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Effect of Temperature on Gravity Assisted Synthesis of Carbon Nanotubes by Spray Pyrolysis

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Carbon nanotubes were prepared along the gravity direction in a spray pyrolysis setup over the silica supported Fe-Co-Ni catalyst. The silica supported Fe-Co-Ni catalyst coated by jet nebulized spray pyrolysis method over copper strip was inverted to face downward, so that carbon nanotubes can be prepared along the direction of gravity. From the point of view of green chemistry, instead of commonly used hydrocarbons, a plant based natural precursor, pine oil is used as carbon precursor for preparation of carbon nanotubes. The effect of temperature on yield and morphology of carbon nanotubes grown along gravity was studied. The yield of carbon nanotubes was calculated as mass percentage of catalyst and support. The carbon nanotubes were characterized using XRD, SEM, Raman and TGA techniques. The carbon deposit obtained at 650 ºC contains multi-walled carbon nanotubes in larger quantity with very less amorphous carbon. A narrow, lengthy and well graphitized multi-walled carbon nanotubes were formed when the carbon nanotubes grow along the gravity.

Keywords: Carbon nanotubes, Effect of temperature, Along gravity, Spray pyrolysis, Natural precursor.

INTRODUCTION

Carbon nanotubes exhibits unique physical and chemical properties, which generally depends on its morphology and structure. These unique properties are potential for application in the field of environmental remedies, gas sensors, hydrogen storage and energy storage devices [1-4]. Preparation of high quality carbon nanotubes has been demonstrated *via* several methods. Among them, chemical vapour deposition (CVD) method seems to be the simple with scale up possibilities for bulk production. The choice of catalyst, precursor, preparation method, have been studied by several research groups in order to improve the quality of carbon nanotubes with respect to yield, length, size, structure and morphology [5-7]. A wide variety of combination of transition metals has been studied for the growth of carbon nanotubes. The catalysts used in CVD process are usually prepared by wet chemical route, which are less likely useful to control uniform particle size in nano scale. In this work, catalyst was prepared by jet nebulizer spray pyrolysis method, through which particle size can be controlled [8]. Silica supported multi metal catalyst is used to prepare carbon nanotubes, owing to its synergistic effect on controlling carbon nanortubes properties.

Among several factors which influence the carbon nanotubes growth properties, pyrolysis temperature is an important factor in CVD process. The tip growth mechanism, which is normally observed in CVD process, contains catalyst at the tip of carbon nanotubes. Owing to heavier catalyst particle at the tip of the light weight carbon tube, during growth of carbon nanotubes in a boat type setup, it bends and results in entangled carbon nanotubes. To deal with this, Yeh *et al*. [9,10] prepared SWCNTs in a gravity assisted chemical vapour deposition process using Co/Si(100)Co/Si(100) substrate. It is reported that all the carbon nanotubes are lined up with the direction of gravity and the length of SWCNTs increases with growth time.

To meet the requirements of the green chemistry principle, it is the need of the present era to use a natural renewable precursor as carbon source to synthesize multi-walled carbon nanotubes [11]. In order to avoid the bending of tube and also to use a natural precursor, the carbon nanotubes are grown along gravity, *i.e.* downward from the surface of the catalyst support using natural precursor pine oil by spray pyrolysis method. The results show that a nanosize, narrow, lengthy carbon nanotubes can be prepared at optimum parameter conditions.

EXPERIMENTAL

In present work, botanical hydrocarbon oil, pine oil, having boiling temperature around 200 ºC is used as carbon precursor for synthesis of carbon nanotubes (CNTs). Pine oil is an essential oil obtained from various parts of pine tree (*Pinus sylvestris*) by distillation. Chemically, pine oil consists mainly of α-terpineol, cyclic terpene alcohols.The biosource is readily available, cheap and also user-friendly to use in spray pyrolysis method. The spray pyrolysis method is more or less similar to chemical vapour deposition method. The spray pyrolysis method differs from CVD in the way of approach that the vaporization and pyrolysis of carbon source occurs simultaneously in spray pyrolysis whereas in CVD it is a two step process [12]. Since the precursor pine oil, evaporates at relatively higher temperature, spray pyrolysis method is adopted for synthesis of CNTs. The chosen catalyst silica supported Fe-Co-Ni is coated over the copper substrate using jet nebulized spray pyrolysis and kept inside the tubular furnace in such a way that the catalyst orients downward enabling carbon nanotubes to grow along the gravity direction. The spray pyrolysis temperature varied from 550 to 750 ºC under optimum conditions of other reaction parameters to obtain good quality carbon nanotubes with high yield.

