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Gas flow and temperature synthesis dependence on the CNTs structure and yield

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Abstract

Recently, research on CNTs received great attention because of their potential applications in field emission, energy storage, chemical sensors and microelectronic devises. The study in this paper is based on the comparison between EtOH and C_2H_4 decomposition over Fe-Co/MgO support using different gas flow and at different synthesis temperature. So, we have systematically studied the effect of EtOH, C_2H_4 and synthesis temperature on the CNTs structure and yield using the CCVD process. The CNTs yield increases significantly with increasing gas flow. In addition, with reactor temperature above to 900 °C, we obtain more SWCNTs than MWNTs using EtOH and ethylene, as carbon precursor, respectively. Finally, the obtained products were qualitatively characterized by TEM and FESEM.

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1. Introduction

Recently, there has been much active interest in the production, processing, manipulation and incorporation of carbon nanotubes "CNTs" to improve properties of materials [1]. After their discovery, NTs were found to possess many interesting properties and potential applications, which gives a strong impetus in the work devoted to understand and to improve their production. Most of the current work is on SWCNTs because of their superior thermal, mechanical and electrical properties compared to MWCNTs [2, 3].

Among the many different routes leading to the production of CNTs, the CVD process seems at present to be the most easily up scalable towards an economically viable scale. Specially, Catalytic CVD method, which is regarded as a way of industrialization foreground to synthesize large-scale pure CNTs [4], has been adopted widely by scientists over the word. Several parameters, such as species and catalyst size, temperature, reaction and carrier gas kind and flow, … have an impact on the CNTs grown by CCVD [5-10]. The synthesis of CNTs by CCVD involves the catalytic decomposition of a carbon precursor (e.g., hydrocarbons or alcohols) on nanostructured transition metal catalysts. Consequently, the synthesis of CNTs with a controlled diameters and number of walls is an important issue. The use of alcohol with much less formation of soot, or solid carbon, is known from an alcohol flame compared to a hydrocarbon flame [11].

Many researches on CNTs have been carried out to understand the growth mechanism of CNTs, which will depend on the synthesis method [12]. The generally growth processes of CNTs by CCVD, involve adsorption and decomposition of hydrocarbon gases containing carbon on metal surfaces, dissolution and diffusion of the released carbon atoms in catalyst, furthermore precipitation of the graphite like-layers. Regarding the CNTs synthesis, many previous researches have indicated that the CCVD process is one of the most promising ways [13-15].

The motivation of the present work is to gain a detailed understanding of CNTs-CCVD formation using two kinds of carbon precursors: ethanol vapor (EtOH) and ethylene gas (C_2H_4). Our specific objectives are to identify the obtained CNTs structure (outer and inner diameters, walls number and length) over a range of operating conditions (carbon source and temperature synthesis).

2. Experimental procedure

We have used the impregnating method in this work to prepare our metal salts mixture in the appropriate concentration (Fe-Co/MgO catalyst) [14]. The catalytic CVD synthesis was carried out in a fixed – bed reactor (quartz tube of 50 mm inner diameter and 1000 mm in length) inside a carbolite horizontal furnace. For each experiment, a quartz boat containing about 0.5 g of white-yellow catalyst powder was placed in the center of the furnace. We have chosen two kinds of carbon precursors: ethanol (C_2H_5OH, absolute, 99.85 % purity) and ethylene (C_2H_4) with 300 and 405 ml/min nitrogen (N_2) as carrier gas. After N_2 purging reactor for 15 min, alcohol vapor or ethylene gas flow was supplied to the quartz reactor for typically 30 min. Subsequently, the reactor was cooled at 25 °C under 300 ml/min N_2 for 15 min. After cooling down, the blackened sample in the boat was weighed and analysed by different characterization method. Following CCVD growth, the catalyst (support and metal particles) was removed by simple acidic treatment where MgO presents the advantage over other supports, it can be readily dissolved in acids. The carbon deposit (wt %) by EtOH and C_2H_4 decomposition over Fe-Co at different reacting gas flow and synthesis temperature was calculated.

In order to study the effect of the CCVD experimental parameters such as carbon source and CNTs formation temperature, we have varied the EtOH vapor pressure by controlling the EtOH reservoir temperature (0, 16 and 25 °C) and the C_2H_4 flow (0, 30 and 60 ml/min). Specifically, we have studied the effect of carbon precursor and concentration as well as growth temperature to further emphasize their effect on the CNTs products.

