



## On the Morphological Dependency of CNTs on Catalyst Support in a CVD Reactor

\*Kariim, I<sup>1,2</sup>, Abdulkareem, A. S<sup>1,2</sup>, Abubakre, O. K<sup>2,3</sup>, Aliyu, A<sup>4</sup>, Isa, R. O<sup>1</sup>

<sup>1</sup>Chemical Engineering Department, Federal University of Technology, PMB 65 Minna Niger State, Nigeria

<sup>2</sup>Center for Genetic Engineering and Biotechnology (CGEB), Federal University of Technology, PMB 65 Minna Niger State, Nigeria

<sup>3</sup>Materials and Metallurgical Engineering, Federal University of Technology, PMB 65 Minna Niger State, Nigeria

<sup>4</sup>Department of Chemical Sciences, Federal University, P.M.B 1020, Wukari, Taraba State, Nigeria

\*Corresponding author email: k.ishaq@futminna.edu.ng, +2348032502867

### ABSTRACT

The structural and morphological dependency of CNTs on the decomposition of acetylene gas on varied catalyst mixed in CVD reactor has been explored. Wet impregnation method was adopted for the catalyst preparation via the application of activated carbon and alumina as supported material. The effects of nickel ferrites doping on the activated carbon and alumina on the structural morphology of CNTs were also examined. The result of the Scanning Electron Microscope (SEM) revealed the formation of tailored morphology resulting to a dense and long strand of CNTs when support materials were doped with nickel ferrites. Furthermore, the X-Ray diffractometer (XRD) analysis revealed the formation of graphitic carbon at diffraction angle of 25.67 and 43.28° for both the CNTs produced from pure activated carbon and that of Fe-Ni/activated carbon. In addition to these graphitic phase formation on both CNTs, the presence of nickel ferrites were also observed. The average crystallite particle size of the CNTs produced from pure activated carbon and Fe-Ni/activated carbon were estimated to be 2.31 and 7.11 nm. The results of the analysis are indications to the potential characteristic properties of activated carbon as an excellent support material for the synthesized of tailored CNTs in CVD reactor.

**Keywords:** Activated carbon, Alumina, CNTs, Morphology, SEM, XRD

### 1 INTRODUCTION

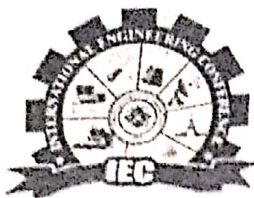
Since the discovery of carbon nanotubes (CNTs) by Iijima in the early 1991, CNTs have received tremendous interest from researchers around the worldwide. The attentions of researchers' to this promising area of research are due to their exceptional characteristics properties of CNTs amongst other synthetic engineering materials. Such properties include but not limited to high mechanical strength, large aspect ratio (length/diameter ratios), distinct tubular structures that are well known for their outstanding thermal and electrical stability in the field of materials engineering (Kariim et al., 2015). The itemized properties have made CNTs exceptional raw materials in various areas of applications as energy storage device, nanoelectric devices, hydrogen storage, reinforced composite materials, field emission and chemical sensors (Yeoh et al., 2009). Therefore, there is need to synthesis tailored CNTs whose properties would be channeled for specific area of application aiming at solving immediate challenges.

Reports have shown that the most efficient and effective active part of catalyst for catalyst vapour deposition techniques are the Fe, Ni and Co (Yeoh et al., 2009). The effect of process parameters and nature of active part of catalyst on the morphology of CNTs is still on research, and the impact of catalyst supporting material on the growth of carbon nanotubes using catalytic

chemical vapor deposition reactor systems are on continuous investigation. Precise understanding and knowledge of the catalyst on a stated supporting substance would lead to controlled growth of CNTs, which is a yardstick for various potential applications

Up till date, there are three major methods reported for the synthesis of CNTs, which include the arc discharge, laser ablation and catalytic vapour deposition (CVD) method. However, the CVD equipment/technique remains the most widely used methods of synthesizing CNTs with distinct structural morphology at large scale (Terrado et al., 2006). The highest level of dependency of researchers and industrial personnel on CVD technique is due to its fabulous mode of operation considering the cost effectiveness, ease of operation, high quality CNTs, ability to vary the operation parameters (optimization) to enhance mass production of this promising nanomaterials (Lee et al., 2002 and Aliyu 2016). Therefore, there is need to carefully and technically manipulate the process parameters of CVD technique towards high yield, quality and oriented CNTs growth.

The application of CVD equipment for the growth of CNTs requires the synthesis of high grade, effective and efficient catalyst particles. Over the years, sol gel method, co-precipitation and wet impregnation are widely reported as an effective mode of catalyst preparation method for the growth of CNTs. Though the application of wet impregnation method outweighs



others methods of catalysts preparation as reported by several researchers. Most of the highlighted techniques for the catalyst synthesis require the use of active metallic part usually transition metals (Fe, Ni and Co, as well as their alloy) (Yeoh et al., 2009) on support materials which include, alumina, MgO, Zeolite, CaCO<sub>3</sub>, SiO<sub>2</sub>, kaolin (Quian, et al., 2003, Pelech et al., 2009 and Yeoh et al., 2009). These supported materials offer a suitable location for the CNTs growth in the CVD technique. The presence of these metal(s) in the catalyst mix, the nature of support material and the growth conditions resulted in the formation of metallic impurities in the synthesized CNTs when used in CVD techniques (Kruusenberg et al., 2011).

