

DYNAMIC STUDY OF CARBON NANOTUBES PRODUCTION BY CHEMICAL VAPOR DEPOSITION OF ALCOHOLS

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Received: April 29, 2005

Abstract. The rate of deposition of carbon nanotubes, their purity and wall thickness was investigated employing different Chemical Vapor Deposition (CVD) processes. Two catalysts, consisting of Al_2O_3 and Fe_2O_3 of variable composition, were used, while the carbon precursor was an alcohol (ethanol or methanol). The experiments were carried out in a thermogravimetric CVD reactor which enables continuous monitoring of the evolution of the mass of carbon with time. The final product was analyzed using Scanning Electron Microscopy and Raman Spectroscopy. It was found that product purity and wall thickness was depended on process temperature, the carbon precursor, the concentration of Fe_2O_3 in the catalyst and the use of hydrogen for catalyst reduction, before or during deposition.

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1. INTRODUCTION

The production of carbon filaments, using the decomposition of various gaseous carbon-containing compounds, in presence or absence of catalyst, is already known since the 1970's [1,2]. In the '80s, researchers tried to produce filaments with diameters of one or several μm . In 1984, Tibbets [3] noticed that carbon filaments with a tubular structure can form. Although this was a remarkable observation, no further research was carried out in this field until the discovery of fullerene by Kroto and Smalley [4] in 1985. Interest in the production of carbon nanotubes was revived following the observation of Iijima [5] in 1991, that filamentous carbon which is produced during the evaporation of carbon electrodes using the arc-discharge method, has nanometer size tube structure. These tubes consist of two or more

tubular walls of carbon atoms in hexagonal order, which are open at the edge or close with a hemispherical structure, such as the spherical structure of carbon (fullerene). Two years later, in 1993, Bethune [6] and also Iijima [7] reported the production of carbon nanotubes with only one wall, known as single-wall carbon nanotubes (SWNTs).

Since then, carbon nanotubes continue to draw much attention for their many potential applications, which derive from their unusual structural as well as electronic and mechanical properties [8]. For this purpose, several methods of producing carbon nanotubes have been reported. The three most important ones are: 1) the electric arc – discharge technique [6,9], 2) the laser evaporation technique [9], and 3) the chemical vapor deposition method [10-12].

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The arc-discharge method is capable of producing large quantities of nanotubes of rather low purity. For this reason efforts have concentrated toward production processes which offer more controllable routes to the synthesis of nanotubes. A family of processes which seems to offer the best chance of obtaining a controllable route for the selective production of nanotubes with defined properties is chemical vapor deposition. The thermal catalytic CVD method, which is the method used in the present study, is considered to be the best process for low-cost and large-scale synthesis of high-quality carbon nanotubes, using a variety of gaseous hydrocarbons and liquid alcohols as the carbon sources. The growth mechanism of the CVD synthesis of carbon nanotubes involves decomposition of the carbon source, followed by dissolution of the carbon phase into metal catalytic nanoparticles and redeposition of carbon on the catalyst surfaces [9].

The use of hydrocarbons as the carbon precursors in this process has already been studied by many researchers [2,11,13-15]. The capability of using alcohol as the carbon precursor to produce carbon filaments has been established since 1968 [16]. Since then, it has been reported that chemical vapor deposition using alcohol also resulted in the production of carbon nanotubes [10,17-22].

In the present communication we report a dynamic study of the kinetics of nanotube synthesis at low temperature, using the chemical vapor deposition method and vapors of methanol or ethanol as the carbon precursor. Two catalysts consisting of Al_2O_3 and Fe_2O_3 of different composition were used. The results show that both catalysts are equivalent with respect to the deposition rate with time. However, higher yield of carbon nanotubes was observed over the catalyst with the higher concentration on Fe_2O_3 . With this catalyst, a yield of 780% in two hours of deposition was achieved. In either case, multi-wall carbon nanotubes were produced.

