Available online at www.sciencedirect.com
ScienceDirect
Thermochimica Acta 463 (2007) 53–59
thermochimica acta
www.elsevier.com/locate/tca

Investigation of the synthesis strategy of CNTs from CCVD by thermal analysis

D. Porwal*, K. Mukhopadhyay, K. Ram, G.N. Mathur[1]

Nanoscience and Technology Division, Defence Materials & Stores Research & Development Establishment,
DMSRDE Post Office, G.T. Road, Kanpur 208013, Uttar Pradesh, India

Abstract

Thermogravimetry (TG) is found to be a simple process to see the effect of the experimental condition on the some properties of synthesized carbon nanotubes (CNTs). A comparative study of thermogravimetry (TG) and derivative thermogravimetry (DTG) curves of CNTs, prepared under different experimental conditions is useful to investigate the influence of synthesis strategy on the thermal stability, yield and the nature of crystallinity of the CNTs. Single step in DTG profile under air atmosphere and high degradation temperature of sample in a TG curve shows the good quality and high yield of the CNTs. The samples of CNTs are prepared by CCVD of acetylene over Fe/Co and Fe/Mo in ratio of 1:1 by weight supported on aluminium isopropoxide (AIP) in the temperature range of 700–900 °C. The investigations from the TG curves help to optimize the experimental conditions for the synthesis of CNTs by CCVD method.

Keywords: Carbon nanotubes; Chemical vapour deposition; Scanning electron microscopy; Thermogravimetric analysis

1. Introduction

The discovery of carbon nanotubes (CNTs) by Iijima [1] continues to draw much attention for their myriad potential applications [2] largely deriving from their structural, electronic and mechanical properties. CNTs are successfully synthesized by arc discharge [3], laser ablation [4], and catalytic chemical vapour deposition (CCVD) method [5]. Out of these three methods CCVD is the most promising method for the scale up low cost production of CNTs. The growth mechanism for CCVD synthesis involves the decomposition of carbon source, followed by the dissolution of carbon phase into metal catalytic nanoparticles and redeposition of carbon on the catalyst surface. In this method catalyst, furnace temperature, flow rate of hydrocarbon (the source of carbon) and the inert gas are the variable parameters for the controlled production of CNTs. These parameters affect the quality of as prepared CNTs. In CCVD method transition metals (Fe, Co or Ni) supported on oxides or zeolite are used as catalyst precursors [5]. Till now both monometallic and bimetallic combinations of these transition metals are used for the synthesis of CNTs. It has already been explained that in case of bimetallic catalyst an alloy phase is formed. The relatively high yield and quality of CNTs synthesized by bimetallic catalysts have been explained by characteristic behaviour of this alloy phase [6], which is different from the properties of its individual component.

CNTs prepared under different experimental conditions of CCVD method have difference in their crystallinity and the thermal stability. TG in air [7] is a good technique for the characterization of yield and thermal stability of CNTs. It is useful for the oxidative purification of raw CNTs. The impurities present in the CNTs as amorphous carbon and defected outer layers on CNTs surface are oxidized by thermal treatment in oxidizing atmosphere. The various oxidizing agent are air [7], CO_2 [8], O_3 [9], O_2 [10] and acids [11]. In this report the degradation profiles of the different samples of CNTs in air have been recorded. TG measurements show that the thermal stability and the yield of CNTs vary from sample to sample with their experimental conditions and the type of the catalyst. The comparative studies of these TG curves of CNTs samples give significant information to select the optimum experimental con-

---

* Corresponding author. Mob.: +91 9450509342.
E-mail address: dipitiporwal@rediffmail.com (D. Porwal).

[1] Visiting Professor, Department of Chemical Engineering, IIT Kanpur 208016, Uttar Pradesh, India.

0040-6031/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2007.07.014

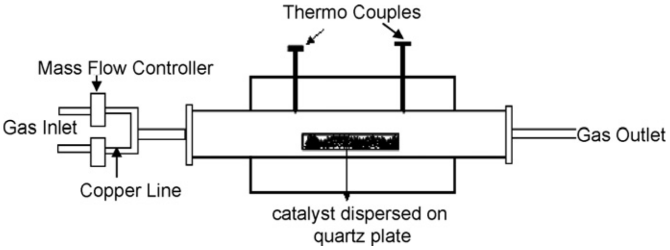

Fig. 1. The pyrolysis apparatus employed for the synthesis CNTs.

ditions for the synthesis of CNTs with different catalyst/support systems.