In this present research work, CNTs are produced via two distinct supported materials separately loaded on nickel-ferrites. The catalysts were produced using wet impregnation method and CVD technique was employed for the synthesis of CNTs. The synthesized CNTs were analyzed via the SEM and XRD for the determination of the surface morphology and crystallinity.

## 2 METHODOLOGY

### 2.1 MATERIALS

The gases used were sourced from BOC Nigeria and were of analytical grade with percentage purity of 99.99%. These gases include acetylene and argon. While all chemicals were supplied by Sigma Aldrich: Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, and alumina (Al<sub>2</sub>O<sub>3</sub>) were of analytical grade with 99.99% purity. The activated carbon (AC) used was supplied by the center for genetic engineering and biotechnology (CGEB) and was used without any purification and the properties of the activated carbon were reported elsewhere (Kariim et al., 2015a).

### 2.2 SYNTHESIS OF NICKEL-FERRITE CATALYSTS

Three equal concentration of 0.25M of Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O were prepared and 6 g of support material (alumina, activated carbon and equal percentage alumina/activated carbon) were added to separate solutions. The mixtures were left to impregnate overnight and the slurries were dried at a static oven at a temperature of 120 °C for 6 hrs. The semi-dried products were calcined in air furnace at 300 °C for 1.5 hrs under the flow of inert gas, then cooled, grinded and sieved through 150 µm sieves. Also, 1.0 g of both Fe-Ni/AC and Fe-Ni/Al<sub>2</sub>O<sub>3</sub> was formulated as a separate catalyst mix with varied properties from the starting materials.

### 2.3 CARBON NANOTUBES PRODUCTION

1.0 g of the developed catalyst (Pure AC, Fe-Ni/AC, Fe-Ni/Al<sub>2</sub>O<sub>3</sub> and mixture of Fe-Ni/AC-Fe-Ni/Al<sub>2</sub>O<sub>3</sub> at ratio 1:1) were weighed and channeled into horizontal reactor's tube via the quartz tube. The system was purged

at 20 ml/min from room temperature to the reaction temperature of 700 °C to evacuate air and any other gaseous impurity from the system. The reactant, acetylene was passed through the catalytic reactor at 100 ml/min for 30 min while the flow of the inert gas was increased to 200 ml/min to serve as a carrier gas. The acetylene flow was truncated and reactor was purged at 20 ml/min until it cooled to room temperature. The CNTs produced with each of the catalysts (Pure AC, Fe-Ni/AC, Fe-Ni/Al<sub>2</sub>O<sub>3</sub> and mixture of Fe-Ni/AC-Fe-Ni/Al<sub>2</sub>O<sub>3</sub> at ratio 1:1) were removed, packaged and analyzed to determine their properties.

## 3 RESULTS AND DISCUSSION

The needs for developing high quality CNTs are pertinent to the creative and skillful approach of nanotechnologist researchers on the basic factors affecting the process of CNTs synthesis. One of the most important factors is the nature, method and composition of the catalyst (active metals to supported materials) used. In this present study, several catalysts were developed and used for the synthesis of high grade, and morphology controlled CNTs.

The BET surface areas of the prepared catalyst were determined under a continuous flow of N<sub>2</sub> and the results are presented in Table 1. According to Table 1, the BET surface area of the pure AC, Fe-Ni/AC, Fe-Ni/Al<sub>2</sub>O<sub>3</sub> and Mixed Fe-Ni/AC/Fe-Ni/Al<sub>2</sub>O<sub>3</sub> (1:1) were 840.30, 714.32, 915.17 and 848.78 m<sup>2</sup>/g respectively. The decrease in the surface area of the pure AC after impregnated with Fe-Ni may be attributed to the incorporation of the metal particle into the pores of the AC. While the surface area of the Mix Fe-Ni/AC/Fe-Ni/Al<sub>2</sub>O<sub>3</sub> (1:1) above the pure AC might be due to the structural changes of the supported materials.

TABLE 1: BET SUFACE AREA OF THE PREPARED CATALYST

Catalyst	BET surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Pore size (nm)
Pure AC	840.38	0.299	2.0507
Fe-Ni/AC	714.323	0.2542	1.7431
Fe-Ni/Al <sub>2</sub> O <sub>3</sub>	915.17	0.3256	2.2332
Mix Fe-Ni/AC/Fe-Ni/Al <sub>2</sub> O <sub>3</sub> (1:1)	848.7838	0.3020	2.0712

The results of the scanning electron microscope (SEM) showing the morphology of the produced CNTs from pure activated carbon and the Fe-Ni impregnated activated carbon are depicted in Figure 1 (A-D).