2. EXPERIMENTAL

The experimental apparatus which was used to synthesize carbon nanostructures consisted of a vertical quartz tube with inner diameter of 15 mm, heated with a resistance furnace, in a length of 22 cm. The almost isothermal band of the reactor was approximately 17 cm. Temperature was controlled by a controller with two Pt / PtRh thermocouples. The catalyst was placed in a flat vessel made from platinum, and it was positioned in the middle of the isothermal band of the reactor. It was connected with a microbalance (CAHN D-101) with 1 μg sensitivity

and with an interface to a computer, where the weight measurements were continuously recorded. Simultaneously, the reactor functioned as the sample tube of a thermo gravity device (TGA). The experimental device was completed with the delivery system, which was based on mass flow controllers and read-out units.

After stabilization of the system at the desirable reaction temperature, which varied between 550 °C and 800 °C, under the flow, the deposition mixture consisting of helium (He), methanol (CH_3OH) or ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) vapors and, in some cases, hydrogen (H_2) was channeled into the reactor. Helium and hydrogen were supplied from regulated gas cylinders, contrary to methanol and ethanol which were delivered from a bubbler using helium as a carrier gas. In some cases, hydrogen was used either before the deposition to prereduce the catalytic materials, which would otherwise be slowly reduced by the alcohol during the deposition reaction, or during the process as a mixture with the vapors of alcohol. The flow rate of the reagents was measured and controlled with mass flow controllers. The composition of the feed mixture was 4.5% methanol, or 3% ethanol and 5% hydrogen, whenever it was used, balance He.

The catalysts which were used in these experiments consisted of Al_2O_3 and Fe_2O_3 in two different concentrations. Specifically, the Fe_2O_3 content of catalyst C2 was 2.5 times that of catalyst C1. The specific surface area of both catalysts was measured and was found to be 134 m^2/g for catalyst C1 and 204 m^2/g for catalyst C2.

Upon completion of the deposition experiments, the final products were analyzed with Scanning Electron Microscopy (SEM) and Raman spectroscopy. The SEM – JEOL JSM 5200 scanning microscope and the T-64000 micro-Raman system of Jobin Yvon (ISA-Horiba group) were 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).

3. RESULTS AND DISCUSSION

Fig. 1 displays the in situ measurements of the relative weight changes of the sample with respect to time of exposure during carbon deposition on the catalysts C1 and C2. It is noted that catalyst C2 is the one with the higher concentration of Fe_2O_3 . In particular, Fig. 1(i) shows the relative weight gain when the catalysts are exposed to ethanol vapors at 800 °C. Both catalysts exhibit the same qualitative characteristics, namely a relative stable rate of

deposition during the initial 2000 s of the experiment, followed by a substantial decline in the rate which becomes nearly zero after 4000 s. However, the rate of carbon deposition over the catalyst C2 is substantially higher than that of catalyst C1. From the curves shown in Fig. 1(i) it is estimated that the initial rate of carbon deposition on catalyst C2 is 0.002 mg/s, while on catalyst C1 it is 3 times lower. As a result, the yield of carbon deposit defined after 1 h of experiment is approximately 350% for catalyst C2, as compared to 120% on catalyst C1.

As indicated earlier, the only difference between the two catalysts is the concentration of Fe_2O_3 , which in C2 is 2.5 times more than that in C1. Apparently, then, the observed difference in the rate of carbon deposition may be attributed to this parameter, namely the higher concentration of active sites (presumably metallic Fe) which lead to the formation of carbon nanotubes. However, while the amount of Fe_2O_3 in catalyst C2 is 2.5 times higher than that in C1, the rate of carbon deposition is 3 times higher. This observation may indicate that a synergistic effect may be operable between the two components of the catalytic material, namely Fe_2O_3 and Al_2O_3 . It is well known [23] that Al_2O_3 can effectively dehydrate ethanol producing ethylene which may be a precursor at the building block of carbon nanotubes.

