

Role of Metal Catalyst and Substrate Site for the Growth of Carbon Nanomaterials

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Abstract

The work reported in this paper relates to preparation and characterization of carbon nanomaterials by CVD method on different substrates by decomposition of certain hydrocarbons at 550-800°C using a horizontal quartz tube reactor. Monometallic and bimetallic catalyst system of iron and nickel were used for the preparation of different carbon nanomaterials. The influence of various parameters such as substrate/catalyst preparation parameters, the nature of substrate, catalyst concentration, reaction time and temperature on the growth, yield and alignment of carbon nanotubes has been studied. The characterization of carbon nanomaterials has been carried out using SEM, TEM and TGA. The carbon nanomaterials developed were vertically aligned on a large area of flat quartz substrate.

Keywords : Carbon nanomaterials, Chemical vapour deposition, Hydrocarbons, Catalytic growth, TEM

1. Introduction

Carbon nanomaterials exist in various forms, as layered materials, nanospheres, nanofibers and nanotubes. Carbon nanotubes have attracted much interest since their discovery in 1991 by Iijima [1]. These have become one of the most exciting materials to emerge from recent scientific research mainly because of their unique electrical as well as mechanical properties [2-4] and potential applications in electronic devices [5], nanotechnology tools [6, 7] and novel nanoscale materials [8, 9]. Various methods have been explored to produce nanostructured carbon materials. Carbon nanomaterials are synthesized using arc-discharge, laser evaporation, chemical vapour deposition and plasma-enhanced CVD methods [10-13]. Amongst all these methods, catalytic chemical vapour deposition method promises to be simple, more controllable and suitable for large-scale production of CNTs since sufficient expertise is available for production of carbon materials using CVD. Catalytic chemical vapour deposition uses transition metals such as Fe, Co, Ni and Cr as active catalyst to catalyze the formation of carbon nanomaterials on the surface of suitable substrates using appropriate carbon source. In fact, catalytic activity of a metal-support system depends on a variety of factors ranging from the size and dispersion of the metal catalyst to chemical composition of vapour as well as on the crystalline phase of the support materials itself. Several studies have been focused on the control of MWNTs growth by the introduction of monometallic and bimetallic catalyst nanoparticles, using carrier gas, in to the reaction chamber under

decomposition of ethylene, methane, ethane and solid carbon [14-17]. In bimetallic systems the introduction of another highly active metal species (e.g. nickel) may increase the activity and stability of the iron based catalyst [18]. Though, a good number of papers have been published on the growth of carbon nanotubes and correlation with processing parameters, these have been studied in isolation or mainly deal with type and structure of carbon nanotubes.

This paper describes the effect of various processing parameters such as substrate/catalyst combined effect, the nature of substrate, catalyst concentration, reaction time and temperature on nanomaterials production.

2. Experimental

2.1. Materials used

Different types of carbon sources, catalyst and substrates were used for the growth of carbon nanomaterials. Carbon sources used were xylene, benzene, pyridine, methanol and acetylene while ferrocene, iron, cobalt and nickel were used as catalyst. Cobalt and Nickel were used as solid particles on the substrate while ferrocene was used in the solution form. Fe/Ni based bimetallic complex was calcined at 450°C and then used as catalyst medium. Quartz and nickel were used as rectangular plates to find out the effect on the growth of different carbon nanostructures.

