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SYNTHESIS OF CNTS VIA CHEMICAL VAPOR DEPOSITION OF ACETYLENE AS A CARBON SOURCE IN THE PRESENCE OF CO-MO/MGO CATALYST

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Abstract

Carbon nanotubes were synthesized via the chemical vapor deposition (CVD) method, using Co-Mo/MgO as a catalyst and C_2H_2, abundant and economical carbon source. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM), along with the results from xray diffraction (XRD) analysis confirmed the successful formation of MWNTs. The bimetallic catalyst was found to produce MWCNTs of 218 % with BET surface area of 289m^2/g. The average length and diameter were found to be 33µm and 32nm. The study has demonstrated that high quality MWNTs can be obtained from Co-Mo/MgO catalyst via wet impregnation followed by CVD technique.

Keywords:- Chemical Vapour Deposition, Acetylene, Co-Mo/Mgo Catalyst

INTRODUCTION

Since its discovery in 1991, Carbon nanotubes (CNT) has attracted huge research interest globally. Its unique physical and chemical properties leads numerous number of its applications such as additives for high-strength polymer composites, electrode materials for high-capacity batteries, efficient field-emitters as electron sources, and functional components for nanoscale electronic devices (Thess *et al.,* 1996). Carbon nanotubes can be seen as a single or multi-layered piece of curly and geometric seamless graphite tube. Experiments revealed that it has high elastic modulus, up to 1000 GN/m^2 (modulus of elasticity of diamond is 1200 GN/m^2) and strength in the order of 100 GN/m^2. Different methods of synthesizing CNTs such as laser ablation, spray pyrolysis, arc discharge and catalytic chemical vapour deposition (CVD) have been reported in literatures (Yerima *et al.,* 2016). However, of all the methods, CVD is considered rather simple, easy to scale up and a cost-effective technique in terms of production of carbon nanotubes of high quality yield and purity, better structural growth, and mass production compared to the other methods (Terrado *et al.,* 2006).

Over the years, there have been considerable increases in the utilization CVD techniques for CNT synthesis based on the aforementioned advantages. The choice of metallic catalyst with or without support materials influences the yield and morphology of synthesized carbon nanotubes. Not only that the mechanism of CNT growth is complex and not fully understood (Kumar, 2012).It is also noteworthy to mention that, catalyst design, catalyst type, support material as well as their properties are integral components in the synthesis of controlled-growth of carbon nanotubes (CNTs) for various applications (Mhlanga *et al.*, 2009). The role of catalyst support in supported-catalyst lies in its ability to determine accessibility of active sites, and to influence certain properties such as the pore volume and pore-size distribution which are essential parameters in catalyst design. Thus, the efficiency of the CVD method for CNT growth is a function of catalysts preparation and metals loading (Terredo *et al.*, 2006).

Transition metals consisting of Fe, Co, Ni, either in single or mixtures of them is generally used as a catalyst that acts as the active components. To increase its mechanical strength and specific surface area, the catalyst was deposited on porous media such as MgO, Al2O3, SiO2, CaCO3, which acts as a catalyst support (Jeong *et al.*, 2010). It has been revealed that the metal is used and its loading, reaction temperature, and catalyst support are the variable which is considered controlling the quality (diameter, thickness, the degree of graphitization, purity) and yield of CNT (Tang *et al.*, 2001). Moreover, both of quality and yield were also influenced by the diameter of the metal and the degree of dispersion (Jeong *et al.*, 2010). Observation has proved that the catalyst performance could be improved drastically by mixing two or more metal. Besides improving the quality of the resulting CNT, this action will also reduce the reaction temperature (Dupuis, 2005)

One of the requirements of a good support material is easily separated from the product CNT. In this case, MgO was considered superior to others because it can be removed by a simple acid treatment (Ago, 2011). It was also reported that the use of MgO-supported Fe has shown excellent performance. The strong interaction between the MgO support and the metal which resulted in the good dispersion of the metal catalyst was considered to be the determining factor.