The influence of the extent of reduction of the catalyst on the rate of carbon deposition was investigated by either co-feeding H_2 , along with ethanol (5% H_2 , 3% $\text{CH}_3\text{CH}_2\text{OH}$) during the experiment, or by pre-reducing the catalyst inflowing hydrogen at 800 °C. The results, in the form of relative weight gain in respect to time are shown in Fig. 1(ii). Comparison of curves (a) and (c) clearly shows that pre-reduction of the catalyst sample is highly beneficial for carbon deposition, indicating that, in most probability, the active sites for the initiation of the nanotube structure is metallic iron. In the case in which the catalyst used was as prepared (curve c), the catalyst is probably reduced in situ, at a flow rate, by ethanol or species produced by the decomposition of ethanol, such as H_2 , CH_4 , CO etc. The case, in which the catalyst is as prepared while hydrogen is included in the feed mixture at a concentration of 5%, as would be expected, presents an intermediate situation (curve b). In this case the reduction of the catalyst is faster but still it does not reach the level of the ex-situ pre-reduced catalyst (curve a).

The type of alcohol used as carbon source makes a significant difference in the rate of carbon nanotube deposition as well as on the overall yield. This is

illustrated in Fig. 1(iii) in which the relative weight gain over catalyst C2 with respect to time—on-stream, for ethanol (curve a) and methanol (curves b and c) is shown. The rate of deposition depends on temperature, as expected and as is illustrated in the insert of Fig. 1(iii) which is blow-up of the curves b and c near the origin. The huge difference in the rate of deposition between ethanol and methanol can not be attributed to the temperature difference of the experiment. This observation may be attributed to the fact that, in the presence of Al_2O_3 , ethanol dehydrates to produce ethylene which is a very active building block for the production of carbon nanotubes.

Finally, all materials produced by the experiments described earlier were characterized using Scanning Electron Microscopy and Raman spectroscopy. Fig. 2 shows typical SEM microphotographs CNT material produced of vapors of ethanol at 800 °C on catalyst C1 (Fig. 2a) and on catalyst C2 (Fig. 2b). In both cases we observed multi-wall carbon nanotubes (MWNTs). As we also present in the insert image of Fig. 2a, fine and long bundles of MWNTs exist in the materials while no carbon or catalytic particles are detected, indicating that the material may be of high purity. The most luminous regions of the images are attributed to the curved and tangled bundles of MWNTs, which mostly appear in the materials produced. Similar images were also recorded from CNT materials which were prepared when hydrogen was used before or during the deposition to enhance the reduction of the catalyst. Nevertheless, catalytic particles were observed, in combination with MWNTs, when vapors of methanol were used as the carbon precursor in both the deposition temperatures of 550 and 700 °C. This behavior is attributed to the lower yield of deposition, which leads to the conclusion that not the whole catalyst had contributed toward production of carbon nanotubes.

Characterization of product deposits was completed by analysis of m-Raman measurements. The laser excitation wavelength was 514.5 nm and the laser's power focused on the sample was 1.93 mW. The spectra were acquired using a back – scattering geometry at room temperature. Fig. 3 displays the spectra in the frequency range of 1200 – 1800 cm^{-1} . The two main first – order peaks which correspond to MWNTs are present. A strong band at $\sim 1576 \text{ cm}^{-1}$ (G-band), which is the Raman – allowed phonon high – frequency E_{2g} first – order mode and which is attributed to the movements of carbon atoms in opposite directions along the surface of a