2.2. Description of the CVD apparatus

The experimental setup used for the preparation of the

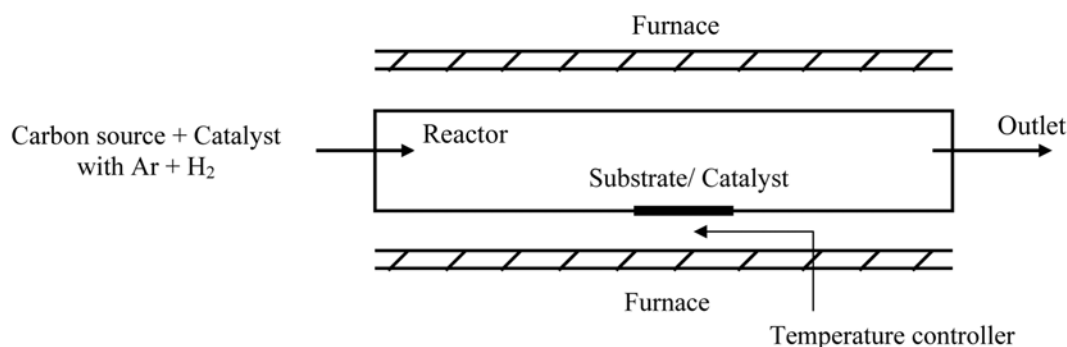


Fig. 1. The schematic diagram of experimental set-up used for the preparation of carbon nanomaterials by CVD method.

carbon nanomaterials is schematically shown in Fig. 1. The reactor is made of 550 mm long quartz tube of 35 mm inner diameter with provisions of inlet of reactants and outlet of spent vapours. The reactor is placed in a tubular electrical furnace. The substrates are placed in pyrolysis zone of the horizontal quartz reactor.

2.3. Carbon nanofibers/tubes from liquid hydrocarbons

For development of carbon nanofibers, methanol vapour were used as carbon source with argon as carrier. In this case the reaction temperature was varied between 550-800 °C.

For development of carbon nanotubes, ferrocene-xylene/benzene/pyridine solutions were used as precursors with quartz as a substrate, while with metallic substrates xylene alone and ferrocene-xylene solutions were used. The temperature of pyrolysis zone was kept at 700-800 °C. On attainment of the temperature, the gas mixture of argon and hydrogen was introduced into the quartz reactor. The carbon source with or without catalyst solution (ferrocene) was then injected (injection feed rate 0.2-0.5 ml/min) in the reactor by syringe pump for different reaction time (15-60 min). After the reaction, the furnace was allowed to cool under argon atmosphere. All substrates, used in these studies were weighed before and after the reaction to determine the amount of carbon produced.

2.4. Characterization of carbon nanomaterials

The samples were viewed under Scanning Electron microscope (SEM) Hitachi S-3000N to ascertain formation of ultra thin elongated structures (fibers or tubes). Transmission electron microscope (TEM) Philips, Tecnai-20 was used to examine the tubular nature of the samples. TGA of carbon materials was carried out on Mettler Thermal Analysis system TA 4000 with TG50 for getting information about amount of catalyst present in the product and also to study oxidation behaviour of carbon nanotubes. TGA of carbon materials was carried out in presence of zero air at flow rate of 200 cc/min and heating rate up to 900 °C.

3. Results and Discussion

3.1. Carbon nanofibers through thermal decomposition of alcohol

Fig. 2 shows the SEM image of carbon nanofibers grown by decomposition of methanol on Fe:Ni (5:5) based catalyst at 700 °C under argon and hydrogen atmosphere. It shows that carbon nanofibers are randomly grown on the surface of catalyst. The nanofibers are of about 100 nm diameter and about 10 to 20 μm length.

Thermogravimetric study on carbon nanomaterials gives information on thermal stability of carbon nanomaterials, which can also be indicative of structure of nanomaterials. Since carbon materials with different microstructure start oxidizing at different temperatures. Fig. 3 shows TGA graph of carbon nanofibers obtained from methanol. Nanofibers prepared on Fe:Ni (5:5) based catalyst at 550 °C (MFeNi550) exhibit lower oxidation initiation temperature, thereby indicating that these nanofibers have lower thermal stability as compared to fibers prepared on Fe:Ni (5:5) based catalyst at 800 °C (MFeNi800). It is known that unorganized carbon exhibit oxidation at lower temperatures than organized carbon. Therefore, from Fig. 3 it can be inferred that nanofibers prepared at higher temperatures have better oriented

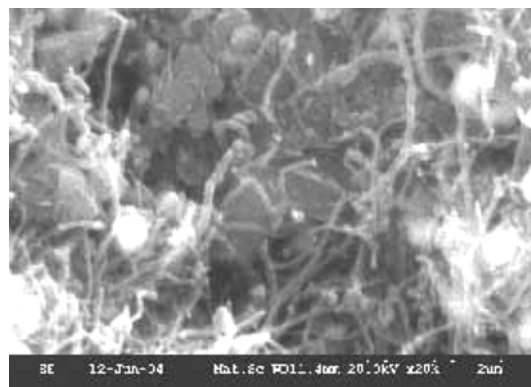


Fig. 2. SEM images of as produced nanocarbon from methanol with Fe/Ni(5:5) based catalyst at 700 °C.

