Synthesis and Characterization of Carbon Nanotubes by Catalytic Decomposition of Acetylene with Co/Zn/Al, Co/Fe/Mg and $(C_5H_7O_2)_3Mn$/Al as Catalysts

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ABSTRACT

We report our studies of the effect of various catalysts in the synthesis of carbon nanomaterials. The as-prepared carbon nanomaterials were characterized by Raman spectroscopy, Scanning electron microscopy, high resolution transmission electron microscopy and X-ray diffraction. The catalysts Co/Fe/MgO and Co/Zn/Al produced cylindrical carbon nanotubes while tris(acetylacetonato) manganese produced carbon nanospheres in a catalytic chemical vapor decomposition chamber.

Keywords: Carbon nanotube, Carbon nanospheres, Catalyst, Co/Zn/Al, Co/Fe/Mg, $Mn(C_5H_7O_2)_3$/Al

1 INTRODUCTION

The ability of carbon to hybridize into forming *sp, sp^2 and sp^3* bonds [1] results in the formation of structures such as carbon nanotubes (CNT) [2-5], fullerenes [6], nanofibers [7-10] and carbon nanospheres (CNS) among other structures [11-13]. Carbon nanospheres have a semi-crystalline structure which is a reflection of their unique properties of low density, high porosity, increased surface area and relatively high chemical and thermal stability [1]. The synthesis of molecular carbon structures and other fullerenes [14], has attracted enormous attention because of their unique structural, mechanical and electrical properties [2] and also because of the wide range and versatility of their potential applications [15]. The role of the catalyst is crucial to get high activity and specially selectivity towards CNT formation. Cobalt and other ferrous metals and their alloys are the active metals usually employed in the constitution of the catalyst [16,17]. During this study, cobalt and zinc supported on aluminium oxide, (Co/Zn/Al), iron and cobalt supported on magnesium oxide, (Co/Fe/Mg), and tris(2,4-pentanedionnato)manganese(III) supported on aluminium oxide, ($Mn(C_5H_7O_2)_3Al$), as catalysts have been used for the synthesis of carbon nanomaterial with ethyne (acetylene) as carbon source. Synthesized carbon nanomaterials have been characterized by Raman spectroscopy, scanning electron microscopy, transmission electron microscopy and X-ray diffraction to determine the effect of catalyst in the synthesis.

2 EXPERIMENTAL

Materials

All chemicals used in the study were of analytical grade purchased from Sigma Aldrich, South Africa and used without further purification. All solutions were prepared with deionized water. Catalytic Chemical Vapor Deposition (CCVD) reactor was obtained from Elite Thermal Systems Limited, South Africa, Mass flow meter and PowerPod 400 multichannel power supply instrument were obtained from Teledyne Hastings Instruments, USA.

Preparation of catalysts

The catalysts Co/Zn/Al and Co/Fe/Mg were prepared by co-precipitation method This was achieved by mixing aqueous solution of chlorides of the metals with an aqueous solution of sodium carbonate and sodium hydroxide at room temperature. The pH of the synthesis was kept at a constant value of pH 9 by drop wise addition of a 1 M sodium hydroxide solution from a burette. The molar ratios used were 1:1:2. The slurry obtained was dried in the oven for different periods of time (10, 30, 60 180 and 300 min) at 125^{o}C. The precipitates were then washed and dried at 40^{o}C in an open air oven. The catalyst samples were calcined at 600^{o}C in air. The final temperature was maintained for two hours. Tris(2,4-pentanedionato)manganese(III) was prepared by dissolving manganese chloride tetrahydrate 0.52 g with sodium acetate 1.4 g in 20 mL of distilled water and 2.5 mL of acetylacetone in a beaker. A solution of 6 mL of potassium permanganate was added and the reaction mixture stirred while heated. Black powder of tris(2,4-pentanedionnato)manganese(III) were obtained which were filtered, washed then dried in in a desicator over calcium chloride. Yield:71%. FTIR (neat liquid); ν/cm^{-1} 3005w, 2921 (s, aliphatic C-H stretch), 1567 (s, υC=C, δC=CH), 1505 (s, sym. ring stretch), 1386 (s, δCH_3), 1338 (w, CH_3 bending vibration), 1254 (m, υC=C, υC–CH_3), 1190 (s, δC=CH), 1012 (s, γCH_3), 923 (υC–CH_3), 773 (s, πC-H), 671 (υC–CH_3, υMn-O, δO=C-CH_3).