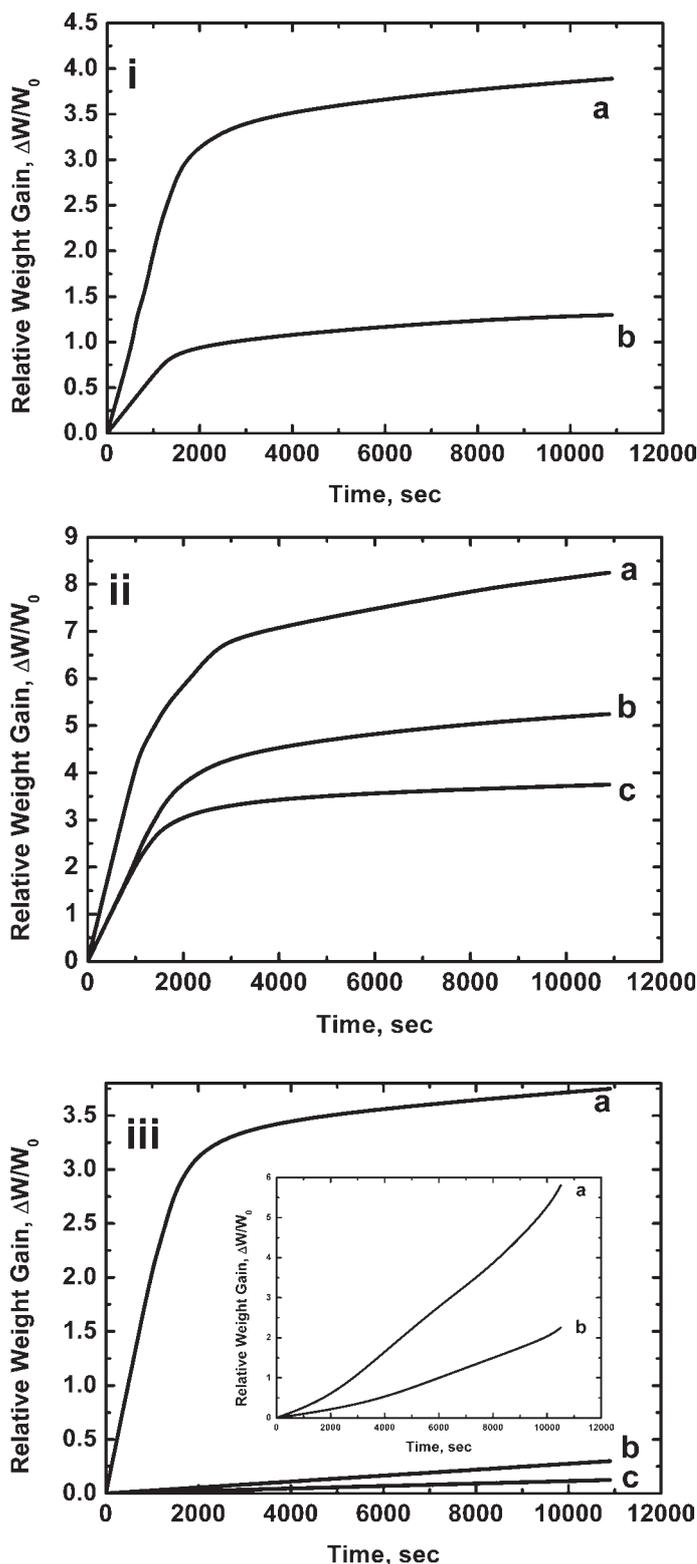


Fig. 1. Relative weight gain of carbon nanotubes with respect to time under various conditions:
 (i) Carbon precursor: ethanol, deposition temperature: 800 °C, catalyst: C2 (curve a), C1 (curve b), as produced.
 (ii) Carbon precursor: ethanol, deposition temperature: 800 °C, catalyst: (a) C2, pre-reduced in flowing H_2 at 800 °C, (b) C2, exposed simultaneously to ethanol- H_2 mixture, (5% H_2 , 3% Ethanol), (c) C2, as produced (as in (i), curve a)).
 (iii) Catalyst C2, as produced, carbon precursor: ethanol (curve a), methanol (curves b and c), deposition temperatures: 800 °C (curve a); 700 °C (curve b); 550 °C (curve c).