The addition of Molybdenum could enhance the synergism among the mixture of Fe or Co metal catalyst. The role of Mo would be as a promoter or activator which will improve the catalyst performance in term of increasing the yield and produce better CNT morphology (Dupuis, 2005; Perez *et al.*, 2005). Wei *et al.* (2008) was reported that the addition of Mo to Fe metal catalyst will prevent sintering of Fe metal catalyst, so the presence of both metals in the catalyst system will prevent rapid deactivation of the catalyst due to sintering. Several researchers have reported on the synthesis of high purity MWNT through CVD teqnique, for instance Inusa *et al.* (2013) demonstrated that SWNTs with narrow chirality and diameter distribution were synthesized through the decomposition of methane at 800 ^{0}C and 900 ^{0}C over Fe-MgO catalyst. The catalyst was prepared following wet impregnation method in which, 2wt% Fe of Fe(NO$_3$).9H-$_2$O and 0.5g of MgO were dispersed in 80ml distilled water. The slurry was dried and calcined at 120 ^{0}C and 500 ^{0}C for 12 and 4 hours respectively. Images obtained from high resolution transmission electron microscopy (HRTEM) revealed the formation of 0.8 – 2 nm diameter SWNT bundles. The carbon yield reported was however, very low ranging between 16 - 18%. This is in contrast to the results obtained by Evangelous *et al.* (2013), in an experiment where Acetylene was decomposed at intervals between 600 ^{0}C and 800 ^{0}C in presence of helium.Further investigation using thermogravimetric analysis (TGA) showed that the MWNTs were stable up to 653 ^{0}C while Xray diffractomety (XRD) results showed that the main intense peak at 2θ is 26.3^0 as compared to 26.5^0 of normal graphite.

In this study, bi-metallic (Co-Mo) catalyst supported on magnesium oxide were synthesized and utilised to prepare CNT through CVD method using acetylene as the carbon source.

Experimental Procedure

Synthesis of Bimetallic Catalyst

19.4 g and 1.19g of Cobalt II Nitrate $(Co(NO_3)2.6H_2O)$ and Ammonium Molybdate $((NH_4)6Mo_7O_{24}\ 4H_2O)$ were dissolved in 50ml of distilled water followed by addition of MgO under continuous stirring for 30 minutes. The slurry was then dried at 115 °C for 11hrs then ground into fine powder. The resulting powder was calcined at 600 °C for 2 h in air.

Synthesis of CNTs

In this study, a cylindrical tube reactor of length 1010 mm with internal and external diameter of 52 mm and 60 mm respectively and thickness of 4 mm was used. 05 g of the supported bimetallic catalyst (Co-Mo/MgO) was weighed and spread evenly on a quartz boat placed at the central part of the horizontal tube. The heating rate, temperature, gas flow rates were maintained at the desired rate. The entrapped gases in the quartz tube were expelled using nitrogen as the carrier gas at a flow rate of 30 ml/min. At a temperature of 700 0C, the flow of acetylene was released into the quartz tube of catalytic reactor at 250 ml/min for 45 min with immediate increment in the flow rate of the carrier gas (nitrogen) to 250 ml/min. As the residence time (45 minutes) of the reaction was attained, the flow of acetylene was stopped and the nitrogen gas was left flowing at 30 ml/min until the reactor cooled to room temperature. The sample was removed, weighed and analysed. The yield of the deposited carbon was therefore determined using Equation (Yeoh *et al.*, 2009; Taleshi, 2012).

$$\text{CNT yield (\%)} = \frac{M\ total - M\ catalyst}{M\ catalyst} \times 100\%$$

Thermo-Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA)

The thermal stability, compositional and percentage purity of materials were determined using TGA 4000 (PerkinElmer). Samples were analysed in nitrogen environment at a flow rate of 20 ml/min, pressure of 2.5 bars and heating rate of 10 ^{0}C/min. To a zeroed thermal balance, sample was loaded and recorded into the equipment using pyris manager software. The analysis was then initiated after constant weight was noted using the created heating profile (temperature scan). The test results were then analysed using pyris manager for proximate and compositional analysis.

High Resolution Scanning Electron Microscope (HRSEM)

The surface morphology and microstructure of the synthesised materials were characterized using Zeiss Auriga HRSEM. A small quantity of the synthesized materials was sprinkled on a sample holder and sputter coated with Au-Pd using Quorum T15OT for 5 minutes prior to analysis. The sputter coated samples was firmly attached to the carbon adhesive tape and analysed using ZeissAuriga HRSEM equipped with In-lens standard detector at 30 kV. The microscope was operated with electron high tension (EHT) of 5 kV for imaging.

X-Ray Diffraction Patterns (XRD)

The crystal phase identification of the powdered materials were performed using Bruker AXS D8 X-ray diffractometer system coupled with Cu-Kα radiation of 40 kV and a current of 40 mA. The λ for Kα was 0.1541 nm, scanning rate was 1.5 °/min, while a step width of 0.05° was used over the 2θ range value of 20 – 80 °. The crystallite size of the catalyst was calculated from the XRD data using the Scherer equation as shown (Kariim *et al.*, 2016).

$$D = \frac{K\lambda}{\beta COS\theta}$$

Where D is the particle size diameter, β is the full width at half maximum, λ is the wave length of X-ray (0.1541 nm), θ is the diffraction angle and K is the Scherer constant (0.94).