The silica supported Fe-Co-Ni catalyst coated over copper strip in inverted position is placed inside the electrical heating furnace. The carrier gas nitrogen (100 mL min^{-1}) is flushed out to remove air and create nitrogen atmosphere. The temperature is increased from room temperature upto the desired CNTs growing temperature. Subsequently, the carbon precursor pine oil was introduced into the quartz tube through spray nozzle at the rate of 0.5 mL min^{-1} for 40 min at the choosen temperature. Nitrogen flow was maintained until the furnace was cooled to room temperature. The product collected was then weighed and stored in air tight container for further characterizations. The carbon deposit was characterized using SEM, XRD, Raman and TGA techniques. Raman spectrum was recorded with Ar ion laser (514.5 nm). Thermogravimetric analysis was carried out at a heating rate of 10 ºC min^{-1} under air atmosphere.

RESULTS AND DISCUSSION

Morphological studies: The carbon deposit grown along gravity over silica supp-orted Fe-Co-Ni catalyst at 550, 650 and 750 ºC using natural precursor pine oil is shown in Fig. 1.

Fig. 1a depicts the morphology of carbon materials obtained at 550 ºC. The image shows that the carbon materials formed are mixture of amorphous carbon and carbon nanotubes. At this temperature (550 ºC), the carbon nanotubes are formed not only sparingly but with more defective surface. The surface of the carbon nanotubes is not smooth. The average diameter and length of the carbon nanotubes are 50 nm and 2 μm, respectively. The irregular surface and shorter length of carbon nanotubes formed at this temperature (550 ºC) are attributed to the insufficient heat for effective pyrolysis of natural precursor, pine oil [13].

The SEM image recorded for the carbon deposit obtained at 650 ºC is shown in Fig. 1b. The image shows that the carbon nanotubes are narrow and lengthy with smooth surface. The diameter and length of the carbon nanotubes formed are in the range 30-50 nm and 10-15 μm, respectively. These facts can be attributed to the optimum temperature for effective pyrolysis of pine oil. The growth of lengthy carbon nanotubes is attributed to almost equal rate of pyrolysis and growth of carbon nanotubes. Moreover, the tip growth mechanism, most probably observed in CVD process, is favourable for lengthy and narrow carbon nanotubes growth along gravity direction [14]. The curved carbon nanotubes observed in the SEM image is due to the disorder occurred during purification.

Fig. 1c shows the morphology of the carbon nanotubes formed at 750 ºC. The image indicates that the carbon deposit formed contains mostly amorphous carbon and low carbon nanotubes population. It is observed that the catalyst particles are covered with amorphous carbon. The sparingly formed carbon nanotubes are shorter 3 μm and larger 80 nm in size. These observations are attributed to the relatively high temperature (750 °C) used for pyrolysis of pine oil. The faster cracking of pine oil than the growth rate of carbon nanotubes results in