2. Experimental

2.1. Sample preparation

The CNTs are prepared by CCVD process. For the synthesis of CNTs, catalysts have been prepared by impregnation method. The bimetallic combination of the salts of Fe, Mo and Co (98–99%) of Aldrich are dissolved in least amount of alcohol and then sonicated for 30 min. The salts used are iron(III) acetylacetonate, cobalt acetate and ammonium molybdate for Fe, Co and Mo, respectively. The sonicated solutions of these salts are poured on hydrolysed aluminium isopropoxide (98%) (AIP) of Acros with constant stirring. After the complete mixing of salt solution with support the final product is dried in an oven at 100 °C followed by grinding to convert it into a fine powder. The prepared catalyst/support systems are Fe/Co/AIP and Fe/Mo/AIP. In each catalyst the metal content is in the ratio of 1:1 by weight and 10 wt.% of each metal with respect to the support.

In order to synthesize CNTs the prepared catalysts dispersed on a quartz plate are placed in pyrolysis apparatus, shown in Fig. 1. After placing the catalyst in furnace, the temperature was raised to 700, 800 and 900 °C within 90 min. During rising of temperature, nitrogen gas (99%) flow was maintained through the furnace at the rate of 300 ml/min. After reaching desired temperature acetylene (99.99%) was introduced into the furnace at the rate of 100 ml/min for 30 min. The main variables in our experiments are catalyst support system and temperature of CNTs synthesis. Besides of CNTs grown at various temperatures and catalysts CNTs are also prepared at 700 °C under modified atmosphere in the presence of hydrogen (reducing agent) with flow rate of 100 ml/min for each catalyst/support system. After half an hour the flow of acetylene/hydrogen was stopped and furnace is allowed to cool in nitrogen atmosphere. Different experimental conditions with respect to different catalyst support system are as given in Table 1. From each experiment a black carbon product deposited on quartz plate is collected for further characterizations.

2.2. Instrumentations

The pyrolysis apparatus used for the synthesis of CNTs is shown in Fig. 1. The apparatus consists of copper gas flow lines and an electrically heated horizontal tubular (5 cm diameter and 150 cm length) furnace. The furnace has two heating zone and the temperature of each zone is controlled by separate PID controller for the homogenous heating of furnace tube. Here the PID controller means a temperature controller program based on Proportional, Integration and Differential (PID) formula. The prepared samples are characterized by scanning electron microscopy (SEM-JEOL JSM 840) in order to describe morphology.

The raw CNTs are used to see the effect of experimental conditions on the yield and thermal stability in air applying a high resolution thermogravimetric analyser (Hi-Res. TGA H2950-TA Instruments) under dynamic air at a flow rate of 60 ml/min and with a heating rate of 10 °C/min for the samples. Raman spectroscopy measurements (Renishaw Raman) are performed at 514.5 nm wavelength used as an Ar ion laser line to excite the CNTs.

3. Results and discussion

The raw CNTs from CCVD methods are used for the thermal treatment with no further purification. During thermal degradation of CNTs in air, carbon content are removed as CO and CO_2 and metal particles are converted into its metal oxide. For a given set of experimental condition, thermal oxidation results into the same type of metal impurities in samples. The TG curves (Fig. 2) of the CNTs prepared by Fe/Co/AIP catalyst support system at 700 (in the presence of H_2), 700, 800 and 900 °C are recorded and symbolized as 1, 2, 3 and 4 of SET-1, respectively. The onset temperatures (T_i) determined from TG curves referred to the temperatures at which the degradation (oxidation) process

Table 1
Experimental conditions

Number	Catalyst	C_2H_2 Flow rate (ml/min)	N_2 flow rate (ml/min)	Reaction temperature (°C)	Sample code	Reaction time (min)
SET-1	Fe/Co/AIP	100	300	700[a] 700 800 900	1 2 3 4	30
SET-2	Fe/Mo/AIP	100	300	700[a] 700 800 900	1 2 3 4	30

[a] At this temperature CNTs are also prepared in presence of H_2 gas with flow rate of 100 ml/min.

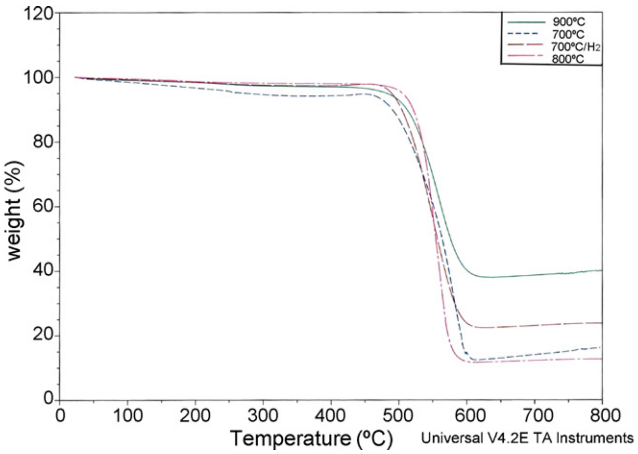

Fig. 2. TG curves of the products obtained by the CVD of the C_2H_2 in the presence of Fe/Co/AIP.