Preparation of carbon nanotubes

A catalytic chemical vapor deposition (CCVD) reactor was used in the synthesis. The reactor consisted of a 40 mm *o.d* x 70 cm long quartz tube heated by an electrical tube furnace with a temperature controller. Nitrogen gas flowing at 40 ml min^{-1} was passed through the reactor for approximately 70 min., after stabilization for 10 min, the nitrogen gas flow was maintained at 240 mL min^{-1}. The ethyne gas with a flow rate of 90 mL min^{-1} was then passed through the reactor for 60 min. The catalyst placed on a quartz boat was placed in the centre of the furnace during the synthesis. The flow rate of the gases was controlled by a mass flow controller (MFC). After the reaction had taken place, the reactor was cooled to room temperature with nitrogen flowing at 40 mL min^{-1} for 3 to 4 hrs. The samples obtained by this method were then characterized as described below.

Characterization

Morphological features of carbon nanomaterial were analyzed by Raman spectroscopy, FE-SEM and HR-TEM. The Raman spectra were obtained by a Raman spectroscope, Jobin-Yvon HR800 UV-VIS-NIR Raman spectrometer equipped with an Olympus BX 40 attachment. The excitation wavelength was 514.5 nm with an energy setting of 1.2 mV from a coherent Innova model 308 argon-ion laser. The Raman spectra were collected by means of back scattering geometry with an acquisition time of 50 seconds. The surface morphology, SEM, measurements were recorded with a JEOL 7500F Field Emission scanning electron microscope. The HR-TEM images of the sample were obtained by a CM 200 electron microscope operated at 100 kV. IR spectra were recorded using Perkin-Elmer Spectrum 400 FT-IR/FT-NIR spectrometer in the range 400 – 4000 cm^{-1}. UV-vis spectra were recorded on a Perkin-Elmer lambda 25 UV-vis spectrometer.

3 RESULTS AND DISCUSSION

Raman spectroscopy is a powerful tool used in the characterization of nanomaterials. [1,14-16] The Raman spectra of the as-prepared nanomaterial produced from the catalysts Co/Zn/Al, Co/Fe/Mg and $Mn(C_5H_7O_2)_3$/Al are presented in figure 1. The Raman spectra obtained show peaks corresponding to the D and G bands of carbon nanotubes. The *D*-bands are observed at 1322, 1340 and 1338 cm^{-1} while the *G*-bands are observed at 1596, 1575 and 1585 cm^{-1}. The *D*-bands are indicative of the presences surface defects and amorphous graphitic carbon while the *G*-bands indicate the presence of crystalline graphitic carbon in the as-prepared carbon nanomaterial. The purity of carbon nanotubes or carbon nanomaterial obtained in a synthesis is determined by the presence of an overtone peak due to the *D* and *G* bands which resonates at about 2600 cm^{-1}. A resonance peak is observed in figure 1(b) indicating the purity of the as-prepared nanomaterial obtained from the catalyst, Co/Fe/Mg over the other catalysts. The intensity ratio of the *D* and *G* bands (I_D/I_G), a parameter that is reminiscent of the quality of carbon nanomaterial synthesized is found to be 0.8645 for Co/Zn/Al catalyst, 0.8722 for Co/Fe/Mg catalyst and 0.9994 for

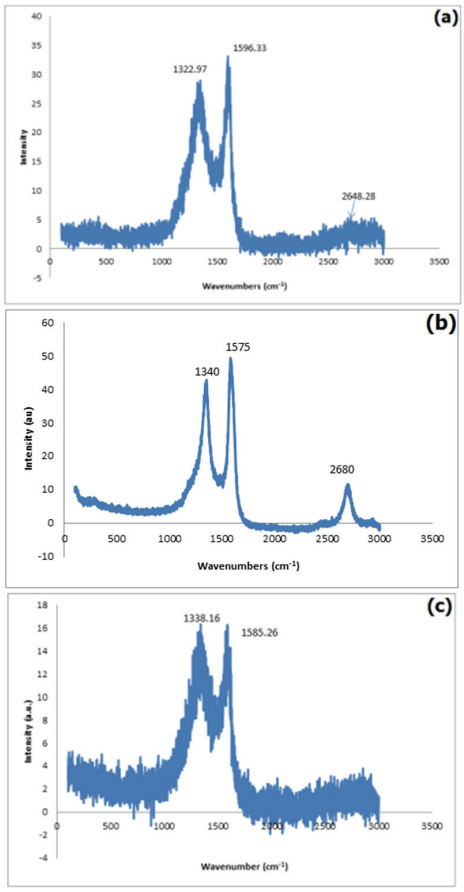

Figure 1: Raman spectra of carbon nanomaterial obtained from (a) Co/Zn/Al, (b) Co/Fe/Mg and (c) $Mn(C_5H_7O_2)_3$/Al

$Mn(C_5H_7O_2)_3$/Al catalyst. The higher the (I_D/I_G) ratio, the poorer the quality of nanomaterial synthesized. The Raman spectra presented here show a high (I_D/I_G) ratio and the absence of an overtone peak for the organometallic catalyst $Mn(C_5H_7O_2)_3$/Al, this is therefore an indication of the effect of a catalyst in synthesis.