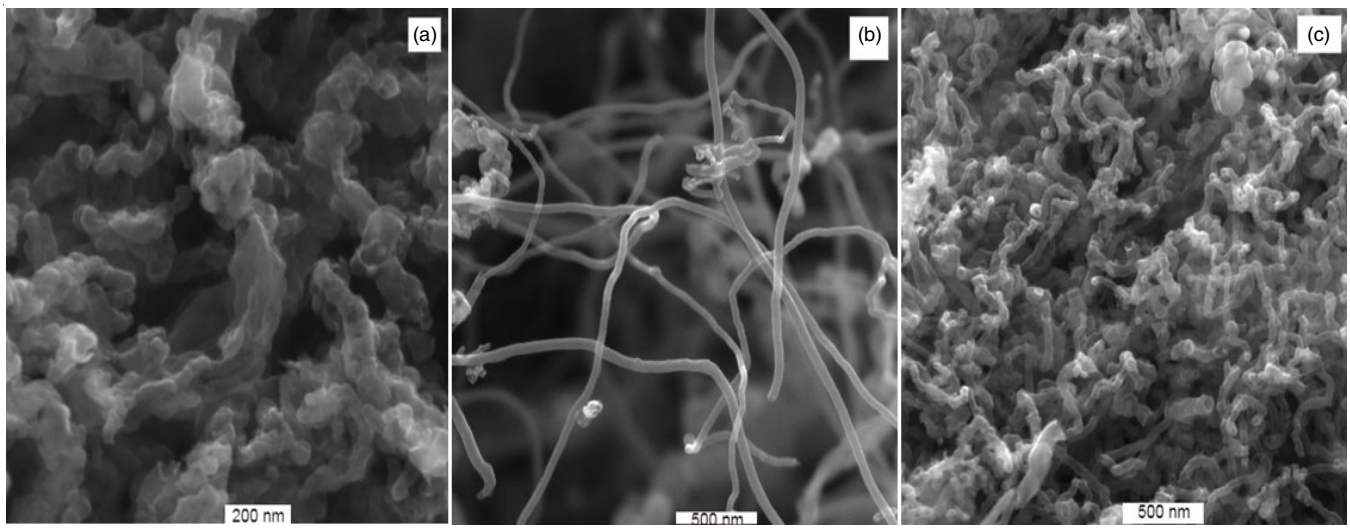

Fig. 1. SEM image of the carbon deposit grown along gravity over silica supported Fe-Co-Ni catalyst at 550, 650 and 750 °C using natural precursor pine oil for the precursor flow rate 20 mL per hour

the deposition of carbon over the outer layer of the liquid state catalyst, particularly forms as layer, when the carbon particles content exceeds the rate of assimilation by catalyst to form carbon nanotubes. As the carbon deposited as layer covering the catalyst surface, the pyrolysis of precursor is discontinued due to unavailability of fresh catalyst surface for cracking precursor pine oil. The fact can be the reason for poor yield of carbon nanotubes. Moreover, at this high temperature, the catalyst particles are sintered and strongly adhered to the substrate surface. These catalyst particles are unable to depart from the support due to strong adhering and thus poor yield of carbon nanotubes.

XRD studies: The X-ray diffraction patterns recorded for the carbon deposit obtained along the gravity over silica supported Fe-Co-Ni catalyst at 550, 650 and 750 °C are given in Fig. 2. The XRD pattern of carbon deposit obtained at 550 ºC (Fig. 2a) indicated that the carbon deposit consist more of amorphous carbon. Absence of sharp intense peak indicates carbons are not well crystallized as graphitic layers. Fig. 2b shows the XRD pattern of carbon deposit obtained at 650 ºC. Two sharp peaks are observed at (2θ) 26.3º and 44.8º. The inter planner distance calculated for these planes are 0.341 and 0.205 nm, respectively. The sharp and intense peak indicates that the carbon deposit obtained at 650 ºC is well crystallized and the inter-planar distance value shows the existence of graphitic layers. The crystalline nature of carbon deposit obtained at 750 ºC is predicted using the XRD pattern of the deposit recorded (Fig. 2c), which shows that the carbon deposits consist of mixture of amorphous and crystalline carbon.

Raman spectra: Raman spectra of the carbon deposit obtained at different reaction temperatures (550, 650 and 750 ºC) are shown in Fig. 3. The Raman spectrum of carbon deposit obtained at 550 ºC (Fig. 3a) shows the characteristic peaks at 1334.5 cm^{-1} and 1572.6 cm^{-1} which corresponds to D and G peak. The ratio of G and D peak, I_G/I_D, is 0.72. The relatively low value of I_G/I_D confirms that the carbon deposit consist of carbon nanotubes with more of amorphous or defective layers. The presence of G peak and absence of RBM peak, the characteristic peak in the region 400-100 cm^{-1} for single walled carbon nanotubes, indicates the carbon deposits are of multi-walled carbon nanotubes type.

