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Effect of Multi-catalysts on Carbon Nanofiber Synthesis in CVD

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The catalytic chemical vapor deposition (CVD) method has been widely utilized for synthesis of carbon nanomaterials. One of important key parameters in catalytic CVD to synthesize the carbon nanofibers or nanotubes is an appropriate selection of catalytic agents. In the present study, first, various kinds of micron-size powder catalysts and their mixtures were combinatorially tested, concerning to the macroscopic disposition of carbon in CVD with C_2H_2 source gas. It was found that the catalytic efforts of some composite catalysts brought remarkable enhancement as compared with single metal catalysts. The maximum fibrilliform carbonaceous deposition was obtained when using Fe+Ni+Sn mixture catalyst. Through the first experiment, unique formation shapes of carbon nanomaterials were obtained using $NiO+In_2O_3$ combination catalyst, called nanotube-bur-particle (NBP) and jointed-fiber-web (JFW). Secondarily, the influence of CVD process parameters such as gas flow rate, deposition time, temperature, and position, on these unique materials synthesis was experimentally investigated.

Keywords: carbon nanofiber, multi-element catalysts, CVD, nanotube bur particle, jointed fiber web

1. INTRODUCTION

Carbon nanomaterials such as nanotubes, nanofibers, and nanocoils, have been attracting numerous scientific and engineering attentions because of their unique structure and properties [1]. A variety of synthesis methods of such materials have been developed, including arc-discharge [2, 3], laser ablation [4], and chemical vapor deposition (CVD) [5, 6]. The CVD technique is a simple and low-cost method, and is thought to be realized the mass production. In CVD method, catalyst is required for the growth of carbon nanomaterials. Typical catalysts are the transition metals of Fe, Co, Ni, their oxides and alloys [7]. Recently, it was reported that when the other element was mixed, unique nanofibers has been obtained. The carbon nanocoils and nanotwist have been synthesized by using Fe/ITO (indium tin oxide) [8], and Ni/Cu or Zn/Cu film/substrate [9] as catalyst. This indicates that the selection of appropriate combination of elemental catalysts is one of the key factors to fabricate carbon nanomaterials in controlled shape or mass-production.

In the present study of carbon nanomaterials synthesis in CVD, first, various combinations of catalysts were tested and the production rate of carbonaceous materials was investigated. During that experiment, the combination of NiO and In_2O_3 provided unique structural carbonaceous materials. Then the influences of the process parameters on the production of the materials were experimentally investigated.

2. EXPERIMENTAL

The CVD apparatus with a cylindrical quartz tube reactor (300 mm long, 40 mm inner diameter) has been shown in previous paper [9]. However, a hot-filament was not used this time. In the present study, commercial powders of Fe, Ni, Sn, In, and their oxides with 1-3 μm diameter were used as catalyst, scattering on the quartz substrate (7.5 mm × 2.5 mm, 1 mm thickness) as thinner as possible. The basic experimental conditions were as follows: source gas, C_2H_2 (180 sccm); purge and dilute gas, He (420 sccm); process temperature, 700°C; deposition time, 3 min; substrate setting location, center of reactor tube; pressure, 1 atm; total weight of powdery catalyst, 10 mg. When the multi element catalyst was tested, each powder was equally mixed in weight.

The deposited carbonaceous materials were weighted with an electronic balance, and observed and analyzed with a scanning electron microscope SEM (JEOL, JSM-6300), energy dispersive X-ray EDX (PHILIPS, DX-4), and transmission electron microscopy TEM (JEOL, JEM-2010).

3. RESULTS AND DISCUSSION

3.1 Carbon deposition rate

After the deposition process, the weight of the product including the catalyst was measured. Then the carbon deposition rate (CDR) was evaluated, dividing the amount of carbonaceous material by the amount of catalyst and unit time (1 min). Therefore, CDR indicates that how many times the amount of carbonaceous material fabricated in the unit time is higher than the amount of the fed catalyst in weight.

The results of CDRs are listed in Tables I and II, for using Fe and/or Ni and Fe_2O_3 and/or NiO powdery catalyst, respectively. First, it was found that Sn, In, SnO_2, In_2O_3 and their mixture did not work as catalyst for carbon deposition at all. However, these elements obviously worked as additive secondary catalyst to enhance the carbonaceous deposition by using together with primary catalysts of Fe, Ni, Fe_2O_3, and/or NiO.

Concerning to the metallic primary catalyst, Fe or Ni