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PRODUCTION OF CARBON NANOTUBES USING CVD – STUDY OF THE OPERATING PARAMETERS

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Abstract. The present work deals with the study of operating parameters of carbon nanotubes production on Fe/Al_2O_3 catalyst by CVD. Experiments have been carried out on a system assisted by a sensitive microbalance capable to measure in situ the weight changes of the sample in the reactor with time. The experimental results show that the process and the reduction temperature of the iron affects the structure of the catalyst modifying the deposition rate. Increase of the metallic catalyst concentration leads to higher amounts of material deposited. The produced material is studied through scanning electron microscopy (SEM) and Raman spectroscopy revealing multiwall carbon nanotubes.

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1. INTRODUCTION

The Chemical Vapor Deposition (CVD) method for the production of carbon nanotubes (CNTs) is of great interest since it can be used for the production of high quality of CNTs for various applications. It offers the opportunity for large-scale production of nanotubes and control of the deposition process using the suitable catalyst. CVD can produce a quite pure product of carbon nanotubes, measuring up to 2 mm inlength [1], with good alignment, and high yield. Therefore, CVD is the more attractive method for the production of CNTs in industrial scale [2-4] than others.

The production of carbon fibers (CFs) and multiwall carbon nanotubes (MWNTs) by CVD was a well-known method [5-8] even before the 1991 Iijima discovery of CNTs produced by arc-discharge method [9]. CNTs are produced by CVD with supported catalyst of carbon compounds (usually CO or hydrocarbons) on powders of metal as Al_2O_3, SiO_2 and MgO that contain metal catalysts (usually Fe, Co or Ni and combinations), with or without other metals (e.g. Mo). Carbon deposition takes place after decomposition of carbon sources and recombination of carbon atoms on the catalyst at high temperature (between 500 °C –1100 °C).

Many studies have been carried out on the CVD production of carbon fibers or nanotubes, but only a few concern the deposition rate, its dependence from the functional conditions and its development over the whole experimentation time horizon. Conclusions

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for catalyst activation are usually derived from Raman Spectrum and images from Scanning Electron Microscopy (SEM) or Transmission Electron Microscopy (TEM) of the quality of the produced CNTs.

In this paper, results concerning the role of the iron oxide (FejOs) precursor on the catalyst, the reduction of iron oxide and the dependence of carbon nanotubes deposition rate on time on carbon deposited material structure and yield are presented.

2. EXPERIMENTAL SECTION

2.1. Microbalance-CVD Experiments

The apparatus used for carbon deposition consists of a vertical hot wall reactor and a sensitive microbalance (CAHN-101) that allows the continuous monitoring of the sample weight changes with high accuracy. A system of mass flow, pressure controllers and valves controls the gas flow in the reactor.

An amount (~10 mg) of catalyst (Fe_2O_3/Al_2O_3) that originates from thermal decomposition of nonahydrate nitrate salt ($Fe(NO_3)_3 \cdot 9H_2O$ with alumina powder of high purity (Alfa Aesar 99.97% purity, specific surface area = 80-120 m^2/g) [10] is placed in a small container of platinum. The container is hung from the sample arm of the microbalance placed in the middle of the heating zone. In this way, continuous monitoring of the deposition rate is carried out. Many studies have concluded that Fe_2Os should be reduced first in order to begin the [11-13]. This iron oxide reduction can happen either with the effect of hydrocarbon that is contained in the gas deposition mixture or by hydrogen during a stage before the deposition. Moreover, the two different experimentation protocols are used in our experiments and they are reported as: 1) the two-step process which contains: (a) heating at He flow (200 standard cm^3/ min) and (b) carbon deposition at 700 °C (6 standard cm^3/min C_2H_4 at 200 standard cm^3/min total flow) and 2) the three-step process: (a) heating at He flow (200 standard cm^3/min) (b) reduction of iron with H_2 (20 standard cm^3/min H_2 at 200 standard cm^3/min total flow) and (c) deposition of carbon after C_2H_4 (6 standard cm^3/min C_2H_4 at 200 standard cm^3/min total flow) flows into the reactor.

Carbon deposition takes place when carbon atoms from C_2H_4 recombine on the catalyst at high temperature. From the variation of the carbon deposition rate with time, it is possible to determine whether deposition proceeds with appreciable rate over the whole experimentation time horizon, and if catalyst deactivation phenomena take place.