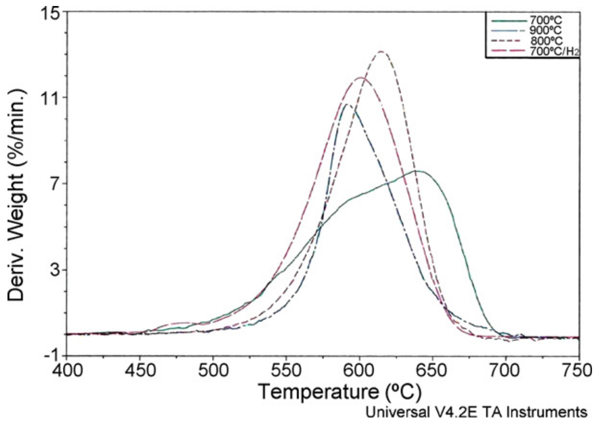

Fig. 3. DTG curves of products obtained by the CVD of the C_2H_2 in the presence of Fe/Co/AIP.

starts and the temperatures at which maximum weight loss are registered ($T_o = dm/dT_{max}$), established from maxima of DTG for four samples of SET-1 are presented in Table 2.

Here T_i describes rather the properties of impurities than nanotubes. It is known that amorphous carbon decomposes around 300–500 °C [12] and causes that CNTs covered by carbon material can be degraded at lower temperature than purified CNTs. While T_o could be assigned to the quality of CNTs, e.g. their crystalline structure and the presence of defected graphite walls. For the samples: 1, 3 and 4 of the SET-1 only one maximum of DTG (T_o peak) is observed while in the sample 2 a broad DTG peak with two maxima is registered, the sharp main maximum at 650 °C and weakly observed elevation at 600 °C.

The single DTG peak is connected with a single carbon phase in CNTs when two maxima of DTG could correspond with two forms of carbon phase, e.g. no defected and defected nanotubes. Defected CNTs are weaker physically and chemically and therefore are oxidized at lower temperature compared to straight, strong nanotubes. The elevation at 600 °C observed in DTG curve of sample 2 can be caused by nanotubes including defects in outer graphite layers, however it can also originate from the amorphous carbon or graphite particles covered nanotubes.

Our results show the influence of the quality of CNTs on their oxidation (degradation) temperature. Hence, the samples from 2 to 4 of SET-1 prepared under the same experimental conditions but at different growth temperatures show that the T_o value decreases while the synthesis temperature increases. The T_o values of CNTs synthesized at 700 and 800 °C are much closer to each other as compared to the sample synthesized at 900 °C. The value of T_o is directly proportional to the thermal stability of the carbon product. Taking T_o values (Fig. 3) into consideration we can conclude that thermal stability of the carbon deposit of sample 4 obtained at 900 °C is worse than for samples 2 and 3. Differences in thermal stability between the samples result from their morphology. Indeed, the SEM images of the samples 2 (Fig. 4a) and 3 (Fig. 4c) show CNTs while the sample 4 (Fig. 4d) composes spherical granules of carbon are called carbon beads. These observations show the effect of synthesis temperature on the morphology and the thermal stability of the samples. It is also clear from the literature [13,14] that for a particular catalyst there is an optimum temperature above which the CNTs synthesis does not take place as well as the quality of CNTs also decreases, due to the deposition of amorphous carbon and more defects in CNTs. A mixture of ferrocene and toluene give maximum yield of CNTs at 760 °C [13] and Harutyunyan et al. [14] found that unreduced iron was active for CNTs growth only from 900 °C whereas it becomes active for CNTs growth at 680 °C with the addition of 20% molybdenum. Along with the higher limit of the synthesis temperature there is also lower limit of the synthesis temperature. Although sample prepared at 700 °C has higher thermal stability but there is a broad hump near about 600 °C which could indicate defected CNTs or larger amount of amorphous carbon as compared to the sample 3 prepared at 800 °C that is characterized by the sharp maximum of DTG at 620 °C.