The morphology of the CCVD crude and purified products was examined by FESEM (JEOL JSM 7500 F field emission scanning electron microscope) and structural analysis was carried out using TEM (Philips Tecnai transmission electron microscope). The specimens for TEM and FESEM analysis were prepared by making a few drops of the suspension (sonicated EtOH with synthesized CNTs) onto a microgrid covered with a holey carbon thin film and a Al pastille, respectively.

3. Results and discussions

The CCVD precursor C_2H_4 or EtOH, as carbon source, is decomposed to form elemental carbon via a sequence of free radical reactions, which then assembled as CNTs. The alcohols are much better carbon sources for CNTs formation than hydrocarbons because of the role of decomposition OH radicals. So, the high purity products were attributed to OH radicals associated with alcohol, which effectively removes the amorphous carbon during the growth.

Our experiments show that the nature and yield of the NTs generated are greatly influenced by the carbon source nature and consequently the interactions with the catalysts. The percentage of carbon deposited on the catalyst due to the catalytic decomposition of EtOH and C_2H_4 over Fe-Co/MgO is represented in the following table. Also, a systematical investigation of N_2 effect, as another reaction parameter, using EtOH and C_2H_4 decomposition shows good results with 405 ml/min and 300 ml/min of N_2 flow, respectively.

The TEM images, displayed afterward, clearly indicate that CNTs structures are linear in nature with a high aspect ratio between their width and length, that is moreover shown in FESEM analysis (see figure 4). These linear structures up to this point have been described as nanotubes graphitic in nature and single, multi-walled or nanofibers depending on CCVD conditions. To favor high quality tubes, homogenous walled CNTs are suggested. Nevertheless, for certain applications, such as gas storage, nanotubes of lower quality are desired [19].

Table 1: Carbon precursors vapor decomposition over Fe-Co/MgO (at 800 °C during 30 min) dependence on CNTs Yield before and after chemical purification (yield defined as the weight ratio of CNTs and catalyst [16]).

Carbon precursors		CNTs Yield (%) Before	after
C_2H_4	30	50	37
(ml/min)	60	41	29
EtOH	0	7	-
(°C)	16	27	13

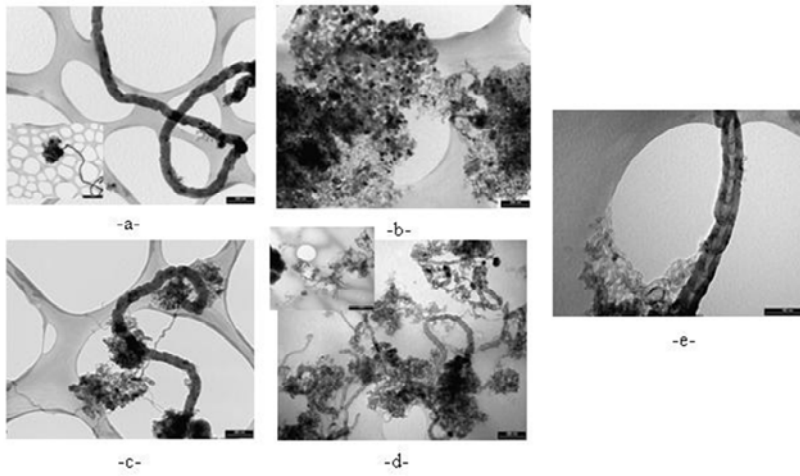


Fig. 1: TEM pictures illustrating the EtOH vapor decomposition over Fe-Co/MgO at 800 °C during 30 min:

- For EtOH/N_2 : (a) 0°C/300 ml/min and (b) 0°C/405 ml/min.
- For EtOH/N_2 : 16°C/405 ml/min : (c) crude, (d) purified product and (e) Bamboo MWNTs.