High Resolution Transmission Electron Microscope (HRTEM)

The diameters and the crystalline nature of as-produced and purified CNTs were determined by Zeiss Auriga HRTEM operated at 3950 V. Small quantity of the materials were suspended in 10 ml methanol and ultrasonicated until the particles completely dissolved. Few drops of the slurry was placed onto the holey carbon grid, dried via exposure to photo light and analysed.

Particle Size Analysis (DLS Technique)

The particle size and the hydrodynamic diameter were determined using Zetasizer Nano S at scattering angle of 173 O operating at 25^{O}C with equilibrating time of 12 secs. 1mg of the samples were dispersed in 10 ml of ethanol then transferred into a polystyrene cuvette using a syringe with 0.22 μm filter coupled to it. This was then placed in the analysis stage of the equipment for analysis.

BET Surface Area

The surface area of the developed and the alumina were determined using a BET method in Nova e-series equipment. Samples were degassed at 250 ^{O}C for 4 hrs for moisture and removal. The degassed samples were then analysed for physisorption of the adsorbate (nitrogen) by the adsorbent in liquid nitrogen environment on the on the surface.

Result and Discussion

Characterization of Catalyst

In order to establish the phases that are present in the catalyst sample, comparison were made between the peaks of its XRD pattern and those in previously reported literatures.

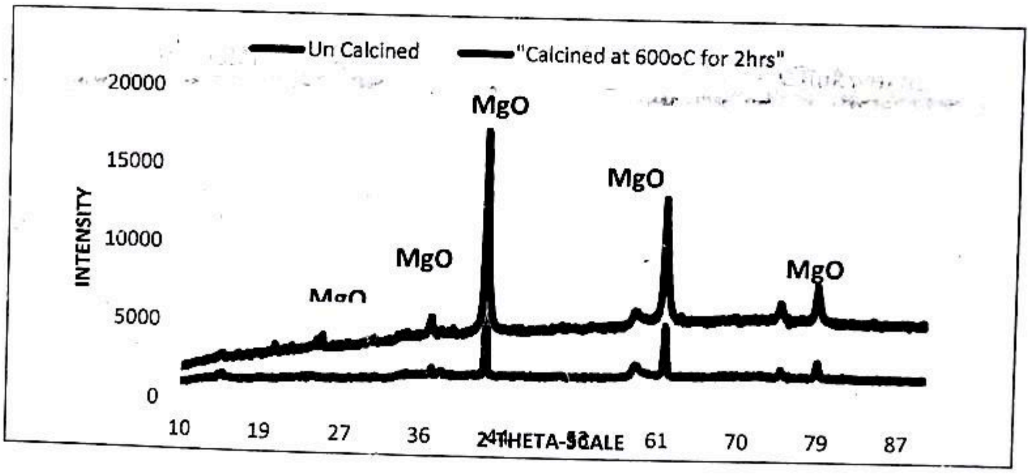

Figure 1: XRD spectra of Co-Mo/MgO catalyst

The XRD pattern in the present study (as shown in Figure 1) showed peak positions at 2θ degrees on 9, 21, 24, 26, 37, 44, 59, 62, 73 and 79° which were assigned to MgO. Setypratomo *et al.* (2015), Ahmed *et al.* (2014) and Wei-Min *et al.* (2013) also obtained a very similar peak at room temperature and attributed all to MgO phase explaining that the pattern showed mainly the presence of MgO peaks. There are no observable peaks of cobalt and Molybdenum particles. This indicate that the loading of these nanoparticles is on a small scale and were well dispersed on the surface of MgO. For this reason. The Co and Mo particles are unable to cause a Bragg reflection. The SEM images in this study also revealed that the Co-Mo nanoparticles were well dispersed on the matrix of MgO support.

The crystallite size was estimated by applying the Deby-scherrer equation (as shown above) (Kariim *et al.,* 2016) to the XRD peak broadening as presented in Figure 1. The result revealed that the bimetallic catalyst crystallite sizes ranges between 23 to 83 nm.