3. RESULTS AND DISCUSSION

3.1. Time development of the carbon deposition rate

Results from the weight development of the sample from carbon deposition following the two-step or the three-step process are presented in Fig. 1A for 6%Fe/Al_2O_3 catalyst. The comparison of the curves shows that the behavior of development of deposition rate is qualitatively the same for the two different experimental processes. When the weight loss coased by the reduction of iron oxide has been overcame by the weight increase from carbon deposition at the two-step process, the development of the sample weight with respect to time indicates the existence of the following stages for both of the curves: a stage where the deposition rate remains almost constant, a second stage where the rate presents relatively high deceleration and a third stage where the deposition rate slows down.

The quantitative and qualitative differences that are presented between the two-step and the three-step process after the flow of C_2H_4 into the reactor result on of the different way of the reduction of iron oxide using the two deposition protocols. The three-step process exhibits higher deposition rate at the initial stage of the process. However, an important deceleration of the deposition rate is exhibited earlier than the one of the two-step process. Finally, the total amount of carbon deposited is lower in the three-step process for long times of deposition. The higher initial rate of carbon deposition at the three-step process obviously confirms the fact that there is an amount of the catalyst being in active form or in form that can easily be activated to promote the carbon deposition prepared during the first step of the process (Fig. 1A, curve (b_1)). Initially, at the two-step process, there is a low deposition rate probably because of the continuous reduction of iron oxide that happens simultaneously. There is an activation of additional iron catalyst that is depicted in the curve (a) of Fig. 1A as a decrease of the weight loss because of the loss of oxygen atoms. Thus, a continuous formation of more activated sites during the deposition process is succeeded and helps keep on the deposition reaction rate for longer period. During the three-step process the reduction of iron oxide to an active or easily activated form to promote carbon deposition, has already occured with hydrogen at the second step of the process. Consequently, the catalyst is expected to be found probably in the form of particles of a size bigger than the minimum size in which the nanotubes grow. Conse-

a)

b)

