

Influence of structural and preparation parameters of Fe₂O₃/Al₂O₃ catalysts on rate of production and quality of carbon nanotubes

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ABSTRACT

The influence of catalytic and operational parameters on the rate of growth and quality of carbon nanotubes has been investigated. A series of Fe₂O₃/Al₂O₃ catalysts prepared by different methods were investigated under conditions of synthesis of CNTs via the process of CVD of ethylene. Deposition experiments were carried out in a thermogravimetric hot-wall reactor, which enables continuous monitoring of the evolution of carbon mass with time. Controlled explosive burning (CEB) of precursor compounds was found to be the most effective method of preparation of the catalyst with respect to rate of deposition and yield of CNTs. This result has been attributed to the presence of hematite particles of small diameter on the catalyst. The presence of hydrogen in the gas feed mixture, even at small concentration, proved to be beneficial for the rate of production of MWCNTs and to result in the synthesis of CNTs of narrower diameter distribution. Yield and quality of MWCNTs depend on the concentration of the carbon source (ethylene) in the feed mixture and on temperature of deposition. Under the present experimental conditions, the optimal reaction temperature was found to be 650 °C. The products of the deposition were characterized using scanning electron microscopy and Raman spectroscopy.

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1. Introduction

In 1991, Iijima observed that filamentous carbon produced during evaporation of carbon electrodes using the arc-discharge method has nanometer size tube structure, consisting of two or more tubular walls of carbon atoms in hexagonal order open at the edge or closed with a hemispherical structure, such as fullerene. These cylindrical structures, which consisted of multi-layered walls were named multi-walled carbon nanotubes (MWCNTs) [1]. Two years later, Iijima reported the production of similar structures, but of single wall carbon nanotubes (SWCNTs) [2]. Ever since, carbon nanotubes continue to draw significant attention due to their various potential applications, deriving from their extraordinary structural, electronic and mechanical properties. CNTs can be either metallic or semiconductive [3]. Moreover, they can be made into room temperature transistors [4] and they can behave as quantum wires [5]. They have also been used as reinforcements in high strength, low weight and high performance composites. Experimental measurements of Young's modulus indicated a value of approximately 1 TPa (steel = 200 GPa) while their tensile strength

has been measured to be about 63 GPa (steel = 1 GPa). Carbon nanotubes can also store electrochemically lithium and hydrogen, or hydrogen molecules by physisorption on their extensive surface area [6]. Significant interest in biological applications has been expressed in recent years, after it has been realized that their high propensity to cross cell membranes is an important feature of functionalized CNTs, allowing their use for delivery of therapeutically active molecules [7].

Several methods of production of CNTs have been reported. These include the electric arc-discharge between two graphite electrodes [2,6], the laser ablation of carbon targets [6,8] and the chemical vapor deposition (CVD) via catalytic decomposition of hydrocarbons, alcohols or CO [6,9]. The latter is one of the most promising methods for large scale production of MWCNTs. This is due to the fact that, in addition to high yield, it can produce CNTs at much lower temperature and with reduced cost [10]. Moreover, excellent alignment and positional control of the growth of CNTs on the nanometer scale can be achieved. It has been reported that alignment can be accomplished with a certain ratio of ammonia to hydrocarbon flow during growth of CNTs [11], while positional control can be achieved with micro-contact printing of the catalyst on the substrate [12]. Control over the diameter, as well as the growth rate of the CNTs can also be maintained.

Frequently, the catalyst consists of particles of a transition metals (i.e. Fe, Co, Ni), or alloys of them, dispersed on supports like SiO₂ [13], MgO [14], Al₂O₃ [9], CNTs [15], zeolites [16], mesoporous

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molecular sieves [17] and minerals [18]. The support plays an important role in influencing the activity of the catalyst and the quality of the nanotubes produced. The interaction between metal or metal oxide crystallites and the support material affects the aggregation tendency of catalyst particles at elevated growth temperatures, i.e. their size. This parameter can be adjusted so as to prepare CNTs with desired diameter, since it is the size of the catalyst particles which controls the diameter of the generated CNTs. Appropriate metal catalysts can preferentially grow single-walled rather than multi-walled carbon nanotubes [10].