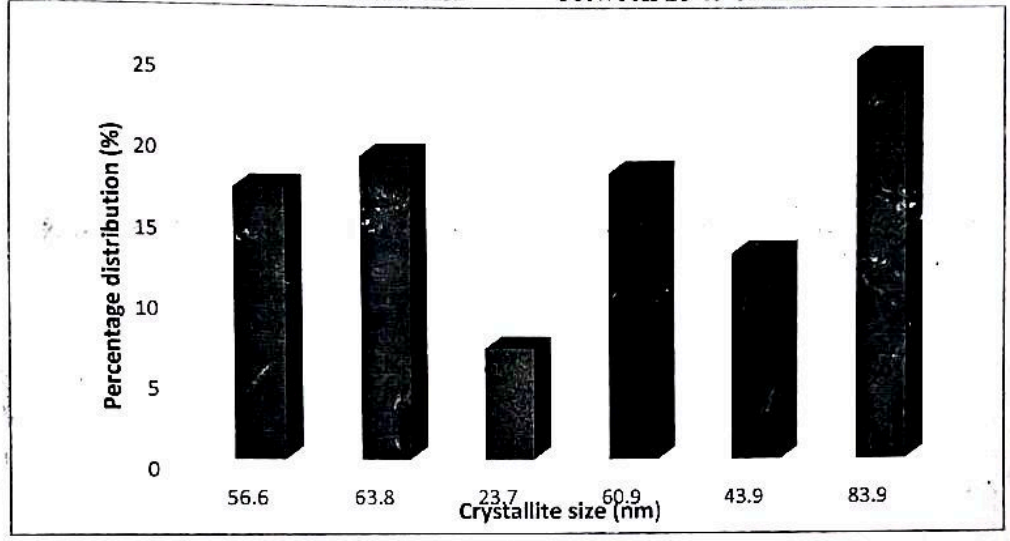

Figure 2: Percentage Population of Particle Sizes from XRD Data

The dominant crystallite size was obtained as of 83.9nm, which is a characteristic of highly crystalline material. Thus, the result indicates the possibility of producing CNTs of nano size when utilizing bimetallic supported catalyst.

The thermal behaviour of catalysts samples that was calcined at 600 °C for 2hrs and the uncalcined were studied using thermogravimetric analysis (TGA). In CVD techniques, catalyst are usually exposed to reaction temperature of 600 °C or above. TGA is necessary to investigate the thermal stability of the catalyst substance within the temperature range of the reaction.

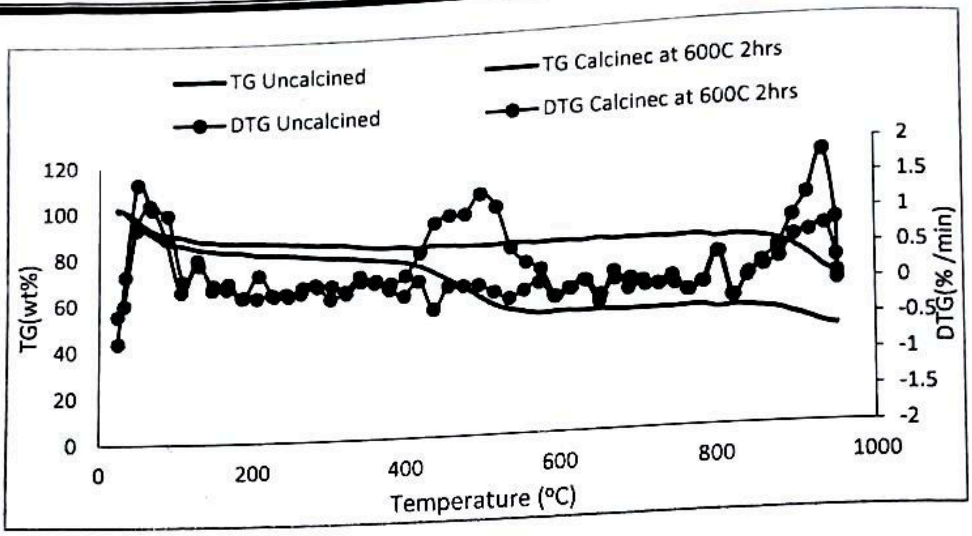

Figure 3: Thermal Behaviour of As-synthesized Catalyst

The results as presented in Figure 3 Above indicates that there were four régimes of weight losses in the TGA curve of the two samples. Al the samples experienced continuous loss in weight from the initial temperature until 400 ^{0}C According to the differential thermal analysis (DTG), this process is endothermic and can be attributed to elimination of water. The differential thermogravimetric (DTG) curves showed significant change which are connected to removal water. In the regime of 400– 550 ^{0}C the samples weight reduction was observed to be faster. This can be attributed to the thermal decomposition of cobalt II nitrate and ammonium molybdate salts as well as the formation of metal oxides (Lobiak *et al.,* 2014). Moreover, within these temperature ranges the DTG curves show the peaks corresponded to crystallization processes of metal oxides. In the following regime of 600 -850 ^{0}C the change of weight was not significant until 850 ^{0}C and above which exhibited another regime of steady weight loss. It can be observed that the weight loss in uncalcined sample was more obvious due to the higher moisture content, cobalt II nitrate and ammonium molybdate salts as compared to the calcined sample. The reason is that during calcination process most of the water content and other impurities in the calcined sample were removed resulting in higher thermal stability.