Table 2
Thermal investigations from SET-1

Sample code	T_i (°C)	T_o (°C)	Residue (%)
1	553.5	580	3.63
2	540.7	650	10.38
3	567.5	620	7.47
4	567.9	570	33.12

The conclusions are confirmed by the SEM images. The CNTs synthesized at 700 °C (SEM image of sample 2, Fig. 4a) are covered by some amorphous carbon while the nanotubes prepared at 800 °C (SEM image of sample 3, Fig. 4c) are clean. Addition of hydrogen gas during CNT growth process at the same synthesis temperature also affects the surface morphology, thermal stability and degradation profile of CNTs. The SEM image (Fig. 4b) shows that the CNTs are of smaller diameter. The TG curve for this sample has higher T_i value as compared to sample without hydrogen. Since hydrogen is a good reducing agent, the presence of hydrogen reduces upper defected layers and the amorphous coating of carbon resulting in the synthesis of CNTs of smaller diameter. DTG curve of the sample prepared at 700 °C with and with out hydrogen shows that the CNTs synthesized in the presence of hydrogen have lower thermal stability

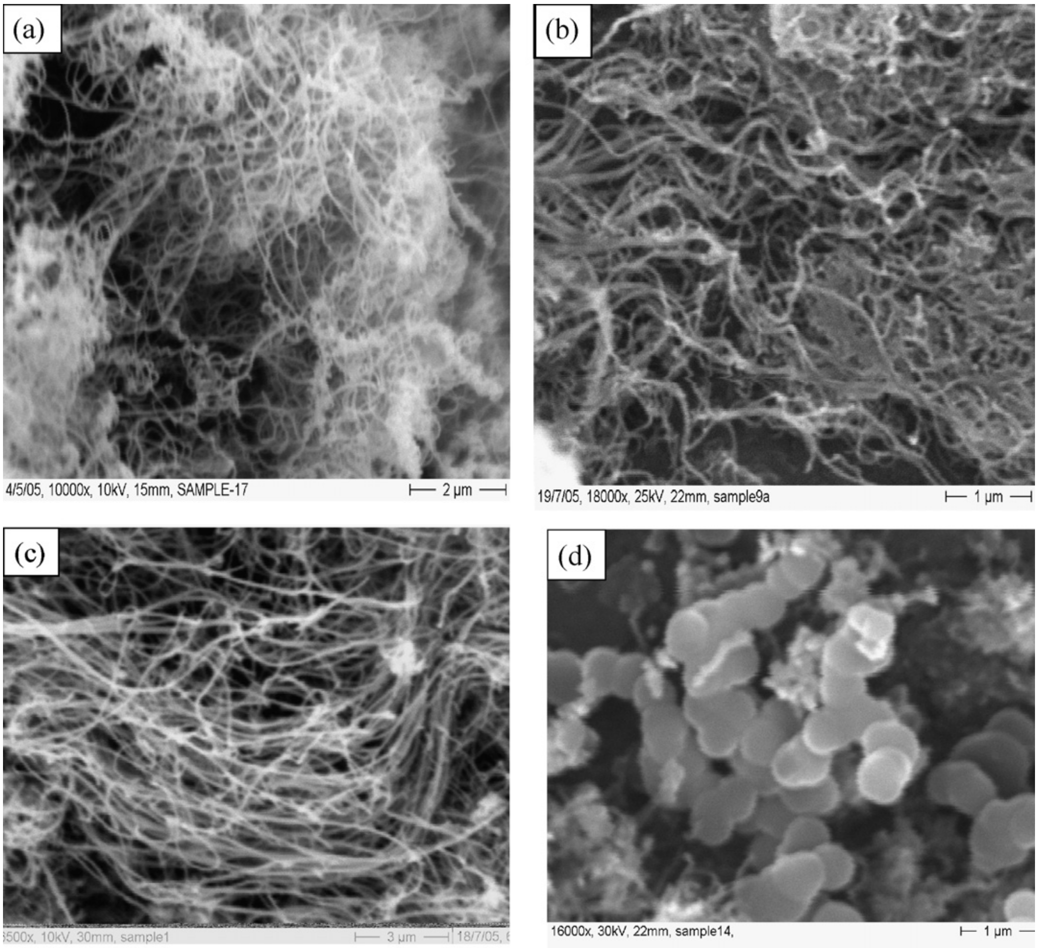

Fig. 4. Scanning electron micrographs of product obtained by the CVD of the C_2H_2 in the presence of Fe/Co/AIP catalyst/support. (a) Fe/Co/AIP-10/10; C_2H_2/N_2: 100/300 ml/min, at 700 °C; (b) Fe/Co/AIP-10/10; $C_2H_2/N_2/H_2$: 100/300/100 ml/min, at 700 °C; (c) Fe/Co/AIP-10/10; C_2H_2/N_2: 100/300 ml/min, at 800 °C;(d) Fe/Co/AIP-10/10; C_2H_2/N_2: 100/300 ml/min, at 900 °C.

however have a single phase of carbon content, results from a sharp DTG peak at 580 °C.

The residue for all these four samples of CNTs are collected in Table 2. The lower amount of residue at 800 °C for the same experimental conditions shows the highest activity of the catalyst because of the maximum deposition of carbon at this temperature. Not only the temperature, the presence of hydrogen for the same temperature also affects the activity of catalyst towards the highest deposition of carbon resulting into less amount of residue. It was found that the degradation profile and the rate of the oxidation are largely affected by the variation in the type of actual metal of the catalyst used.