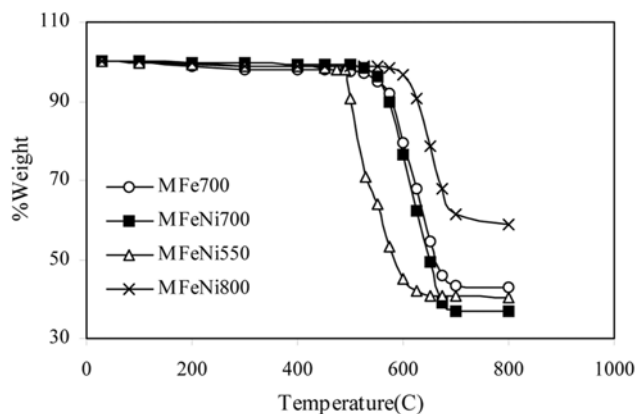


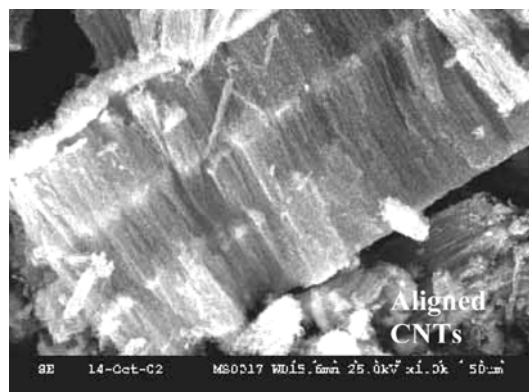
Fig. 3. TGA graph of as produced nanocarbon from methanol with Fe/Ni based catalyst.

structure than those prepared at lower temperatures. On comparing the TGA curves of the samples prepared at 550 °C (MFeNi550), 700 °C (MFeNi700) and 800 °C (MFeNi800), it is found that the residue is maximum for sample prepared at 800 °C as compared to those made at 700 °C and 550 °C. On taking weight loss as the measure of formation of carbon materials (organized and unorganized), it can be inferred that formation of carbons increase with increase in temperature from 550 °C to 700 °C. The carbon yield is found to be lower at 800 °C, thereby meaning that around 700 °C may be the optimum temperature for formation of carbon nanomaterials with methanol as carbon source. Higher oxidation initiation temperature for samples made at 800 °C indicates formation of more organized carbon at higher temperatures. Further, on comparing the TGA graph of the samples prepared at 700 °C on Fe and FeNi as catalyst, it is noticed that bimetallic system (MFeNi700) gives higher carbon growth as compared to single metallic system (MFe700). This again could be enhanced catalytic effectiveness of bimetallic system.

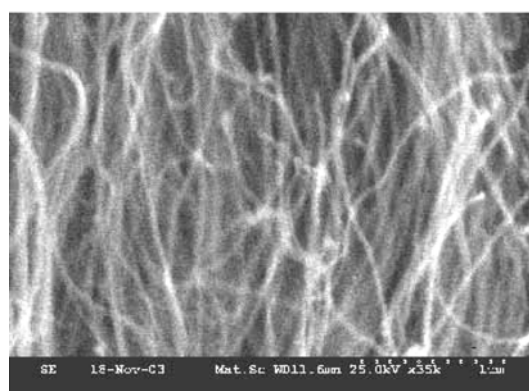
3.2. Carbon nanotubes through thermal decomposition of hydrocarbons

Amongst liquid hydrocarbons, xylene, benzene and pyridine are preferable carbon sources and ferrocene as catalyst for the nanotube formation. Scanning electron microscopy was carried out for carbon nanomaterials obtained through decomposition of hydrocarbons (in the temperature range 700-800 °C) in presence of ferrocene as catalyst over quartz substrate. These nanomaterials are found to be bunch of aligned carbon nanotubes originating from the surface of the substrate. Since the reactor is made up of quartz tube, its inner walls also provided growth sites for aligned CNT arrays. The aligned nanotube arrays deposited on quartz could easily be peeled off from the quartz surface without destroying the arrays integrity.