Surface area analysis was carried out using Brunauer Emmet Teller (BET) in which liquid nitrogen was used as cryogen and nitrogen gas as the adsorbent. The surface area of the uncalcined sample was found to be 209.4 m^2/g, however as the sample was conditioned at 500 ^{0}C for two hours, the surface area slightly increased to 211 m^2/g. The change was not significant because no thermal decomposition of the major catalyst component, MgO would have occurred at a calcination temperature of 500 ^{0}C. As the treatment time increased to four hours, the BET specific surface area increased to 234.5 m^2/g.

Table 1: BET Surface Area of Calcined Co-Mo/MgO Samples

S/N	Calcination Condition	Surface Area (m^2/g)	Pore Volume (cc/g)	Pore Size (°A)
1	**500 C for 2 hrs**	211.1	0.074	32.9
2	**500 C for 4 hrs**	234.5	0.089	30.9
3	**600 C for 2 hrs**	283.2	0.11	31.2
4	**600 C for 4hrs**	278.9	0.098	32.69
5	**Uncalcined**	209.4	0.085	28.3

The dispersion of Co and Mo nanoparticles in the matrix could lead an increase in active surfaces, resulting to an increase in surface area. Setypratomo *et al.* (2015) also reported that calcination of Fe-Co-Mo/MgO catalyst at 500 ^{0}C for four hours is sufficient for the growth of MWNT with specific surface area of 181.1 m^2/g.

Characterization of CNT

The HRSEM micrograph, Figure 5 shows that the produced carbonaceous deposit was black in color with very soft and spongy texture, indicating the presence of CNTs. The preliminary percentage yield of carbonaceous deposit obtained after CVD was 218% on the basis of the weight of catalyst used.

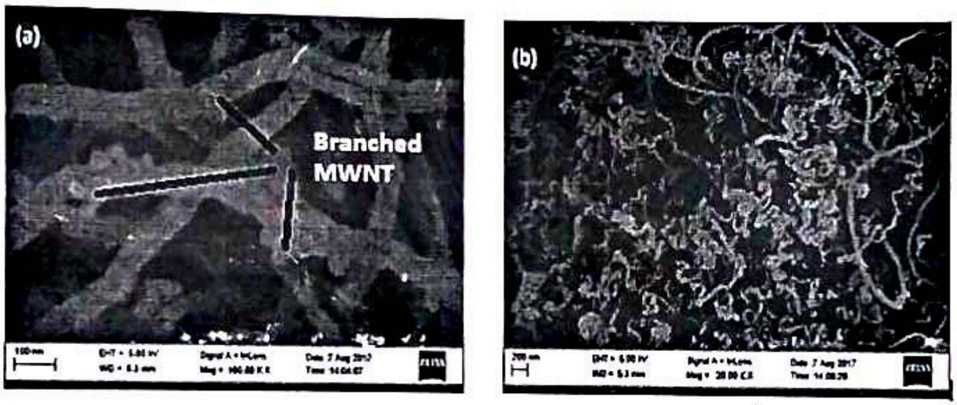

Figure 4: SEM Images of Synthesized MWNTs (a) High Magnification (b) Low Magnification

Transmission electron microscopy analysis carried out in addition to the obtained scanning electron microscopy images. The results revealed that the wall structures of the CNTs varied and diameters ranges between 16 – 36 nm.