The TG curves (Fig. 5) for the samples prepared by using Fe/Mo/AIP (SET-2) under the same conditions as for the previous catalyst have no similar effect. The samples are symbolized as 1, 2, 3 and 4 similar to previous reaction conditions for SET-1.

For this catalyst, TG curves (Fig. 5), DTG curves (Fig. 6) and the resultant amount of residues (Table 3) show that the sample prepared at 700 °C have good quality and the quantity of CNTs in presence of hydrogen. But in absence of hydrogen at this temperature in DTG curve broad hump has been found, which has two peaks at around 525 and 576 °C, respectively. The lower T_o value correspond to the carbon phase having lower thermal stability (defected CNTs or carbonaceous impurities) and higher T_o value correspond to higher thermal stability of CNTs. The degradation profiles of 1 and 2 samples show that the presence of hydrogen has similar effect as described for the earlier for SET-1. SEM images Fig. 7a and b also support this

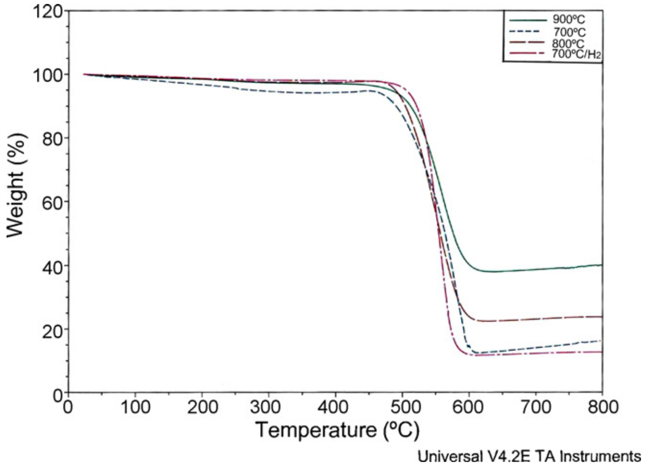

Fig. 5. TG curves of products obtained by the CVD of the C_2H_2 in the presence of Fe/Mo/AIP.

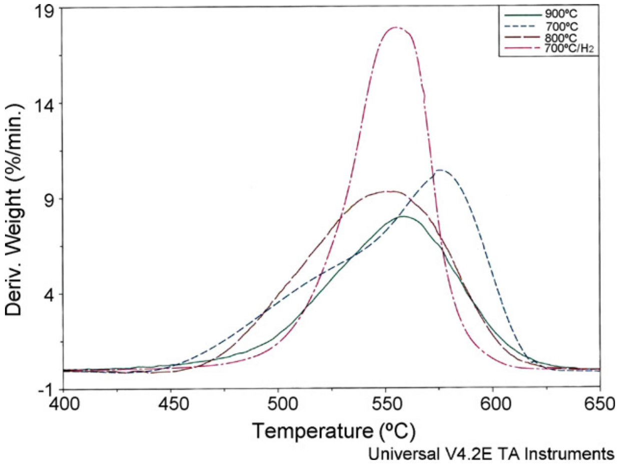

Fig. 6. DTG curves for of products obtained by the CVD of the C_2H_2 in the presence of Fe/Mo/AIP.

observation by DTG curve. These images show that the CNTs prepared in the presence of hydrogen are clean as compared to those in the absence of hydrogen. The SEM image of sample 4 prepared at 900 °C (Fig. 7d) shows the presence of carbon beads. Although the diameter of these carbon beads are much bigger and not homogenous as compared to previous catalyst. For all three samples, respectively, 2, 3 and 4 of SET-2 a broad DTG peaks are found, indicating the mixing of more than one phase of carbon as impurities.

Table 3
Thermal investigations from SET-2

Sample code	T_i (°C)	T_o (°C)	Residue (%)
1	486.7	550	14.80
2	475.6	576	12.65
3	507.5	560	25.15
4	470.9	555	39.46

The residues for all these four samples of CNTs are presented in Table 3. For both the type of catalysts, resultant amount of residue is found minimum for Fe/Co/AIP catalyst/support system. Since out of the Fe, Co and Mo transition metals Fe and Co are the good catalysts for CNTs synthesis in CCVD method [15], the combined effect of these two transition metals enhance the activity for the carbon deposition of Fe/Co/AIP system resulting in higher yield of the product. Here in the TG and DTG curves of all the samples, it has been seen that the samples of SET-1 started to oxidize from ∼540 °C while for the SET-2 the oxi-

