burning method showed highest surface area of 766 m²/g and over 300 times of yield. The finer catalyst particles from the mild burning condition, which deduce the short structural units of CNF, must be one of the reasons for the formation of high surface area.

Figure 1 shows SEM, TEM and STM image of CNFs prepared from Cu-Ni (2/8). STM photograph showed the primary structural units and its packing alignments. Some defects and nano spaces induced from the misalignments of primary structural units clearly appeared. Such nano-spaces might be one of the factors for the high surface area.

Reverse-GC chromatography confirmed that more amounts of methane was dissipated in the CNF growth from Cu-Ni (2/8) prepared by burning method. The defects or nano-space derived from the dissipation of methane that was converted from ethylene and hydrogen.

Acknowledgement

This work was carried out within the framework of the CREST program. The present authors acknowledge the financial support of Japan Science and Technology Corporation (JST).

References

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Table 1 Preparation results

Temperature (°C)	580			
	Cu-Ni(2/8)		Cu-Ni(8/2)	
Catalyst	CB* ¹	Metal* ¹	CB	Metal
* ² Yield (Product/Cat)	317.4	175.1	56.13	19.97
Specific Surface Area (m ² /g)	766	211	253	23

*¹CB=Supported by Carbon Black, Metal=Metal catalyst

*²Gas composition (C₂H₄/H₂)=4/1

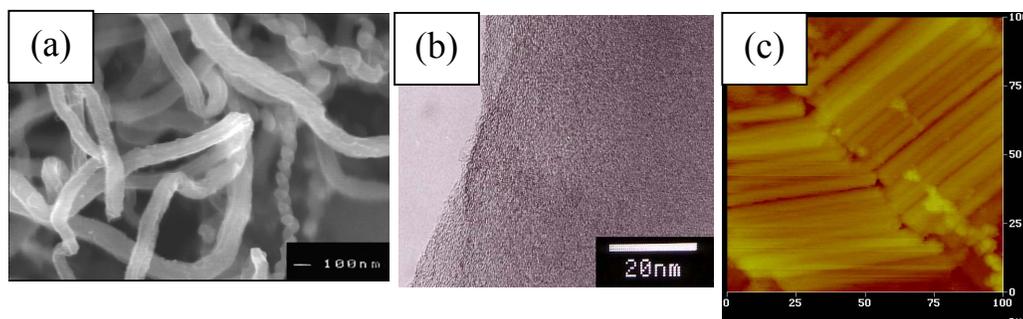


Fig.1 (a) SEM, (b) TEM and (c) SEM photographs of Herringbone CNF produced by Cu-Ni (2/8) metal catalysts