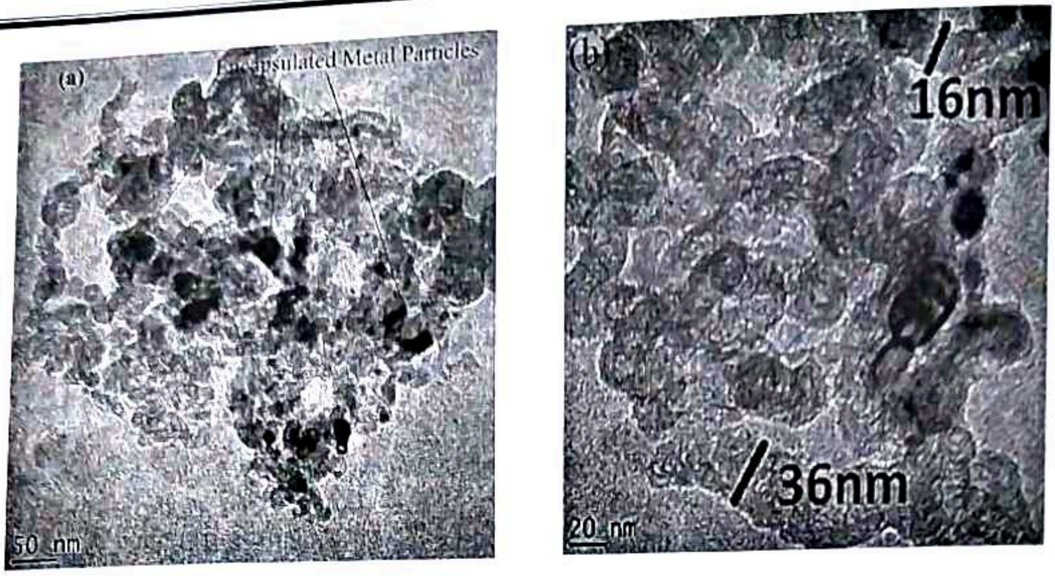

Figure 5: TEM Images of Synthesized MWNTs (a) Low Magnification (b) High Magnification

The Encapsulated metal particles were observed along the inside diameter of most of the nanotubes samples which were introduced by the metal catalyst used for the CNTs growth. Carbon nanotubes can grow either through tip or root mechanism thereby encapsulating metal particles inside the tube (Kariim *et al.*, 2016). This shows that nanometer sized particles can affect the diameter of the produced nanotubes. Another important observation is the large cluster of catalyst found in Figure 5 which is an agglomerate of metal and mainly MgO support material. The produced CNTs contained significant amount of the residual catalyst, impurities and amorphous forms of carbon. This catalyst support material can be removed by acid treatment, however, the location of metal inside the tube causes challenges during purification process (Ahmed *et al.*, 2014). Figures 5 shows clearly that the synthesized CNTs were multiwalled.

Table 2: BET Surface area, pore volume and pore size of synthesized Carbon nanotube

S/No	MORPHOLOGY	
1	Surface Area (m^2/g)	289.5
2	Pore Volume (cc/g)	0.198
3	Pore Size ($\mathring{A}$)	1.688

The BET analysis result from Table 2 indicates that the pore size, pore volume and the surface area of the CNT is 1.688 Å, 0.198 cc/g and 289.5 m^2/g respectively. This result shows that the MWNTs produced has low pore volume, small pore size and a large surface area. This work has a higher surface area than that of Setypratomo *et al.* (2016) who reported a surface area of 181.135 m^2/g for MWNTs grown over Fe-Co-Mo/MgO. The difference observed in the works of Setypratomo *et al.* (2016) may be as a result of the difference of CVD process conditions. Furthermore, the surface area obtained from this work is widely apart from that of Ahmed *et al.* (2014) that reported 190.9 m^2/g for MWNTs produced through the decomposition of natural gas in the presence of Co $-Mo/Al_2O_3$. However, CNTs synthesized is of greater benefit as CNTs with large surface area are known to generally favour metal matrix composite production according to Esawi *et al.* (2010).

The X-ray diffraction technique was used to investigate the crystallinity the produced CNTs.

The XRD pattern in Figure 6, indicates that graphite wall of CNTs are identified by peak C which occurred at 2θ of 26°. Other phases also occurred at 37, 42.5. 62, 74.5 and 78.5°, these were assigned to CoO, MgO and mixed oxides of Co and MgO.

