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Synthesis of Nano-Carbon Fine Particles in Low-Temperature Plasma and Evaluation of their Gas Adsorption Properties

低温プラズマ中でのナノカーボン微粒子の成長とガス吸着特性の評価

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Nano-carbon fine particles were synthesized by plasma-assisted hot-filament chemical vapor deposition. Their properties of hydrogen thermal-desorption (TDS), nitrogen adsorption-isotherm, specific surface area, and hydrogen adsorption-isotherm were evaluated. The results showed that the height of a peak appearing between 100 and 200 ℃ for synthesized carbon fine particles in TDS was one order of magnitude higher than that for CoMoCAT, that the nitrogen specific surface area was 31 m^2/g, and that the volume of hydrogen adsorbed on synthesized fine-particles at atmospheric pressure was 2.2 and 0.13 wt% for 77 K and room temperature, respectively. They suggest that synthesized carbon fine-particles have a higher capacity for hydrogen storage.

1. Introduction

Because nano-caron fine particles like carbon nanotubes (CNTs) generally have large surface area per unit weight, they are expected to be used for gas-adsorption material, especially, hydrogen storage material. Some papers have been published that carbon single-walled carbon nanotubes (SWNTs) show high capacity of hydrogen storage [1-3], while different results were also reported [4-6]. Since the structure and the hydrogen-storage mechanism of nano-carbon materials are complicated, the precise and repeatable data may be difficult to obtain. Therefore manysided analyses should be carried out for the evaluation of hydrogen-storage property of nano-carbon.

We have developed a new chemical-vapor-deposition (CVD) method of gas phase synthesis of carbon fine particles containing catalytic metal and SWNTs applying a radio-frequency (RF) glow discharge plasma along with hot-filaments (plasma-assisted hot-filament CVD), for the purposes of longer growth and structure modification of SWNTs by suspension in a reaction zone for a long time [7-9].

In this paper, we present the results of synthesis of carbon fine particles including SWNTs and their properties of hydrogen thermal-desorption, nitrogen adsorption-isotherm, specific surface area, and hydrogen adsorption-isotherm.

2. Experimental

Fig.1 shows the schematic diagram of the RF glow discharge plasma system with hot-filaments. RF plasma was generated between grounded filaments and an RF-induced cupper plate. Filaments were heated up to 1800-2000 ℃. 40-60 % ethylene diluted in hydrogen containing the vapor of ferrocene ($Fe(C_5H_5)_2$) was allowed to flow toward the hot-filaments. The pressure in the chamber was maintained at 2.66-5.32 kPa (20-40 Torr). The plate of RF electrode was set 15 mm downstream from the hot filaments and placed perpendicular to the flow of reaction gas. Power up to 50 W was applied to the RF plate with the filaments heated for about one hour. Prepared carbon fine-particles were collected on an upper-plate, which also serves as RF electrode, and a bottom-plate.

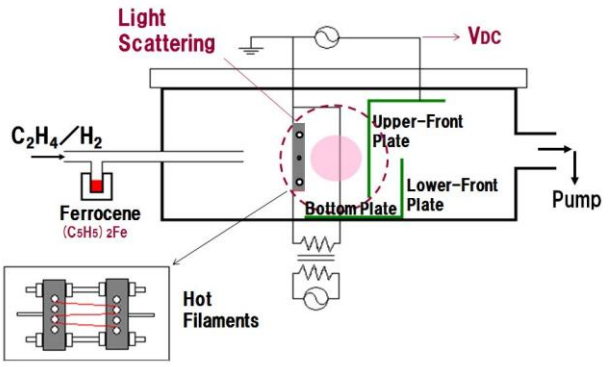

Fig.1. Schematic of plasma-assisted hot-filament chemical vapor deposition system.