The scanning electron micrograph of carbon nanomaterial obtained from the catalyst systems are presented in figure 2. The SEM images show cylindrical nanotubes obtained from the catalysts Co/Zn/Al and Co/Fe/Mg, figure 2(a & b), while the organometallic catalyst, $Mn(C_5H_7O_2)_3$/Al, formed carbon nanospheres, figure 2(c). Despite employing the same synthesis conditions, the effect of catalyst is seen here in the formation of different allotropes of carbon. The catalysts, Co/Zn/Al and Co/Fe/Mg, formed carbon nanotubes while the catalyst $Mn(C_5H_7O_2)_3$/Al formed carbon nanospheres.

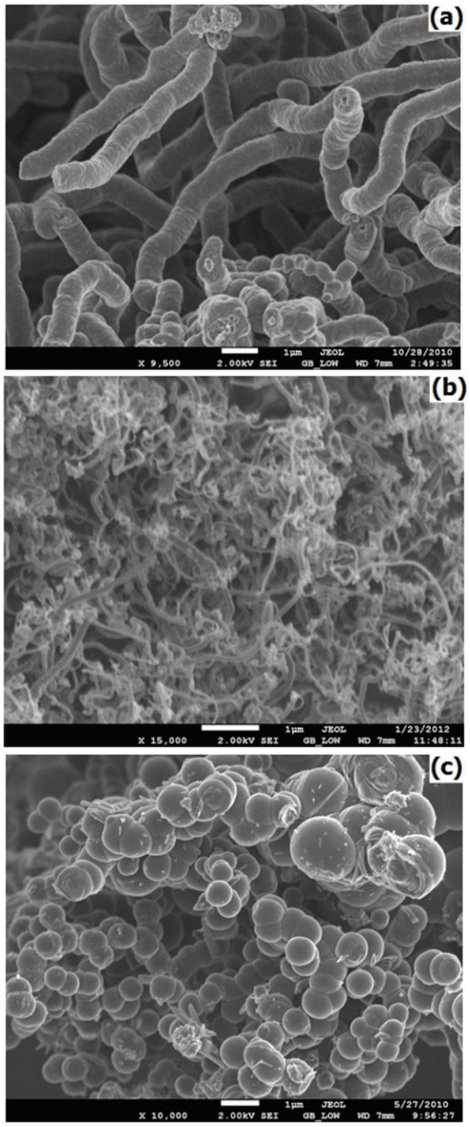

Figure 2: Scanning electron micrograph of carbon nanomaterial obtained from (a) Co/Zn/Al, (b) Co/Fe/Mg and (c) $Mn(C_5H_7O_2)_3$/Al

The use of an organometallic catalyst, such as bis(acetylacetonato) oxovanadium(IV), $VO(acac)_2$, is repored to also produced carbon nanosphere [1].

High resolution transmission electron micrograph of carbon nanomaterial obtained from the catalysts system catalysts Co/Zn/Al, Co/Fe/Mg and $Mn(C_5H_7O_2)_3$/Al are presented in figure 3. Figure 3 (a & b) show cylindrical carbon nanotubes while figure 3(c) show a spherical carbon nanomaterial confirming the SEM observation of carbon nanotubes and carbon nanospheres formed in the synthesis.

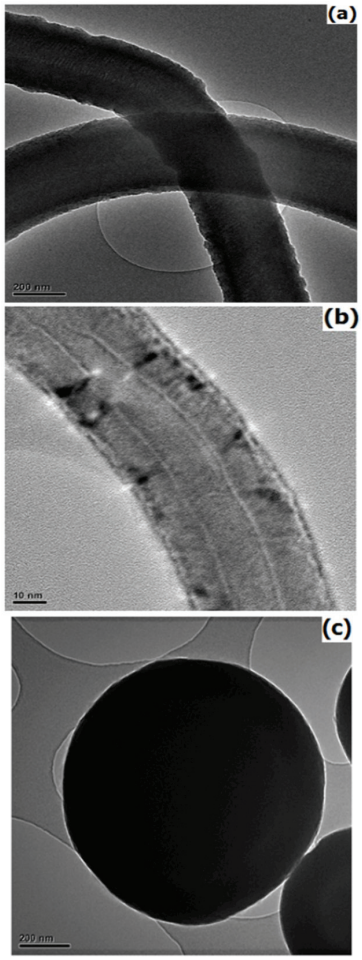

Figure 3: Transmission electron micrograph of carbon nanomaterial obtained from (a) Co/Zn/Al, (b) Co/Fe/Mg and (c) $Mn(C_5H_7O_2)_3$/Al

In figure 3(b), the image shows the carbon nanomaterial as a hollow tube of several graphitic layers.