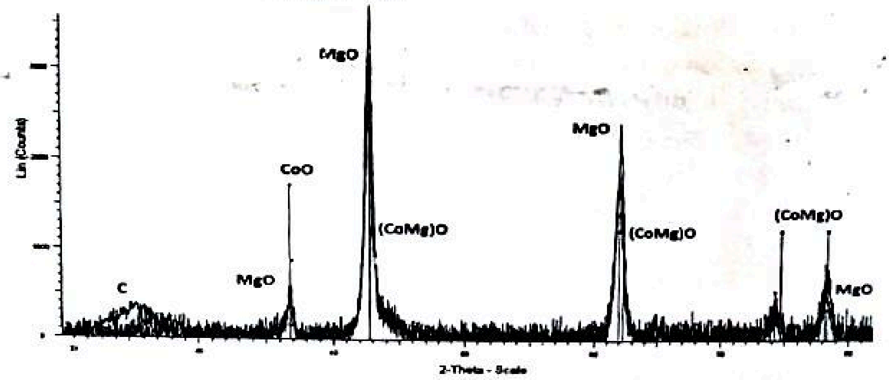

Figure 6: XRD spectra of synthesized CNTs

The XRD did not detect any observable peaks of Molybdenum particles. This indicate that the loading of these nanoparticle is on a small scale and were well dispersed on the surface of MgO. Setypratomo *et al.* (2015) also reported that the presence Co component in a Fe-Co-Mo/MgO catalyst is necessary for the dissociation of CH_4 and the formation of high quality MWNTs.

The diameter of as-produced and purified carbon nanotubes from HRTEM image was related to the Dh (hydrodynamic diameter) using modified Navier-Stokes (Nair *et al.*, 2008) and Stokes-Einstein equation.

Literature values of aspect ratio (L/d), along with Z-average from DLS were substituted to obtain the corresponding length and diameters of the MWNTs produced in the present study. This analysis gives a correlation between the aspect ratio, length and diameter for this MWCNT sample, as shown in the charts.

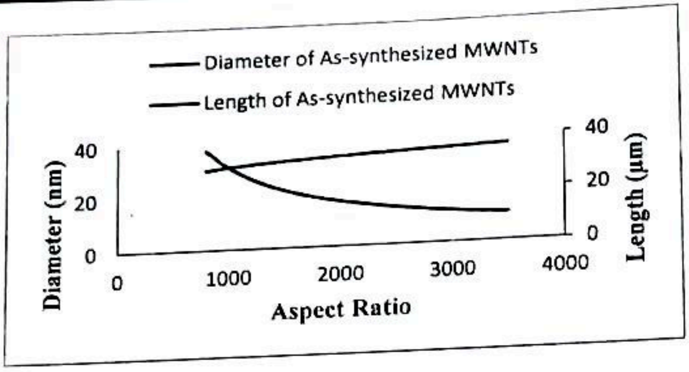

Figure: .7: Aspect Ratio Correlation of Length and Diameter of As-Synthesized MWCNTs

For the MWCNT sample under consideration, an average diameter of 32nm was obtained from the TEM analysis 5. This value suggests an aspect ratio (L/d) of about 1000 and length of 33μm, using the correlation chart. The difference in aspect ratios of samples grown at different CVD conditions also indicates that length and aspect ratios are growth parameters-dependent. Ahmed *et al.* (2014) observed that an increase in the aspect ratio of CNT increases their young's modulus.

Conclusion

Multiwalled carbon nanotubes of 218% yield was successfully produced using the prepared Co-Mo/MgO catalyst. The process conditions were 45 min growth time; 700 °C growth temperature and 250 ml/min for acetylene and nitrogen flow rates. SEM and TEM analysis of the produced MWNTs shows densely populated strand of CNTs with high degree of homogeneity and low porosity 16 to 32nm diameter. The average length and diameter were found to be 33μm and 32nm.The XRD analysis revealed carbon nanotube peak at 2θ of 26° while the BET analysis revealed surface area of 289 m^2/g; pore volume and size of 1.9 cc/g and 1.6 Å respectively.

REFERENCES

Ahmed, E. A., Ateyya, A. A., & Ahmed K. A. (2014) Effect of progressive Co loading on commercial Co–Mo/Al_2O_3 catalyst for natural gas decomposition to COx-free hydrogen production and carbon nanotubes *Energy Conversion and Management* 77 143–151.

Ago, H., Y., Nakamura, Y., Ogawa & Tsuji, M., *Carbon*, 49 (2011) 176.

Dupuis, A., *Progress in Materials Science*, 50 (2005) 929.

Esawi, a. M. K., Morsi, K., Sayed, a., Taher, M., & Lanka, S. (2010). Effect of carbon nanotube (CNT) content on the mechanical properties of CNT-reinforced aluminium composites. *Composites Science and Technology*, *70*(16), 2237–2241. doi:10.1016/j.compscitech.2010.05.004

Evangelos P. F., Stephanos F. N., Andreas A. S., Sergios K. P., Konstantinos L. S., & Athanasios C. M. (2013) High purity multi-walled carbon nanotubes: Preparation, characterization and performance as filler materials in co-polyimide hollow fiber membranes *Separation and Purification Technology* 262–26

Inusa, A., Nataphan, S., & Jose E. H. (2014) Selective synthesis of single-walled carbon nanotubes on Fe–MgO catalyst by chemical vapor deposition of methane *Diamond & Related Materials* 41 84–9

Jeong, S.W., Son, S.Y., and Lee, D.H., *Advanced Powder Technology*, 21 (2010) 93.