In figure 1b, it is observed the presence of some catalysts which are non-actived during the CNTs formation with low concentration EtOH decomposition at 800 °C. Generation of 90 % CNTs-bundles (Φ_{out} between 4 and 38 nm) is observed only in the carbon deposit obtained from reactions based on EtOH carried out at T > 900 °C. This TEM analysis reveals perhaps the presence of SWNTs and/or DWNTs in the sample, but it does not allow us to determine precisely the quantitative ratio between the two types of CNTs. Consequently, these formed products are composed of CNTs in form of MWNTs, bundles or bamboo-MWNTs where the uniformity of this kind of CNTs is affected by the carbon precursor or synthesis temperature. As well, the formation of MWNTs is obtained using C_2H_4 at T < 800 °C. Finally, in all cases according to the previous research, the synthesis of SWNTs seems to be linked to the very small size of the catalyst particles. It is well understood, that the CNTs are formed via the interaction between carbon and metal particles. Therefore, the composition of the EtOH-CCVD (ACCVD process) closely associated with NTs bundles are of interest towards identifying active catalyst particles.

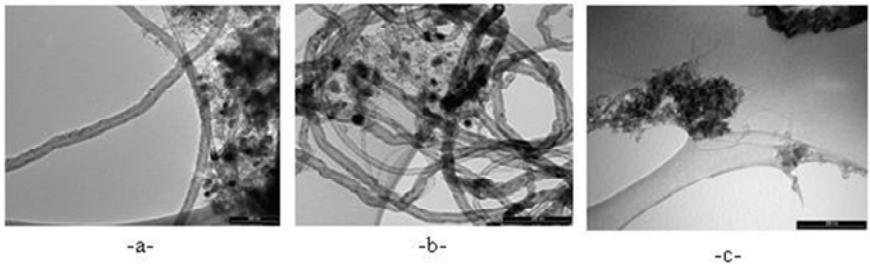


Fig. 2: TEM pictures of CNTs obtained using Ethylene and EtOH carbon source at 800 °C:

- 60 min synthesis period: (a) C_2H_4-N_2 = 30ml/min-300 ml/min and (b) purified product.
- 30 min synthesis period: (b) EtOH-N_2 = 16 °C/405 ml/min purified CNTs.

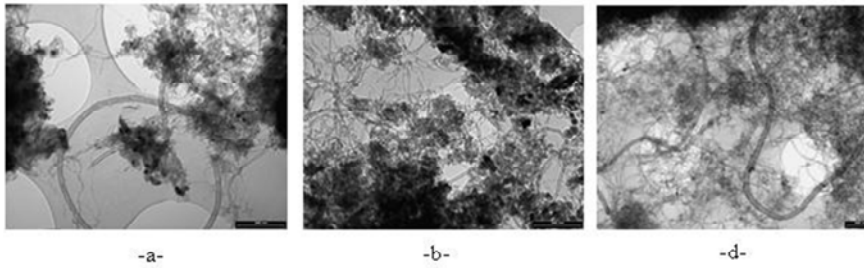
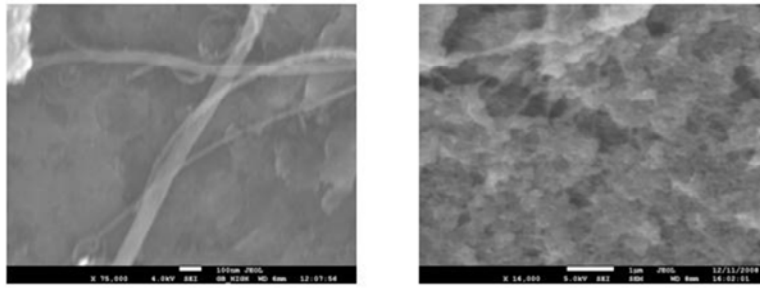


Fig. 3: TEM pictures of CNTs obtained using Ethylene decomposition over Fe-Co/MgO at 700 °C:

- during 60 min: (a) C_2H_4-N_2 = 30ml/min-300 ml/min and (b) C_2H_4-N_2 = 60ml/min-300 ml/min.
- during 30 min: (c) C_2H_4-N_2 = 30ml/min-300 ml/min purified product.