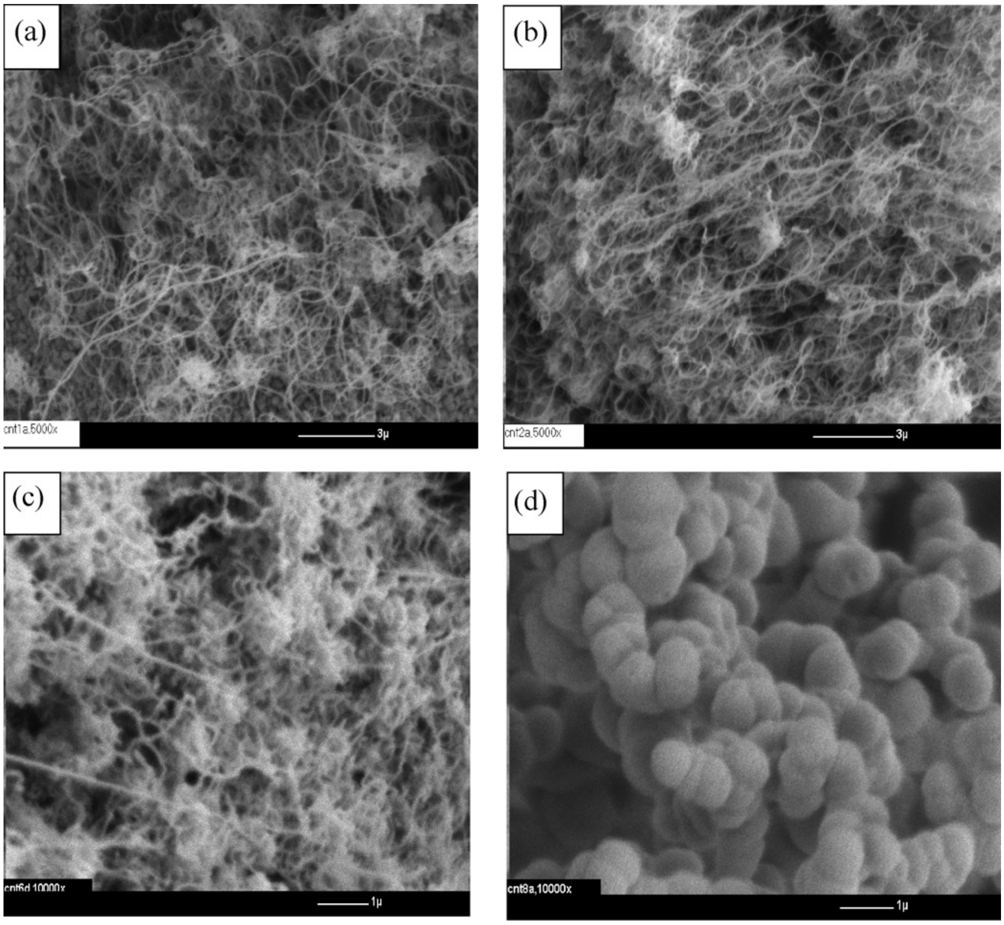

Fig. 7. Scanning electron micrographs of product obtained by the CVD of the C_2H_2 in the presence of Fe/Mo/AIP. (a) Fe/Mo/AIP-10/10; C_2H_2/N_2: 100/300 ml/min,at 700 °C; (b) Fe/Mo/AIP-10/10; $C_2H_2/N_2/H_2$: 100/300/100 ml/min, at 700 °C; (c) Fe/Mo/AIP-10/10; C_2H_2/N_2: 100/300 ml/min, at 800 °C; (d) Fe/Mo/AIP-10/10; C_2H_2/N_2: 100/300 ml/min, at 900 °C.

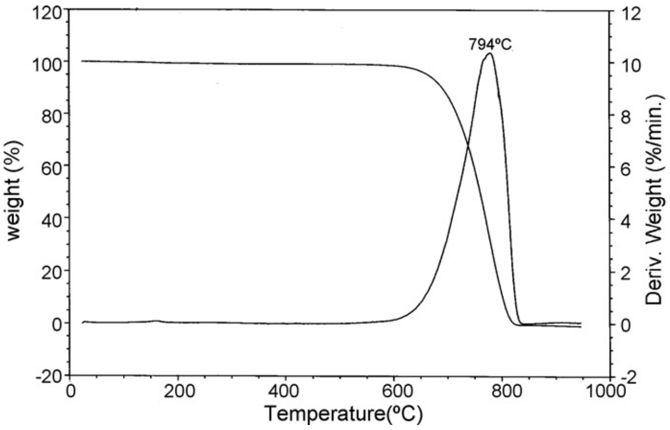

Fig. 8. DTG and TG graphs of graphite.