Fig. 4a shows peeled off arrays of carbon nanotubes made



(a)



(b)

Fig. 4. SEM images of as produced nanocarbon on quartz from (a) 1 wt% ferrocene-xylene mixture and (b) 1 wt% ferrocene-benzene mixture at 800 °C.

from 1 wt% ferrocene-xylene solution at 800 °C on quartz substrate. These layers of CNTs have well defined morphology and all the tubes are almost of same height (more than 50 μm). Fig. 4b shows SEM micrograph at higher magnification of carbon nanotubes made from 1 wt% ferrocene-benzene solution at 800 °C on quartz substrate. It shows aligned nature of the tubes. These aligned carbon nanotubes have a diameter around 100 nm.

Fig. 5 shows effect of quantity of hydrocarbon solution (1 wt% ferrocene in xylene) and solution feed rate on carbon deposition at 800 °C. As seen in Fig. 5 for same feeding rate, i.e. 0.5 ml/min, CNTs deposition increases with feeding time, i.e. with total amount of solution. Further, the deposition is found to be higher for higher feed rate. 15 ml of solution injected at rate of 0.5 ml/min gave higher carbon yield than 20 ml of solution injected at rate of 0.3 ml/min. The continuous feeding method secures the continuous supply of Fe catalyst particles and carbon source during the continuous growth process of aligned carbon nanotubes. These trapped particles may maintain a rapid continuous growth of carbon nanotubes. So, higher feed rate gives better

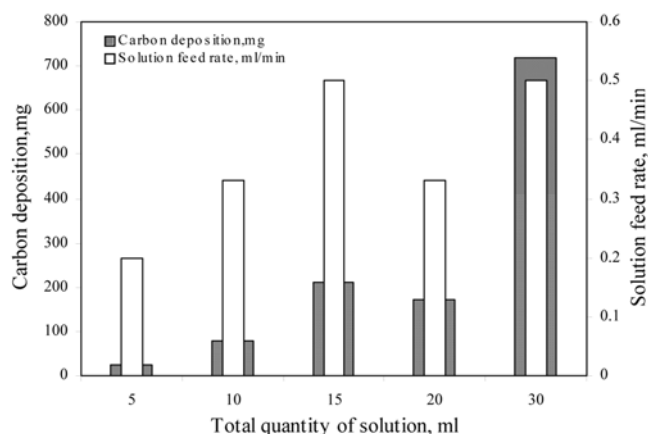
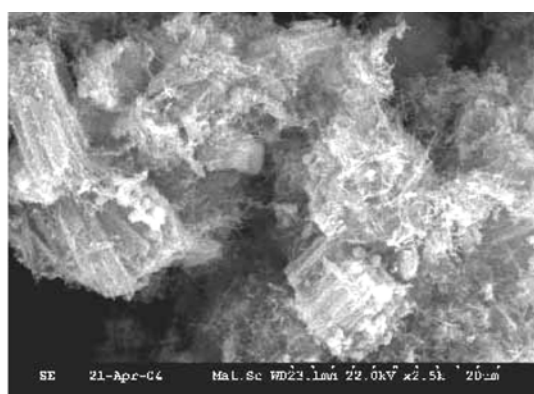
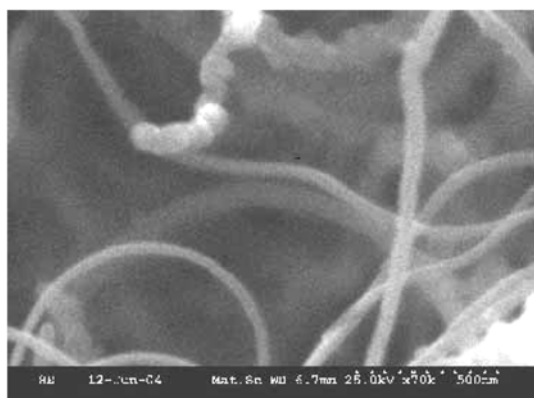


Fig. 5. Effect of quantity of hydrocarbon solution (1 wt% ferrocene in xylene) and solution feed rate on carbon deposition.