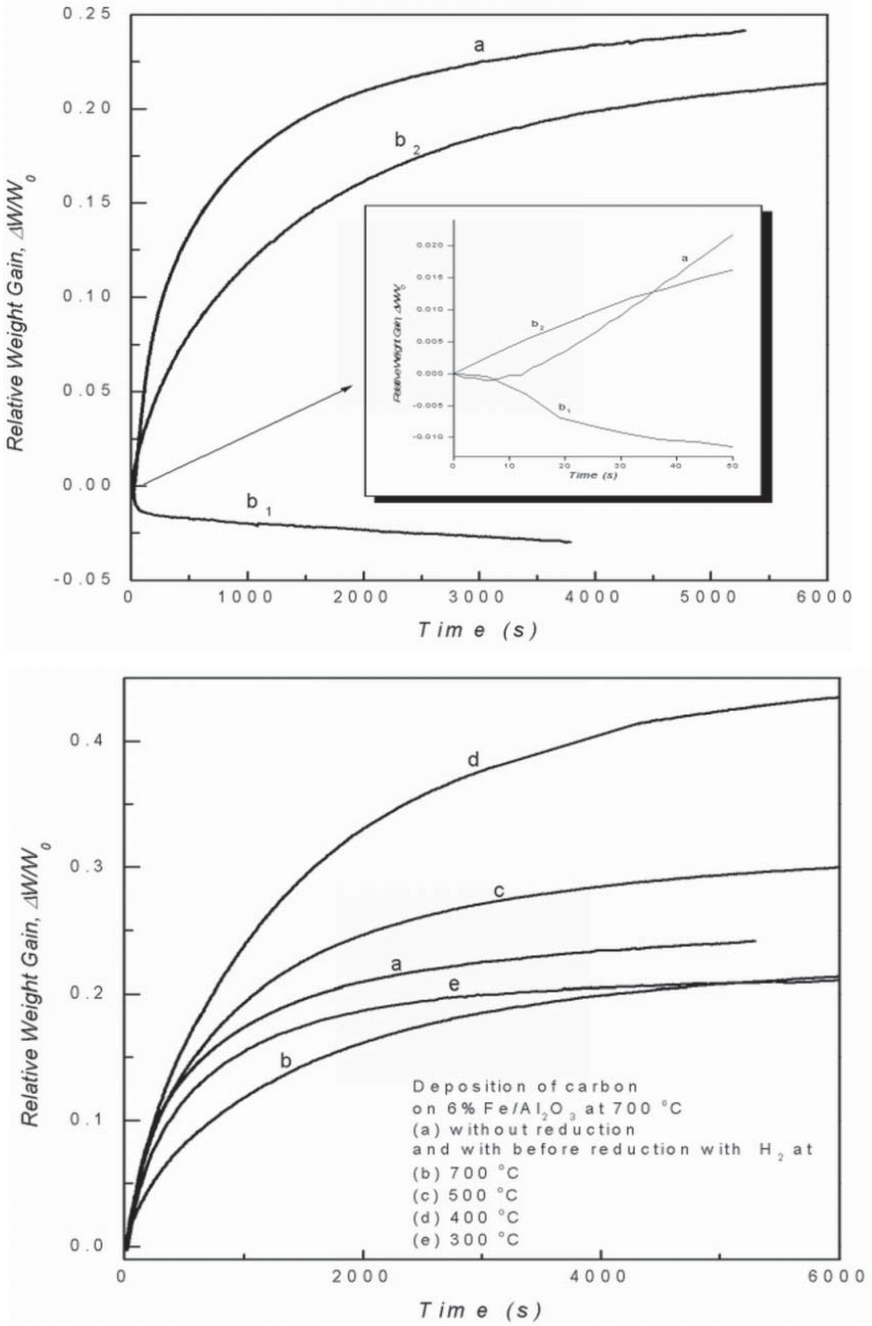


Fig. 1. (a) Relative weight change curves of carbon deposition on Fe/Al_2O_3 catalyst at 700 °C using the two-step (curve (a)) and the three-step (curves (b_1) for the 2nd step and (b_2) for the *3ed* step) process. (b) Curves of the relative weight change from carbon deposition on Fe/Al_2O_3 at 700 °C using the two-step process (curve (a)), and the three-step process at 700 °C (curve (b)), 500 °C (curve (c)), 400 °C (curve (d)), and 300 °C (curve (e)).

quently, the concentration of the activated sites for the carbon deposition after the reduction of iron oxide is expected to be smaller for the three-step process, for the same catalyst (6%Fe/Al_2O_3). It is suggested that this is the reason for which the deposition rate is lower for the initial stages of the two-step process.

3.2. Effect of Catalyst Reduction Temperature

Fig. 1B presents the curves of the sample weight changes with respect to time for carbon deposition (third step) using the three-step process for the 6%Fe/Al_2O_3 catalyst, for various reduction tempera-

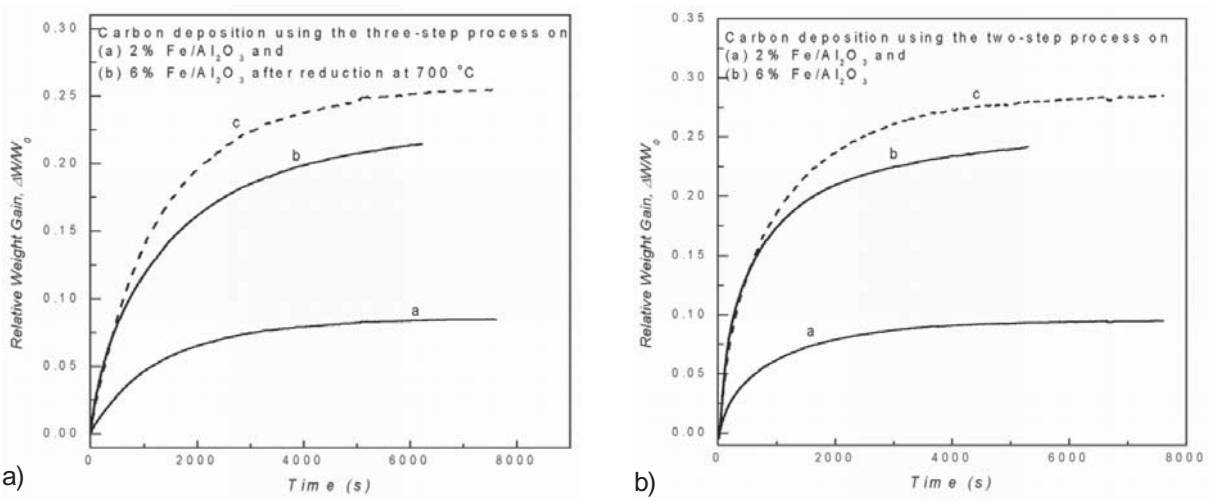


Fig. 2. Relative weight change curves of carbon deposition on 2% Fe/Al_2O_3 catalyst (curves (a)) and 6% Fe/Al_2O_3 (curves (b)) for the three-step process after reduction with H_2 at 700 °C (A) and for the two- step process (B). Curves (c) reprints the curves of the theoretical weight from carbon deposition proportional to the increase of the iron.