Thermal-desorption spectroscopy (TDS) of the properties of synthesized fine particles were evaluated by the use of a qaudrapole mass analyzer

(QMS). Carbon fine particles of 200 mg were put on a silica boat in a hot-wall silica tube. Temperature was raised at the constant rate of 10 °C/min. The change of partial pressure for M/q (the ratio of mass to charge) = 2 to 200 was measured during temperature increase.

The nitrogen and hydrogen adsorption-isotherms of synthesized fine particles were measured by the volumetric method using nitrogen gas in a small stainless cell at the temperature of 77 K and room temperature (Fig.2).

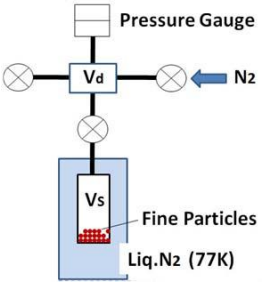

Fig.2. Schematic of adsorption-isotherm measurement system.

3. Results and Discussion

Fine particles including SWNTs were baked in vacuum at 1000 °C for 5 h and immersed in hydrogen gas at atmospheric pressure and room temperature for 15 h, the hydrogen gas was evacuated, and then TDS was carried out. The height of a peak appearing between 100 and 200 ℃ for synthesized carbon fine particles was one order of magnitude higher than that for CoMoCAT, which is commercialized SWNT. The hydrogen storage capacity of synthesized fine particles was calculated to be 0.01 wt% by the integration of the peak determined by TDS appearing at around 200 °C.

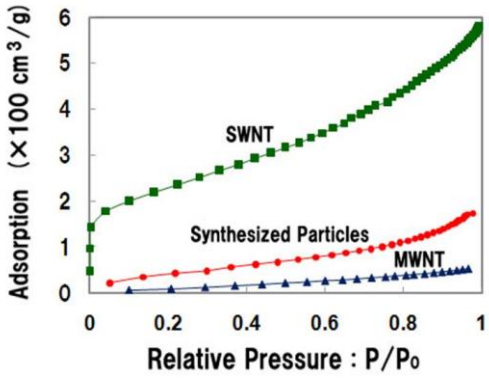

Fig.3. N_2 adsorption isotherms for synthesized fine particles, SWNTs and MWNTs.

Figure 3 shows a nitrogen adsorption isotherm for synthesized fine particles, which were beforehand baked in vacuum at 400 °C for 5 h, along with those for commercialized SWNTs (CoMoCAT) and multi-walled carbon nanotubes (MWNTs) for comparison. While synthesized fine particles show smaller adsorption of nitrogen than SWNTs, they show larger adsorption than MWNTs. Specific surface areas were determined by the BET plot of the adsorption isotherms to be 832, 157, and 31 m^2/g for SWNTs, synthesized fine particles, and MWNTs, respectively.

Figure 4 shows a hydrogen adsorption isotherm at 77 K for synthesized fine particles, which were beforehand baked under the same conditions as above. Since the saturated vapor pressure at 77 K cannot be defined for hydrogen because of the excess of the critical temperature, Fig.4 is plotted against equilibrium evaporation pressure.

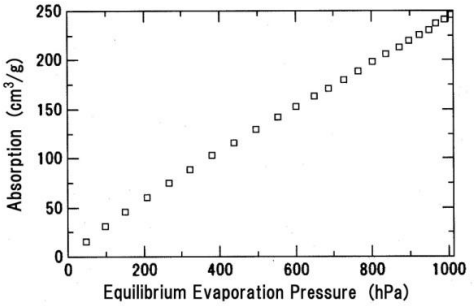

Fig.4. H_2 adsorption isotherm for synthesized fine particles.

The volume of hydrogen adsorbed on synthesized fine-particles at atmospheric pressure (1013 hPa = P_0) and 77 K was comparable to that of nitrogen and was calculated to be 2.2 wt%. The volume of hydrogen adsorbed on synthesized fine-particles at atmospheric pressure and room temperature was also measured and calculated to be 0.13 wt%. The results suggest that synthesized carbon fine-particles have a higher capacity for hydrogen storage.

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