The characteristic D and G peaks for the carbon nanotubes grown at 650 °C are observed at 1332.7 cm^{-1} and 1567.3 cm^{-1}, respectively. I_G/I_D ratio is found to increase to 2.16 on increasing reaction temperature from 550 to 650 ºC for carbon nanotubes preparation. This indicates less amorphous carbon is present and the surface of carbon nanotubes is well graphitized.

Further increase of temperature to 750 ºC for pyrolysing the carbon precursor produced mixture of amorphous and crystalline carbon deposit. The Raman spectra of carbon deposit obtained at 750 °C is shown in Fig. 3c. The I_G/I_D ratio (1.16) of characteristic D and G peaks observed at 1330.2 cm^{-1} and 1569.9 cm^{-1} indicates the existence of both amorphous carbon and defective surface of carbon nanotubes or any of these.

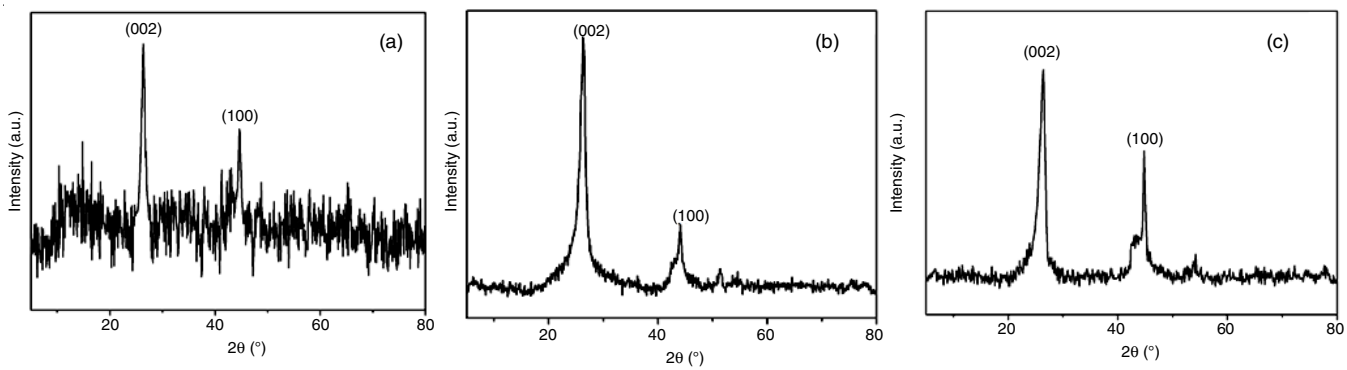

Fig. 2. XRD pattern recorded for the carbon deposit obtained over silica supported Fe-Co-Ni catalyst at 550, 650 and 750 °C using natural precursor pine oil for the precursor flow rate 20 mL h^{-1}