The X-ray diffraction diffractograms of nanomaterial synthesized with the catalyst catalysts Co/Zn/Al, Co/Fe/Mg and $Mn(C_5H_7O_2)_3$/Al are presented in figure 4. XRD is an effective method to investigate the interlayer changes and the crystalline properties of a synthesized material. The XRD diffractograms show similar XRD patterns for the catalysts Co/Zn/Al, and Co/Fe/Mg, figure 4 (a and b), with differences observed in the pattern with the catalyst $Mn(C_5H_7O_2)_3$/Al. Bragg diffraction peaks are observed at $2\theta = 25.97^o$, 36.15^o, and 43.80^o for Co/Zn/Al and at $2\theta = 25.97^o$, 35.27^o, 42.57^o and 44.46^o for Co/Fe/Mg and at $2\theta = 24.87^o$, 35.08^o, 40.70^o, 42.46^o, and 58.82^o for $Mn(C_5H_7O_2)_3$/Al. The strongest peak at $2\theta = 25.97^o$ and 26.00^o correspond to hexagonal graphite lattice of multiwalled carbon nanotubes. The low intensity peaks at $2\theta = 25.76^o$, 25.97^o and 24.87^o in the difractograms corresponds to hexagonal graphite lattice of carbon nanomaterial. The low intensity peaks at $2\theta = 36.21^o$, 35.27^o

and 35.08° indicate the presence of low quality carbon nanomaterial.

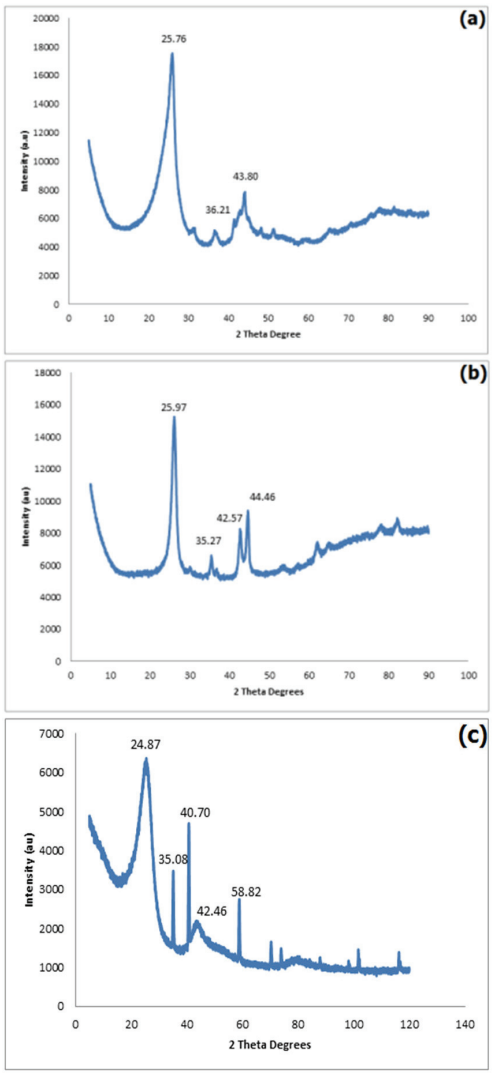

Figure 4: X-ray diffractograms of carbon nanomaterial obtained from (a) Co/Zn/Al, (b) Co/Fe/Mg and (c) $Mn(C_5H_7O_2)_3$/Al

4 CONCLUSIONS

In summary, the analyses we have presented here show the results that were obtained when different metal combinations were employed as catalyst for the synthesis of carbon nanomaterials. The organometallic catalyst, tris(2,4-pentanedionnato)manganese(III), $Mn(C_5H_7O_2)_3$/Al, formed carbon nanospheres as confirmed in the scanning electron and transmission electron micrographs while the inorganic metal catalysts, cobalt-zinc and cobalt-iron supported on aluminium oxide and magnesium oxide respectively formed cylindrical carbon nanotubes.

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