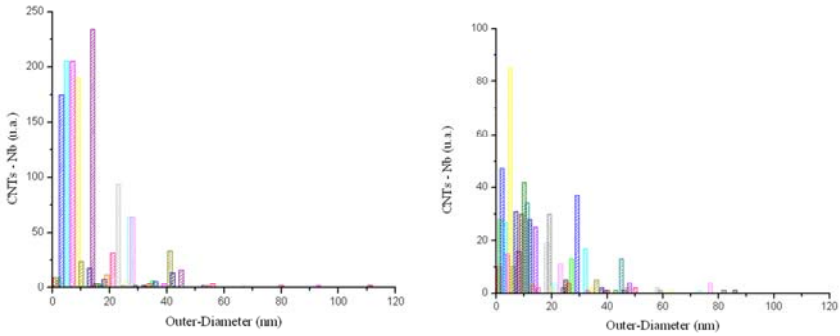


-a- -b-

Fig. 4: FESEM pictures of CNTs obtained using Ethylene and EtOH CCVD technique:

- 800 °C – 60 min: (a) C_2H_4-N_2 = 30ml/min-300 ml/min.
- 800 °C – 30 min: (b) EtOH-N_2 = 16 °C-405 ml/min purified CNTs.

Thus, in order to see the influence of the reacting gas on the CNTs structure, the outer, inner diameters and the walls number have been measured from TEM pictures and presented in figure 5. According to these histograms, 69 % and 29 % of thin MWNTs with 4 % and 14 % of Φ_{out}<10 nm is obtained using 34 torr (EtOH) and 30 ml/min (C_2H_4) at 800°C, respectively.



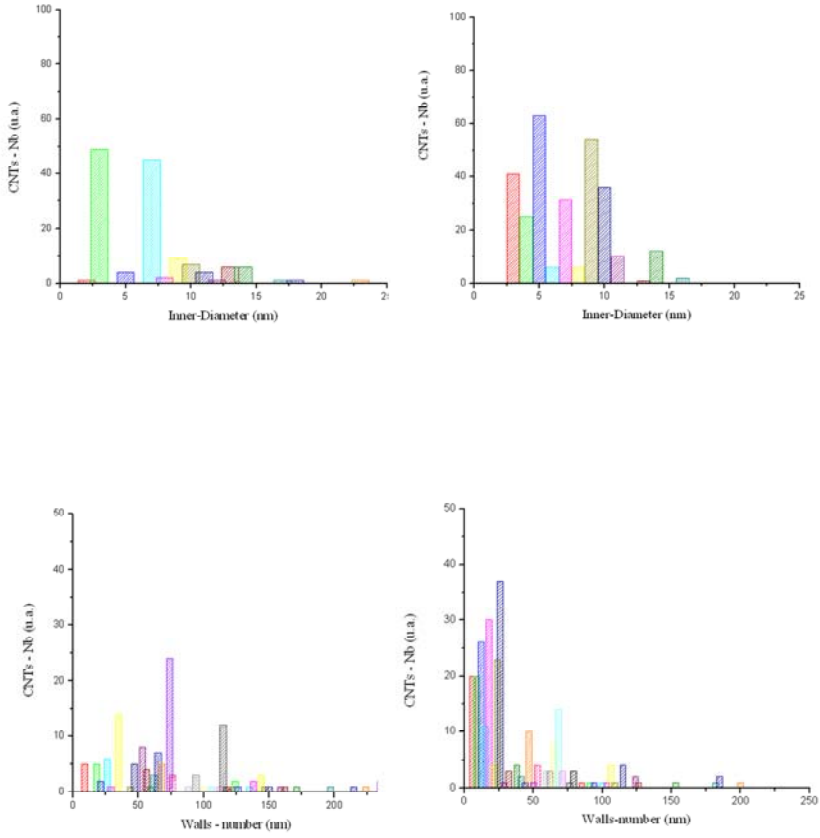


Fig. 5: Outer and inner diameter as well as number of walls distribution histograms of CNTs synthesized over: C_2H_4 – CCVD (right) and EtOH- CCVD (left) at 800 °C.

4. Conclusion

The comparison of physical appearance of as-synthesized carbon deposit from C_2H_4 and with ethanol's one indicated that as-product are thin MWNTs, bamboo-MWNTs and bundles-CNTs according to the CCVD decomposing. The yield of CNTs changes significantly with the EtOH vapor and C_2H_4 flow. The better yield is achieved at 16 °C and 30 ml/min. Furthermore, it is obvious that it is possible to

synthesis thin or thick MWNTs with desired outer diameter distribution and consequently the walls number by choosing the EtOH pressure or ethylene flow associated with 405 ml/min and 300 ml/min of N_2, respectively.

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