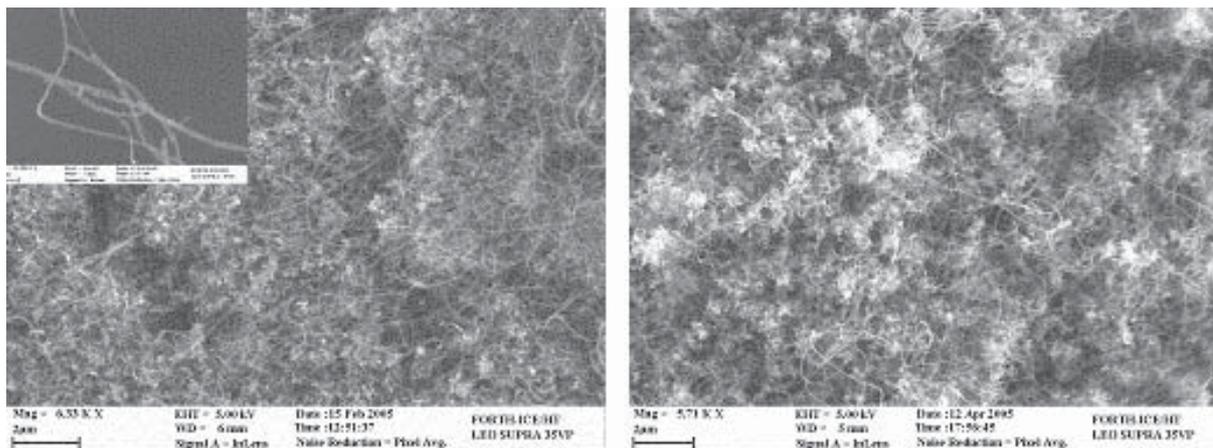


Fig. 2. SEM micrographs of CNTs using vapors of ethanol at 800 °C on catalyst C1 (a), and catalyst C2 (b).

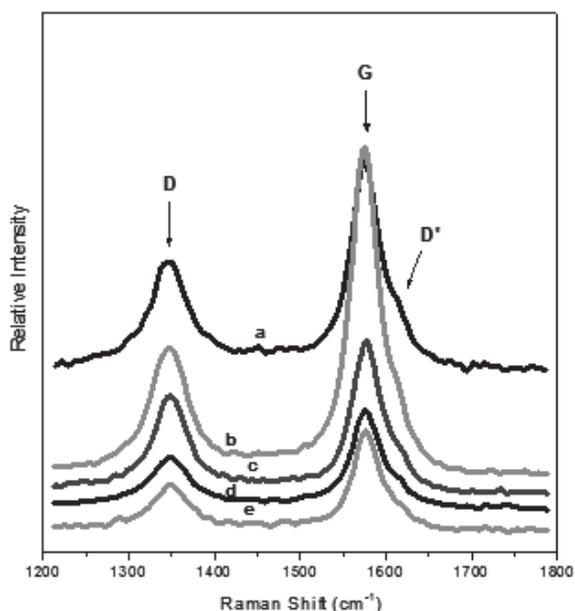


Fig. 3. Micro – Raman spectra collected with 514.5 nm laser excitation from carbon materials deposited at various CVD conditions. (a) Catalyst C1 with deposition of vapors of ethanol at 800 °C, (b) Catalyst C2 with deposition of vapors of ethanol at 800 °C, (c) Catalyst C2 with pre-reduction by hydrogen and deposition of vapors of ethanol at 800 °C, (d) Catalyst C2 with deposition of vapors of methanol at 700 °C and (e) Catalyst C2 with deposition of mixture of vapors of ethanol and hydrogen at 800 °C.

tube [24,25], and a weaker peak at $\sim 1348 \text{ cm}^{-1}$ (D-band) which is originating from defects in the curved graphene sheets, tube ends, or in the presence of carbon coating on the outside of tubular bundles [26,27]. Moreover, a small bump appeared at a higher than G-band energy side, at $\sim 1617 \text{ cm}^{-1}$ (D-band),

which is again assigned to the multiwall nanotubes and is explained as a disorder – induced feature [14,28]. Thereupon, the results of Fig.3 show that for all the experimental procedures which are presented in this paper the material produced is MWNTs.

4. SUMMARY AND CONCLUSIONS

The rate of deposition and the final product (which was found to be multi-wall nanotubes) of different CVD processes on two catalysts were investigated. The results show that the rate of deposition and the final yield depend on carbon nanotube temperature of the process, the carbon precursor (methanol or ethanol), the composition of catalyst ($\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$) as well as the extent of his reduction. The experimental results show that the deposition yield is remarkably higher when catalyst C2 is used and vapors of ethanol are the carbon precursor. Additionally, the yield increases further, approaching 780%, when the catalyst is pre-reduced in flowing hydrogen at 800 °C. The products of the deposition were characterized using Scanning Electron Microscopy and Raman spectroscopy, and the fact that they are MWNTs of high purity is established.

ACKNOWLEDGEMENTS

We would like to thank Prof. Xenophon E. Verykios for all his help, Dr. Amaia Soto Beobide and Dr. Vassilios Dracopoulos for their assistance in the Raman analysis and SEM characterizations, respectively, and GSRT for partial support of this work under the PENED program.

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