Kariim, I., Abdulkareem, A. S., Abubakre O. K., Mohammed, I. A., Bankole, M. T., & Jimoh, O. T. (2016) Studies on the suitability of alumina as bimetallic catalyst support for mwcnts growth in a cvd reactor *proceedings of international conference of Engineering* 295-306

Kumar, M., (2012) *"Carbon Nanotube Synthesis and Growth Mechanism"*, Department of Materials Science & Engineering Meijo University, Nagoya 468-8502 Japan.http://www.intechopen.com, Book chapter 8.

Lobiak, E.V., Shlyakhova, E.V., Bulusheva, L.G., Plyusnin, P.E. Shubin, Y. V., Okotrub, A.V. (2015) Ni–Mo and Co–Mo alloy nanoparticles for catalytic chemical vapor deposition synthesis of carbon nanotubes Journal of Alloys and Compounds 621 351–356

Mhlanga, S. D., Mondal, K. C., Carter, R., Witcomb, M. J., and Coville, N. J., (2009)"The Effect of Synthesis Parameters on the Catalytic Synthesis of Multiwalled Carbon Nanotubes using Fe-Co/CaCO3 Catalysts", *South Africa Journal of Chemistry*, Vol. 62, pp. 67–76.

Nair, N., Kim, W. J., Braatz, R. D., and Strano, RD., (2008)"Dynamics of Suspended Single-Walled Carbon Nanotubes in a Centrifugal Field, Langmuir, Vol. 24, pp. 1790-1795.

Pe´rez-Mendoza, M., Valle´s, C., Maser, W.K., Langlois, M.T. Sauvajol J.L., and Benito, A.M., *Letters to the Editor / Carbon*, 43 (2005) 3002.

Setyopratomo, P., Praswasti, P. D. K. W., & Sudibandriyo, M., (2015) Production of carbon nanotubes: Chemical vapor deposition synthesis from liquefied petroleum gas over Fe-Co-Mo tri-metallic catalyst supported on MgO, *the American Institute of Physics*, 1737, 030007-1–030007-10.
Taleshi, F., (2012)"Evaluation of New Processes to Achieve a High Yield of Carbon Nanotubes by CVD Method", *International Nano Letters*, pp. 2-23.

Tang, S., Zhong, Z., Xiong, Z., Sun, L., Liu, L., Lin, J., Shen Z.X., and Tan, K.L., *Chemical Physics Letters*, 350 (2001) 19.

Terrado, E., Redrado, M., Munoz, E., Maser, W. K., Benito, A. M., and Martinez, M. T., (2006) "Carbon Nanotube Growth on Cobalt-Sprayed Substrates by Thermal CVD", *Material Science and Engineering*, Vol. C26,No (5-7), pp.1185–1188.

Thess, A. Lee, R. Nikolaev, P. Dai, H. Petit, P. Robert, J. Xu, C. Y. Lee, H. Kim, S.G. Rinzler, A.G. Crystalline ropes of metallic carbon nanotubes, *Sci. AAAS-Weekly*
Pap. Ed. 273 (1996) 483e487.

Wei, F., Zhang, Q., Qian, W., Yu, H., Wang, Y., Luo, G., Xu G., and Wang, D., *Powder Technology*, 183 (2008) 10.

Wei, Y., Kim-Yang, L., Siang-Piao, C., Keat-Teong, L., & Abdulrahman, M. (2013)

Synthesis of High purity multi walled carbon nanotubes over Co-Mo/MgO catalyst by the catalytic chemical vapor deposition of methane *New Carbon Materials* 02 -1 19-05

Yeoh, W. M., Lee, K. Y., Chai, S. P., Lee, K. T., and Mohamed, A., (2009)"Synthesis of High Purity Multi- Walled Carbon Nanotubes over Co-Mo/MgO Catalyst by the Catalytic Chemical Vapour Deposition of Methane",*New carbon materials,* Vol. 24, pp. 60041- 60044.

Yerima, M. L., Abdulkareem A. S., Ndaliman, M. B., and Khan, R. H. (2016). Developments in the fabrication of carbon nanotube reinforced metal matrix composites – a review. *Journal of Nigerian Institution of Mechanical Engineers* Vol. 13 55-58.