(a)

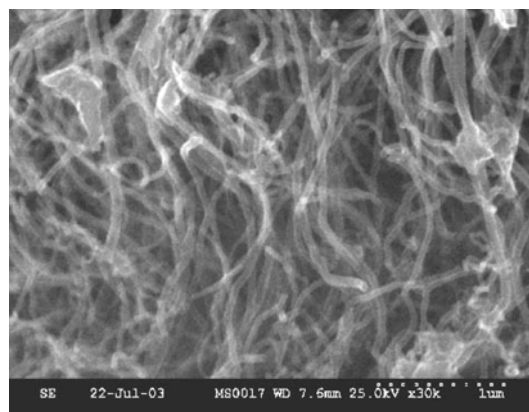


(b)

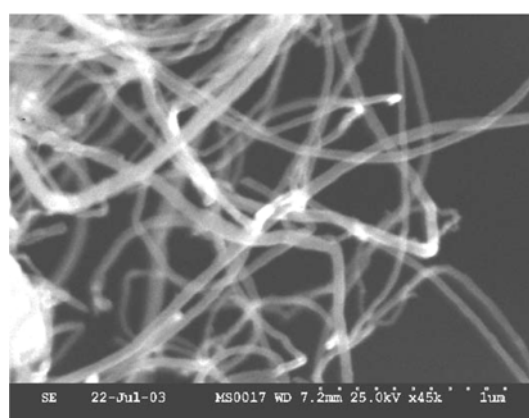
Fig. 6. SEM images of as produced nanocarbon on quartz from 1 wt% ferrocene-pyridine mixture at 800 °C.

results and provides higher growth rate of carbon nanotubes.

Pyridine is widely used precursor for preparation of N-doped carbon nanotubes. In this study, 1 wt% ferrocene-pyridine solution was decomposed at 800 °C on quartz. Fig. 6(a, b) show the SEM micrographs of carbon nanotubes prepared from decomposition of pyridine. It shows bundles



(a)



(b)

Fig. 7. Randomly oriented carbon nanotubes growth on Nickel plate from (a) only xylene and (b) 1 wt% ferrocene-xylene mixture at 800 °C.

of aligned CNTs with diameter less than 100 nm and more than 8 μm length.

To study the combined effect of substrate and catalysts on the growth of nanotubes, systematic experiments were carried out using nickel plate alone or metal balls (containing nickel and cobalt) as metallic substrates. The carbon nanomaterials were obtained through decomposition of only xylene in one set of experiments and solution of xylene and ferrocene in the second set of experiments. Fig. 7a shows carbon nanotube growth on nickel plate from xylene alone and Fig. 7b shows the carbon nanotubes growth on nickel plate from 1 wt% ferrocene-xylene mixture. Carbon nanotubes with diameter less than 100 nm were obtained in case of nickel plate as a substrate. Here one finds that, growth of carbon nanotube is in random fashion. It means that the chemistry and textural properties of supported catalyst and the types of carbon source may affect the tubular structures. Fig. 8 shows the comparative amount of carbon nanomaterials grown on Ni and Ni-Co based substrates from solution containing varying amount of ferrocene catalyst. As seen from the Fig. 8, the growth of carbon nanomaterials is

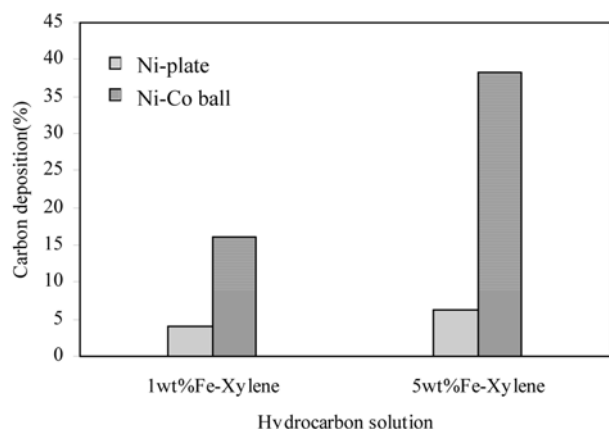


Fig. 8. Effect of catalyst concentration on the carbon deposition.

higher for Ni-Co substrate than on Ni plate. Further, the increase in concentration of ferrocene from 1 wt% to 5 wt% provides abundant Fe particles for the growth of carbon nanotubes. Therefore, the carbon deposition in case of 5 wt% ferrocene-xylene solution is higher on both the substrates under similar reaction conditions. The growth of nanotubes was found to depend on the composition of solution with supported catalyst as well as the types of substrate.