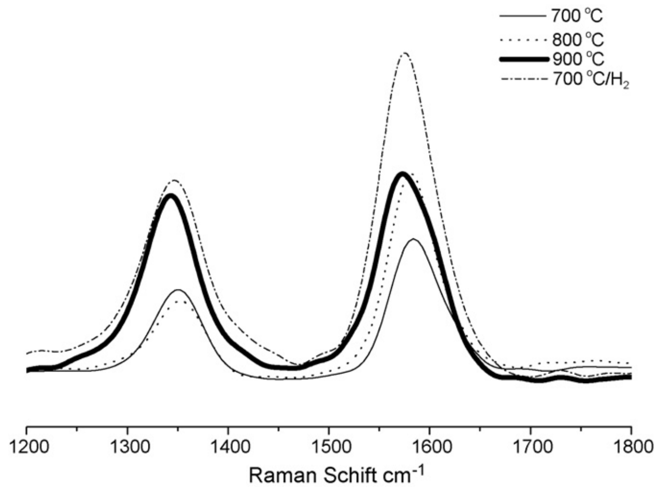

Fig. 9. Raman spectrum of CNTs of SET-1 synthesized at different synthesis temperature.

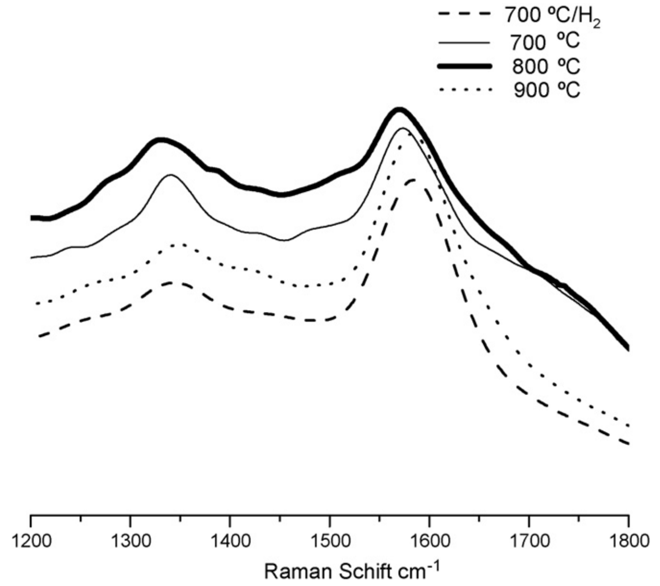

Fig. 10. Raman spectrum of CNTs of SET-2 synthesized at different synthesis temperature.

dation started at 486 °C. The sample 3 of the SET-1 and 1 for SET-2, which are identified as the best samples for synthesized catalyst from TG and DTG curves and the thermal stability of the sample 3 of SET-1 is higher (∼620 °C) than of the Sample1 of SET-2 (560 °C). It is also found that the oxidation temperature is lower for the synthesized CNTs as compared to graphite (Fig. 8) because the CNTs have the impurities of the transition metals, which catalyses the rate of oxidation of carbon [16], resulting the lower oxidation temperature as compared to graphite. Presence of impurities and defects also reduces the oxidation temperature of CNTs.

Raman spectra of CNTs synthesized in SET-1 and SET-2 experiments also confirm the influence of growth conditions on the quality of the deposited carbon products. For the multi-walled carbon nanotubes (MWCNTs) Raman spectrum is dominated by two characteristics peaks around 1350 cm^{-1}, called as D band peak associated with the defected CNTs and around 1580 cm^{-1} called as G band peak [17]. The G band peak is originated in plane stretching mode of sp^2 hybridized carbon bonding. The D band arises from the defects and disorder in graphene sheets [17]. The presence of high intensity of the G band peak provides the evidence of high graphitic order in CNTs. Both G band and D band are used to determine the structural quality of the CNTs. Higher the value of the G/D corresponds to the higher graphitic structure of the CNTs.

The intensity ratio of G:D peaks for the samples: from 1 to 4 synthesized in SET-1 (Fig. 9) are 1.65, 1.58, 2.68 and 1.21, respectively. From these data result that CNTs prepared at 800 °C are characterized by the highest G/D value what indicates their good crystalline quality. The results are consistent with thermal measurements (TG and DTG of sample 3). Similar observation compatible with thermal analysis was registered for samples prepared in SET-2 experiments. G/D values calculated from the Raman spectra (Fig. 10) of samples from 1 to 4 are 1.027, 1.011, 1.007 and 1.023, respectively. The sample 1 prepared at 700 °C in the presence of H_2 has highest the G/D value indicating the good crystalline quality of CNTs in this sample. Hence, these Raman Spectra (Figs. 9 and 10) show the effect of experimental conditions on crystalline nature of carbon product. Analyses of above results show that that the CNTs produced by Fe/Co/AIP catalyst at 800 °C have good crystallinity among all six samples of SET-1 and SET-2.