During CVD synthesis, the decomposition of the gas (carbon precursor) and the growth of nanotubes are activated by the catalyst. The carbon precursor is dissociated catalytically on metal oxide nanoparticles spread on the substrate surface. These particles are then reduced to pure metal and carbon diffuses into them. The resulting density gradient of carbon dissolved in the particle drives the diffusion of carbon into the particle. In order to avoid dangling bonds, the precipitated carbon atoms assemble at a less reactive facet of the particle, which leads to the formation of a nanotube [12]. It is obvious that the catalyst plays an important role in the rate of growth, purity and structural properties of the resulting nanotubes.

In the present communication, the use of iron supported on alumina catalysts for the synthesis of MWCNTs via ethylene decomposition, with a significant production rate and yield, is discussed. In particular, catalyst performance as a function of preparation procedure, calcination and reduction process, reaction temperature and ethylene concentration during deposition are examined. Alumina powders are characterized by enhanced surface acidity, good mechanical resistance, high surface area and stability against sintering. On the other hand, the characteristics of iron oxide include redox behavior, medium to low surface area and ease of sintering [19].

2. Experimental

2.1. Catalyst preparation and characterization

The catalyst used in the present study consists of iron oxide dispersed on alumina carrier. Two different procedures were used for the preparation of the catalyst: co-precipitation (designated as CP) and controlled explosive burning (designated as CEB) of precursor materials. In the first case, the precursors, iron nitrate [$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$] and aluminium nitrate [$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$] were dissolved separately into 3D water under stirring to prepare two homogeneous solutions which were subsequently mixed. The resulting solution was heated to 90 °C and isothermal evaporation was carried out under continuous stirring. The slurry thus obtained was calcined at 500 °C under He flow for 20 min and then ground into fine powder. The catalyst resulting from this procedure is designated as CP-W(H) catalyst. The same procedure was followed using methanol instead of water as solvent to dissolve the precursor materials. The catalyst resulting from this procedure is designated as CP-M(H) catalyst. Finally, another variation of the CP-W method involved calcining the generated slurry in air instead of He. The catalyst resulting from this procedure is designated as CP-W(A) catalyst.

In the controlled explosive burning method, the precursor materials (same as before) were mixed in a vertical quartz tube with one open end. The tube was subsequently encased within a resistance furnace already heated at 500 °C and maintained for 20 min. At this temperature, the nitrate groups decomposed totally [20]. No water was added since the water already contained in the hydrated metal salts was sufficient for the generation of a homogeneous mixture during explosive burning. The resulting product was ground into fine powder. The catalyst resulting from this method is designated as CEB catalyst.

Catalysts were characterized by X-ray diffraction analysis. A Bruker D8 advanced apparatus was employed, using $\text{Cu K}\alpha$ radiation. The diffraction angle was varied between 20° and 80° (2θ), while the operating voltage and electric current were adjusted at 40 kV and 40 mA, respectively. The aperture slit between the X-ray tube and the sample was 0.6 nm.

The specific surface area (SSA) of the catalysts was measured with the BET method, employing nitrogen adsorption at liquid nitrogen temperature (77 K). A Quantachrome Corporation, 440-C, BET instrument was used. Outgassing temperature was set at 150 °C.

Catalysts were also characterized with Raman analysis. The T-64000 micro-Raman system of Jobin Yvon was used. Raman spectra were excited by a linearly polarized monochromatic radiation at 514.5 nm produced by a Spectra Physics air-cooled Ar^+ laser (model 163-A42).