The nanotube arrays could be easily peeled off from the substrate surface without destroying the arrays integrity. Carbon nanotubes grown on two different substrates (quartz and nickel plate) under similar process conditions (30 min deposition time with 15 ml of 1 wt% ferrocene-xylene solution) were found to have distinct features. The growth density of carbon nanotubes per unit area of both the substrates are shown in Fig. 9. The nanotubes growth density on nickel substrate is found to be higher than that on quartz. Moreover, the nanotubes grown on nickel substrate are

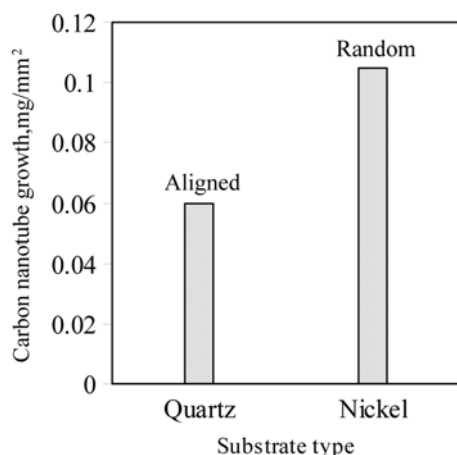
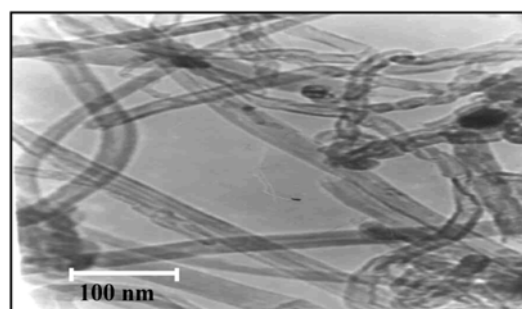
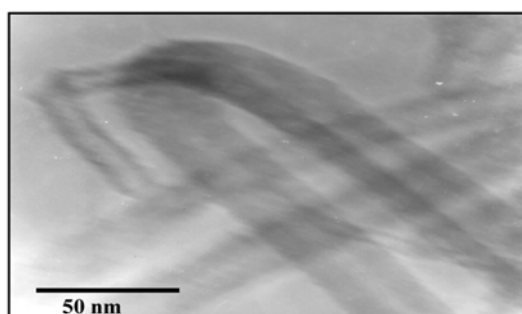


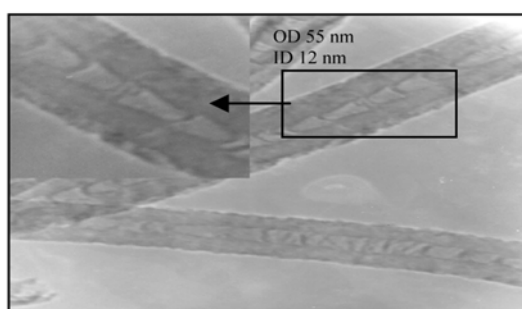
Fig. 9. Carbon nanotube growth from 1 wt% ferrocene-xylene solution on two different (ceramic and metallic) substrates at 800 °C.



(a)



(b)



(c)

Fig. 10. TEM images of as produced nanocarbon from (a) 1 wt% ferrocene-xylene mixture (b, c) 1 wt% ferrocene-pyridine mixture at 800 °C.

randomly oriented (Fig. 7b). The nanotube grown on quartz substrates is found to be aligned (Fig. 4a). This suggests that nickel (metallic) substrate enhances carbon nanotube deposition but disturbs the orientation of tubes.