4. Conclusion

Thermal investigations show the effect of experimental conditions on the structure and thermal stability of CNTs. The results show that the thermal stability of CNTs prepared by CCVD technique is lower than graphite due to the presence of transition metal as catalytic impurities as well as due to the presence of defects in CNTs. The TG and DTG analysis evaluate the percentage of impurities/residue and the thermal stability of CNTs. The reaction temperature for the CNTs synthesis has measurable effect on structure and quality of CNTs. The CNTs obtained from the pyrolysis of acetylene over Fe/Co/AIP catalyst support system at 800 °C has higher thermal stability and less impurities and for the Fe/Co/AIP catalyst support system CNTs synthesized at 700 °C in the presence of hydrogen has higher thermal stability and less impurities. But out of these two samples CNTs prepared from Fe/Co/AIP is the best sample regarding the graphitization, thermal stability and yield of CNTs. It shows that the addition of cobalt enhance the activity of catalyst as compared to molybdenum in a bimetallic catalyst for the production of CNTs. Hence, the TG is a good technique to investigate the quality and quantity of as prepared CNTs. It is also helpful for the optimization of experimental conditions for the synthesis of good quality of CNTs.

Acknowledgements

The corresponding author is grateful to Defense Research & Development Organization (DRDO) for providing fellowship to carry out the research activities. The authors are also thankful to Dr. R.S. Chauhan, DRDE Gwalior and Mr. Anand, SSPL New Delhi for SEM analysis, Mr. C.B. Viswakarma, DMSRDE Kanpur for thermal analysis and Mr. Sanjay for Raman analysis of the samples. The authors are also thankful to our director Dr. K.U. Bhaskar Rao for permission to present the paper.

References

[1] S. Iijima, Nature 354 (1991) 56–58.
[2] E.W. Wong, P.E. Sheehan, C.M. Lieber, Science 277 (1997) 1971–1975.
[3] X. Lv, F. Du, Y. Ma, Q. Wu, Y. Chen, Carbon 43 (2005) 2020–2022.
[4] T. Seeger, G. de la Fuente, W.K. Maser, A.M. Benito, M.A. Callejas, M.T. Martinez, Nanotechnology 14 (2003) 184–187.
[5] K. Mukhopadhyay, G.N. Mathur, Int. J. Nano Sci. 2 (2003) 153–164.
[6] Z. Konya, J. Kiss, A. Oszko, A. Siska, I. Kiricsi, Phys. Chem. Chem. Phys. 3 (2001) 155–158.
[7] D. Bom, R. Andrews, D. Jacques, J. Anthony, B. Chen, M.S. Meier, J.P. Selegue, Nano Lett. 2 (2002) 615–619.
[8] M.R. Smith, S.W. Hedges, R.L. Count, D. Kem, N. Shah, G.P. Huffman, B. Bockrath, Carbon 41 (2003) 1221–1230.
[9] S.C. Tsang, P.J.F. Harris, M.L.H. Green, Nature 362 (1993) 520.
[10] Y.S. Park, Y.G. Choi, K.S. Kim, D.C. Chung, D.J. Boe, K.H. An, S.C. Lim, X.Y. Zhu, Y.H. Lee, Carbon 39 (2001) 655–661.
[11] S.C. Tsang, Y.K. Chen, P.J.F. Harris, M.L.H. Green, Nature 372 (1994) 159–162.
[12] B. Kitiyanan, W.E. Alvarez, J.H. Harwell, D.E. Resasco, Chem. Phys. Lett. 317 (2000) 497–503.
[13] C. Singh, M.S.P. Shaffer, A.H. Windle, Carbon 41 (2003) 359–368.
[14] A.R. Harutyunyan, B.K. Pradhan, U.J. Kim, G. Chen, P.C. Eklund, Nano Lett. 2 (2002) 525–530.
[15] A. Kukovecz, Z. konya, N. Nagarjun, I. Willems, A. Tamasi, A. Fonseca, J.B. Nagy, I. Kiricsi, Phys. Chem. Chem. Phys. 2 (2000) 3071–3076.
[16] J.M. Thomas, Microscopic studies of graphite oxidation, in: P.L. Walker (Ed.), Chemistry and Physics of Carbon, vol. 1, Marcel Dekker, New York, 1965, pp. 121–128.
[17] C.E. Bottani, C. Castiglioni, G. Zerbi, Raman scattering in nanostructures, in: H.S. Nalwa (Ed.), Encyclopedia of Nanoscience and Nanotechnology, vol. 9, 2004, pp. 225–272.