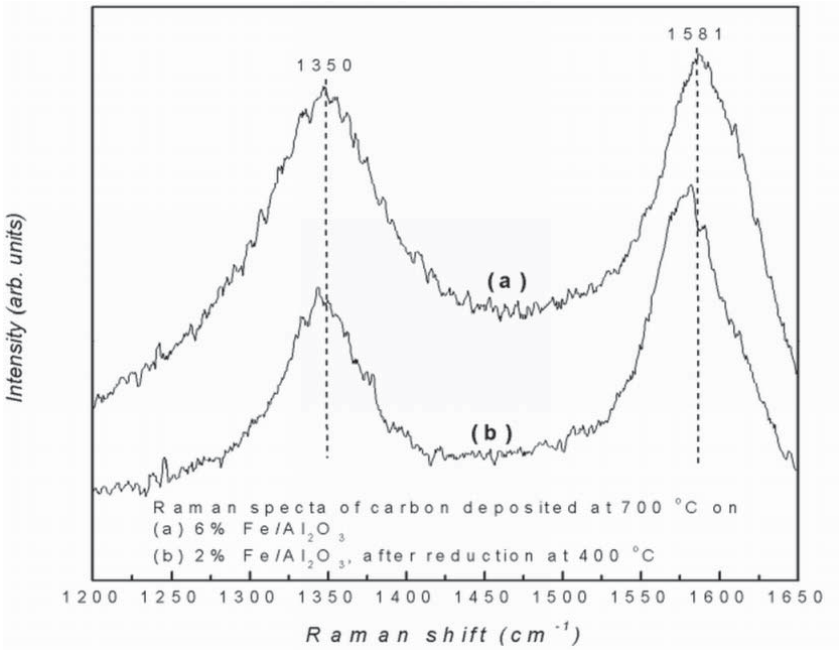
tures (second step) at the same reaction conditions in all cases. Therefore, the catalyst was heated at 700 °C in He flow, and remained at this temperature for 30 minutes. Curve (a) represents the carbon deposition rate without any treatment with H_2. For reduction with H_2, the catalyst was heated at the reduction temperature i.e.700 °C curve (b), 500 °C curve (c), 400 °C curve (d), and 300°C curve (e) for another 10 min before the reduction gas mixture (10%H_2/He) flows into the reactor.

The iron oxide of the sample reduces for different reaction time in each case. For temperatures lower than 600 °C, the weight change for 60 min of reduction is much lower than the one for full reduction of Fe_2O_3 to Fe. Therefore, for temperature lower than 600 °C the process takes place for longer period to succeed in weight loss corresponding to Fe^{3+}/Fe° reduction. Results show that there is a reduction temperature for the activation of the catalyst, where the carbon deposition rate is maximized. The increase of carbon deposition rate by decreasing the reduction temperature is higher between 500 °C and 400 °C than other cases. Thus, the deposition rate increases by increasing the concentration of the activated particles for carbon nanotubes growth because of the reduction size of the catalyst after reduction. The high deposition rate increase for reduction temperature under 500 °C reveals that the form and the size of the activated catalysts is affected from the temperature while for low temperature, there is a change of these characteristics

According to the iron oxide reduction model that was presented before, the temperature of the reduction affects the mechanism of the process and the size of the iron particles and consequently the rate of deposition. It is reported that as the reduction temperature increases, the iron oxide reduction rate increases also [11]. Consequently, for the same time of reaction and for the three-step process, activation of higher amount of iron of the Fe/Al_2O_3 catalyst is expected, as the reduction temperature increases. However, this does not involve necessarily, an increase of the activated sites of the catalyst where carbon was deposited since the increase of temperature can lead to the creation of bigger size particles of the reduced material because of the higher speed of nucleation that affects their morphology.