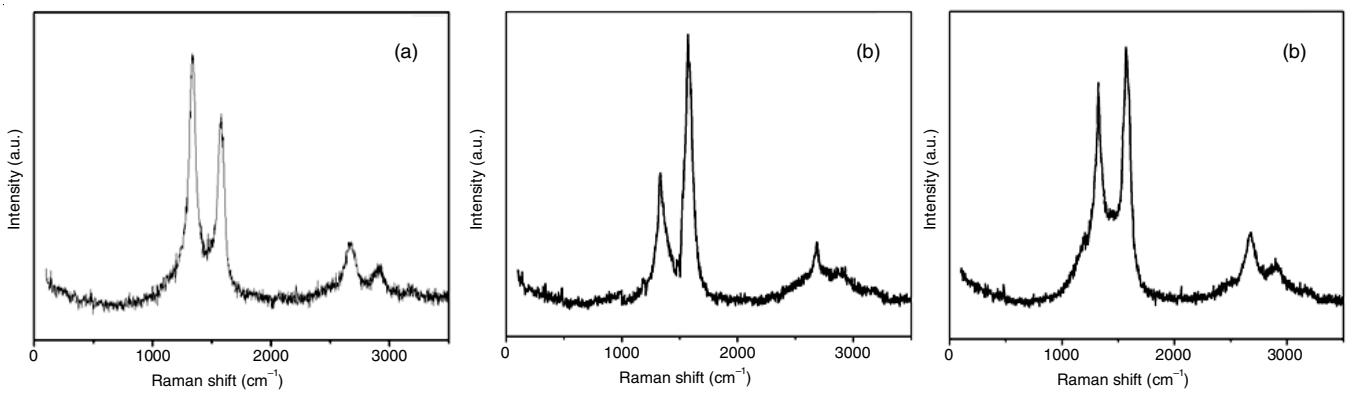

Fig. 3. Raman scattering spectrum for the carbon deposit obtained over silica supported Fe-Co-Ni catalyst at 550, 650 and 750 °C using natural precursor pine oil for the precursor flow rate 20 mL h^{-1}

Increasing temperature to higher level (750 ºC) do not produce well crystallized graphitic structure due to higher the rate of precursor pyrolysis to growth of carbon nanotubes. Radial breathing mode (RBM) of carbon nanotubes is normally observed for single walled carbon nanotubes at lower frequency region (100-400 nm). In RBM mode, all the carbon atoms in a carbon nanotube structure move in the radial direction to the length of the tube synchronously, similar to breathing. The RBM modes are not present in multi-walled carbon nanotubes because the multilayer of tube restrict the breathing mode. Absence of RBM frequency peak indicates absence of single walled carbon nanotubes in the carbon deposit. The general observation is higher temperature favours formation of single walled carbon nanotubes, when small organic molecules are used as precursor. Under the experimental conditions, precursor of larger hydrocarbon, the pine oil, results in formation of multi-walled carbon nanotubes rather than single-walled carbon nanotubes [15]. This is also confirmed with SEM analysis.

Thermal studies: Thermogravimetric analysis is used to characterize the carbon deposit for the existence and population of crystallized carbon nanotubes, amorphous carbon, residual metal catalyst and support. The thermogravimetric results of the carbon deposits obtained at 550, 650 and 750 ºC are shown in Fig. 4. The catalyst and support residue after 800 ºC and the temperature range in which carbon nanotubes decompose for each carbon deposits prepared are calculated. These values provide an idea to ascertain crystalline nature of carbon nanotubes, amorphous carbon presence and residual catalysts in the carbon sample [16]. It is clear from the TGA studies of as-deposited carbon that the residual catalyst quantity (64.3%) is high for the carbon deposit obtained at 550 ºC. The percentage residual catalyst (14.7%) is reduced for the carbon deposit obtained at 650 ºC, whereas, the residue value (47.2 %) increases when temperature (750 ºC) is increased. These facts coincide with the yield of carbon deposits obtained. Low residual catalyst is observed for the high yield condition (650 ºC) where, the population of carbon is high in the deposit.

The oxidative decomposition temperature of carbon is related to the nature of carbon allotropes and catalysts present in the carbon deposit. Raman spectroscopic analysis, through its low I_G/I_D ratio, indicated that carbon deposits obtained at 550 ºC and 750 ºC have mixture of amorphous and defective carbon layers or any one of them. Thermal analysis is used to identify more clearly the existence and population of amorphous carbon as well as carbon nanotubes in the carbon deposit. The oxidative decomposition temperature is related with the thermal stability of carbon nanotubes. The thermal stability of the carbon allotrope is linked with the aromatic nature of carbon, number of walls or layers of carbon nanotubes, nature of catalysts and support material present with it [17]. Amorphous carbon has low thermal stability and thus gets oxidized at lower temperature itself, whereas, multi-walled carbon nanotubes oxidize relatively at higher temperature. The carbon deposit obtained at 550 ºC shows that weight loss initiated around 337 ºC and accelerated around 400 ºC indicates that it contains amorphous carbon (12%). The multi-walled carbon nanotubes present (32%) in the deposit obtained at 550 ºC undergo oxidative decomposition around 550 ºC. The thermogravimetric curve of carbon deposit obtained at 650 ºC (Fig. 4c) shows beginning of weight loss at relatively higher temperature (585 ºC) compare to that of deposit obtained at 550 °C. This indicates presence of multi-walled carbon nanotubes at higher popul-ation in the deposit obtained at 650 ºC. The quantity of multi-walled carbon nanotubes present in the deposit obtained at 650 ºC is 82.4% and residue is found to be 14.7%. The remaining weight loss is attributed to moisture and amorphous carbon.