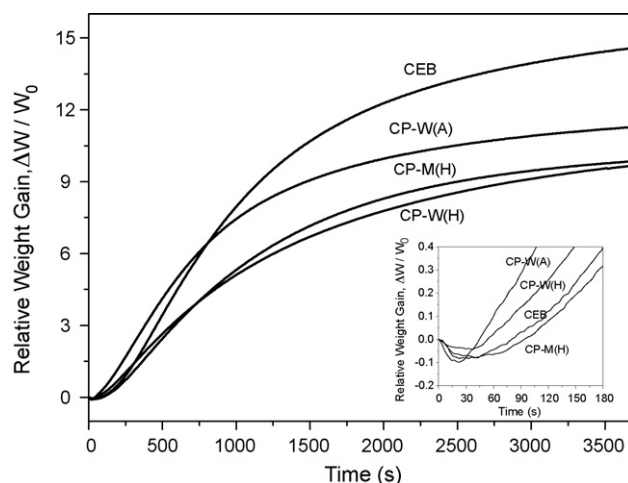


Fig. 1. Influence of catalyst preparation method on rate of production of CNTs over a 45 wt% $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst. Experimental conditions: feed composition: 20% C_2H_4 , 5% H_2 , bal. He. Total flow rate: 200 sccm. Reaction temperature: 650 °C. Insert: Blow-up of growth curves at initial condition.

2.2. Deposition of CNTs by the CVD method

The rate of growth as well as the yield of carbon nanotubes produced employing the CVD method was determined in a sensitive microbalance (CAHN, D-101) which allows for continuous monitoring of changes of sample weight with time. The catalyst sample, approximately 3 mg, was uniformly distributed in a flat vessel positioned in the middle of a vertical quartz tube, encased within a resistance furnace. The sample vessel was connected to the microbalance and its weight was continuously monitored. Buoyancy effects and its dependence on the reaction temperature were taken into account for the accurate calculation of the deposited carbon mass. Temperature was controlled by a PID controller with two Pt/PtRh thermocouples. A system of mass flow controllers and valves controlled gas flow and composition into the reactor.

The catalyst inside the vessel was gradually heated under helium flow (200 sccm) from room temperature to the reaction temperature, which was varied between 500 and 800 °C. After stabilization of the system at the desired reaction temperature, the deposition gas mixture, consisting of ethylene, helium and hydrogen, was channeled into the reactor. Ethylene was used as the carbon source for the formation of nanostructures, via its catalytic decomposition during the CVD process. Deposition time was approximately 1 h. Reaction conditions were varied so as to study the effect of various parameters on the rate of formation of CNTs and yield. After completion of the reaction, the reactor was allowed to cool under He flow.

MWCNTs were examined with scanning electron microscopy (SEM). The SEM-JEOL JSM 5200 scanning microscope was employed, equipped with a ZrO electron gun, coated with W (100), operating at an acceleration voltage between 5 and 15 keV, a working distance of typically 5 mm and a resolution of 1.7 nm at 20 keV. Raman spectroscopy was also employed to characterize the nanotubes. The same micro-Raman system was used with the same operating conditions as in the case of characterization of the catalysts, described earlier.

3. Results and discussion

3.1. Effects of catalyst preparation procedure on rate of production of CNTs

As described earlier, two catalyst preparation procedures were investigated with respect to the rate of carbon deposition: The co-precipitation method and the method of controlled explosive burning. For the first procedure, two preparation parameters were examined: the nature of the solvent (water or methanol) and the atmosphere under which the catalyst was calcined (helium or air). Results of these studies, pertaining to a catalyst invariably consisting of 45% $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$, are presented in Fig. 1. Comparison of CNTs deposition curves which pertain to catalysts CP-W(H) and CP-M(H) indicates that the solvent employed for the preparation of the catalyst (water or methanol) does not influence, in any measurable extent, the rate of production of carbon nanotubes. The insert in Fig. 1 is a blow-up of the initial 3 min of the experiments. During

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