3.3. Effect of iron concentration on the Fe/Al_2O_3 catalyst

In Figs. 2a and 2b the rates of carbon deposition for 2% and 6% Fe/Al_2O_3 are compared for deposition at 700 °C using the two-step and the three-step processes. The dash line of the diagrams represents the relative weight change of the 2% Fe catalyst for iron concentration of 6% (the relative weight curve points of carbon deposition on 2% Fe catalyst multiplied on a factor 3.) The dash line obviously gives the deposition weight change of the material with 6% Fe according to the results for 2% Fe of con-



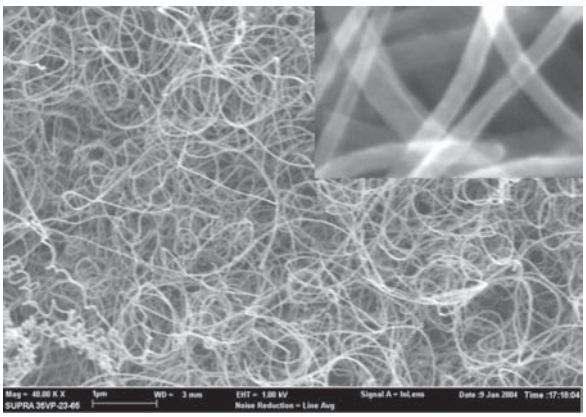


Fig. 3. (A) Raman Spectra from carbon deposited on 6% Fe/Al_2O_3 (a) and 2% Fe/Al_2O_3 (b) catalyst at 700 °C using the three-step process after reduction with H_2 at 400 °C. (B) SEM image of MWNTs deposited on 6% Fe/Al_2O_3 under the same conditions.

centration and for the possibility of the proportional change of deposition rate with the iron concentration. At all procedures, the theoretical carbon deposition rate is higher than the one measured experimentally. Thereupon, the activated sites where carbon nanotubes growth takes place are not increased proportionally with the catalyst concentration.

Therefore, high iron concentration should lead to high concentration of activated sites and to high carbon deposition rate on the catalyst if the population of these is on the iron concentration on the support (alumina). Consequently, kinetically controlled conditions of deposition reaction, for absence of important degree of concentration in the space between the catalyst particles and in their internal surface, the carbon deposition rate is expected to change proportionally with the substrate catalyst. This does not happen probably due to the formation of bigger size catalyst particles that could be the result of the increase of the iron concentration and lower contact (interaction) of iron-alumina.

3.4. Characterization of the carbon material

Carbon nanostructures were measured as produced and were qualitively characterized using Raman Spectroscopy and Scanning Electron Microscopy (SEM), to estimate their type and size. SEM was performed at 20 kV using JEOL JSM-5200 system. A UV Raman system (Dual, 325/441.6 nm, UV/blue) using excitation energy at 441.6 nm (2.8 eV) from a He-Cd laser was also used for the carbon characterization.

Raman spectra present the two main peaks G and D at 1350 cm^{-1} and 1581^{-1} respectively (Fig. 3A). These peaks are characteristic for the graphite structure of MWNTs. The absence of peaks under 300 cm^{-1} (low frequency Raman spectrum) reveals the absence of single-wall carbon nanotubes. Fig. 3B reprints SEM images of MWNTs deposited at 700 °C 6% Al_2O_3 catalyst from 3% C_2H_4 using the three-step process after reduction with 10% H_2 at

400 °C. The nanotubes size ranges from 15 to 30 nm for diameter and length of certain urn.

4. SUMMARY AND CONCLUSIONS

According to the experimental results, carbon deposition takes place during the first 60 min of the deposition process for both experimental protocols we used. Then, the reaction rate presents high deceleration and for long periods, the deposition stops. The reduction temperature also affects the deposition rate at the three-step process. Experiments show that using H_2 as reducing gas, there is always a temperature that produces the more activated sites for carbon deposition with high rates. It is suggested that the deposition rate decreases mainly because of the deposition of carbon on the porous space of alumina which the main part of the support surface while deposition on this surface becomes progressively difficult as the size and the amount of material deposited increases.

The deposition rate increases with the increase of iron concentration for constant reduction and deposition conditions though not proportionally. Therefore, the concentration of activated sites of the catalyst does not increase as the concentrations of iron on the support despite the low iron concentrations that are used, which can be attributed to the presence of the big size of the particles and lower degree of catalyst exploitation. Differences between the two processes are eliminated as the iron concentration decreases. Differences were also found to carbon deposition between two-step and the three-step the process. The two-step process yields the higher prices. The differences in the catalyst particles size are likely the main reason for the different deposition rate between the two-step and the three-step process. As in the two-step process, the catalyst can be used for carbon deposition after the formation of a minimum of a population of activated sites while afterwards deposition increases.

The characterization of the material using SEM showed the presence of MWNTs for both iron concentrations. The results of Raman spectroscopy reveal the characteristic peaks of graphite structure at region 1200–1600 cm^{-1}.

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