It is observed that the onset weight loss, accelerated weight loss and residue attained are at 380 ºC, 420 ºC and 680 ºC respectively for the carbon deposit obtained at 750 ºC. The weight percentage of amorphous carbon, carbon nanotube and residue are found to be approximately 16%, 37% and 47.2%, respectively. It shows that the carbon deposit contains amorphous carbon as well as adhered amorphous carbon over the defective surface of multi-walled carbon nanotubes. The oxidative decomposition of carbon in to carbondioxide happens at higher temperature for multi-walled carbon nanotubes due to its aromatic character. The amorphous carbon which is not crystalline also possess poor aromatic character, decomposed through oxidation at lower temperature itself.

The purity in terms of carbon allotropes is obtained from the derivative curves. The weight loss and derivative curves of the carbon deposits are shown in Fig. 4. Two peaks are observed for carbon deposits obtained at 550 and 750 ºC while single peak for the deposit obtained at 650 ºC. This shows that carbon deposit obtained at 650 ºC contains multi-walled carbon nanotubes in larger quantity with very less amorphous carbon. These results are coinciding with the Raman and SEM studies of these deposits.

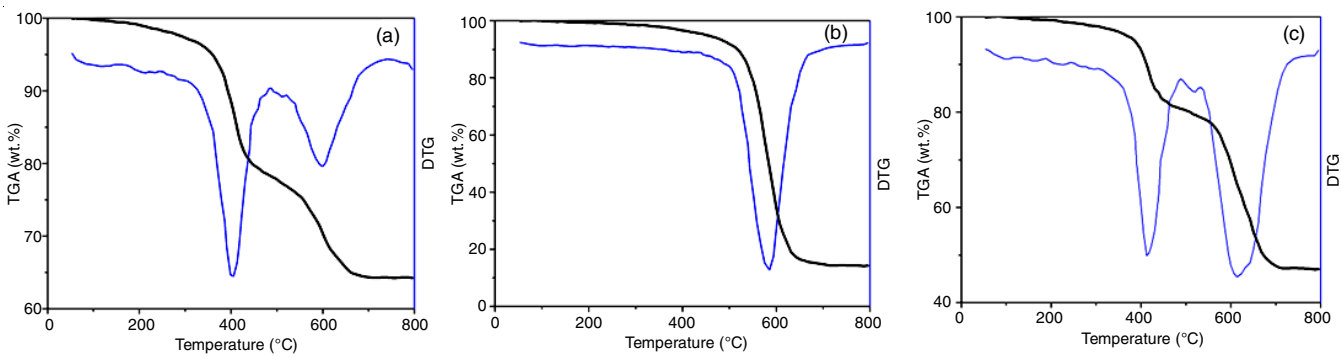

Fig. 4. Thermogravimetric results of the carbon deposits obtained at (a) 550 °C, (b) 650 °C and (c) 750 °C

Conclusion

Narrow and long carbon nanotubes can be prepared along gravity direction in a spray pyrolysis setup over the silica supported Fe-Co-Ni catalyst using plant based natural precursor pine oil. The effect of temperature on yield and morphology of carbon nanotubes grown along gravity is studied. The optimum temperature for pyrolysis of pine oil to produce carbon nanotubes is found to be 650 ºC when other reaction parameters are at optimum condition. The characterization of carbon nanotubes using XRD, SEM, Raman and TGA techniques shows that the carbon nanotubes formed were narrow, long and well graphitized multi-walled type.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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