3.3. Transmission electron microscopy of carbon nanotubes

Fig. 10a shows the TEM micrograph of carbon nanotubes produced from xylene-ferrocene mixture decomposed at 800 °C. The carbon nanotubes in the arrays are found to be clean with uniform diameter of about 25-65 nm.

Fig. 10b & c show TEM micrographs of carbon nanotubes prepared from pyridine-ferrocene solution. These show that CNTs prepared from pyridine-ferrocene decomposition are bamboo shaped as well as some CNTs have simple tubular

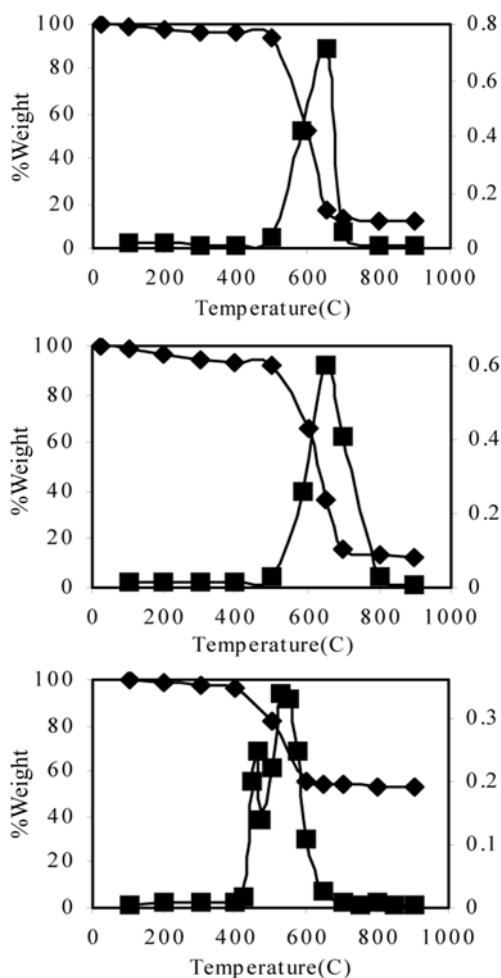


Fig. 11. TGA graph of as produced nanocarbon from (a) xylene (b) benzene and (c) pyridine with 1 wt% ferrocene at 800 °C.

(hollow core) structure. It also shows small diameter nanotube attached with another nanotube. On an average, the outer diameter of the nanotube is around 55 nm while ID is 12 nm.

3.4. Thermal stability of carbon nanotubes

Thermogravimetric analysis studies were performed on as-prepared carbon nanotubes from different carbonaceous precursors. Xylene-based carbon nanotubes (Fig. 11a) and benzene-based carbon nanotubes (Fig. 11b) exhibit higher oxidation onset temperature (500 °C i.e. more thermally stable) than pyridine-based carbon nanotubes (Fig. 11c). It shows that the thermal stability and hence the structure (organized and unorganized) of carbon nanomaterials depend on the carbonaceous precursors though processed under same reaction conditions. Xylene and benzene have more no. of carbon in its structure and can easily decompose under suitable reaction conditions and convert in to organized carbon. But pyridine has nitrogen in its structure and after

decomposition it gives carbon with small amount of nitrogen. The differential thermograms (dw/dt curve) of carbon produced from xylene and benzene indicate one peak whereas two peaks are observed in pyridine based carbon. It indicates unstability of nitrogen in the structure. Further it can be inferred that chemical structure of carbon precursors play major role on the structure and hence thermal behaviour of resultant carbon nanomaterials.

4. Conclusion

Carbon nanomaterials are formed whenever carbon containing precursors impinge on a hot surface containing iron/nickel, heated to temperature of 550-800 °C. Metallic complex catalyst system shows enhanced and random growth of carbon nanotubes. The CVD method provides the basis for synthesis of aligned CNTs on suitable substrate like quartz. The length and diameter of the carbon nanotubes were found to be dependant on reaction time, type of carbonaceous precursor and amount of catalyst present in the carbon precursor. Studies on different metallic substrates revealed that carbon deposition depend on the substrate type and reaction parameters. Growth morphology is mainly depended on the catalyst type under same reaction conditions. The use of different substrates provides choice of selection for producing aligned and random nanofibers/tubes.

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