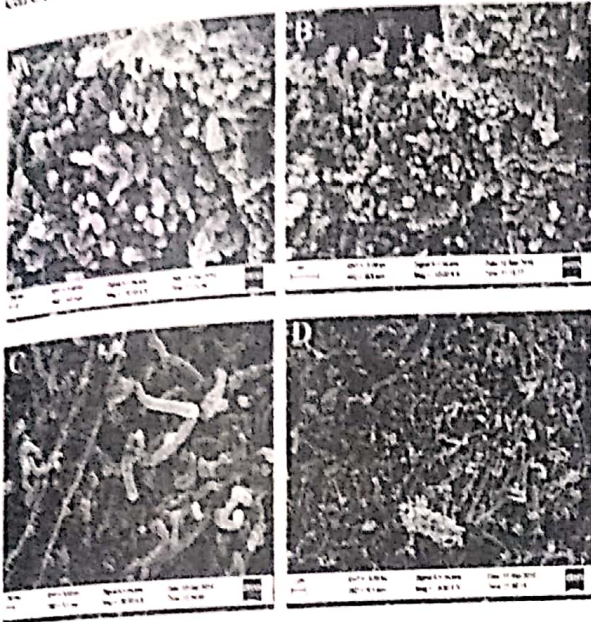


Figure 1: SEM micrograph of CNTs produced from pure activated carbon (A-B) and Fe-Ni supported on activated carbon (C-D)

The results as shown in Figure 1 (A-B) revealed that the CNTs produced are partially formed. There are presences of short and condensed nature of CNTs formation as seen in Figure 1 (A-B). The formation of high dense and populated short-growth of CNTs might be resulted from the absence of inhibitor such as the transition metal(s) (Fe-Ni) which has the ability to enhance the decomposition of the acetylene gas. In the same phase, as depicted in Figure 1 (C-D), the CNTs produced have an improved structural composition with identified and long strand of CNTs formation which was produced at the same operating condition. It can be deduced from Figure 1 (A-D) that, there is need to incorporate active metals into the support material to produce tailored CNTs for any specific area of application.

The SEM Micrograph shown in Figure 1 also revealed that to improve the growth of CNTs synthesis by promoting the decomposition of acetylene, there is need to incorporate transition metals. Furthermore, the result shows that activated carbon is a perfect and good support material for the synthesis of improved and tailored CNTs

for materials engineering application. The use of activated carbon is also an indication for the production of low cost and environmentally friendly material via a CVD technique.

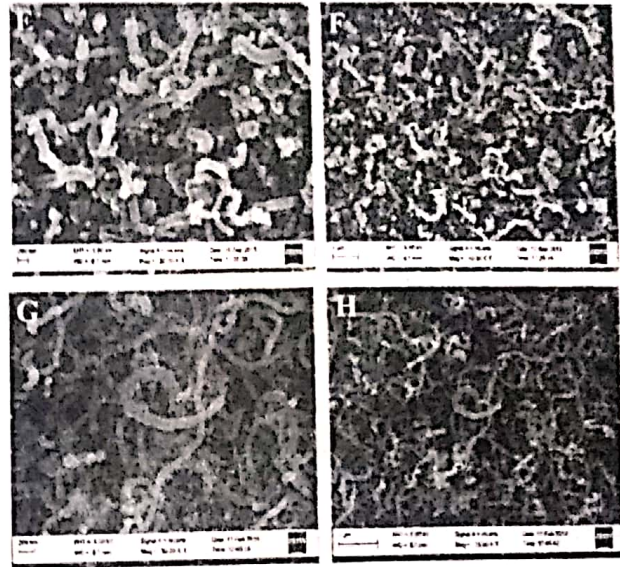


Figure 2: SEM micrograph of CNTs produced from equal percentage of activated carbon and Fe-Ni/Alumina (E-F) and Fe-Ni supported on alumina (G-H)

Furthermore, the effect of incorporation of activated carbon on the surface morphology of CNTs in the mix of Fe-Ni supported on alumina was further determined. The result of the analysis is as depicted in Figure 2 by the scanning electron microscope.

Figure 2 (G-H) depicts the surface morphology of CNTs synthesized from pure alumina impregnated with Fe-Ni catalyst. The depicted SEM (Figure 2 (G-H)) confirms the formation of long and continuous strand of CNTs. This behavior might be resulted from the presence of Nickel ferrite on the surface of the alumina support and its pores which enhances the catalytic breaking down of acetylene in the CVD reactor. This assertion was due to the formation of the structure produced when the Fe-Ni/alumina was doped with activated carbon. It was shown that the doping of the catalyst with activated carbon reduces the rate and quality of CNTs produced and this can be attributed to the suppression of the functionality of the existing nickel ferrites at the surface of the alumina.

The phase changes and identification of component of the developed CNTs were determined via



X-Ray Diffractometer (XRD) technique. The result of the analysis is presented in Figure 3.

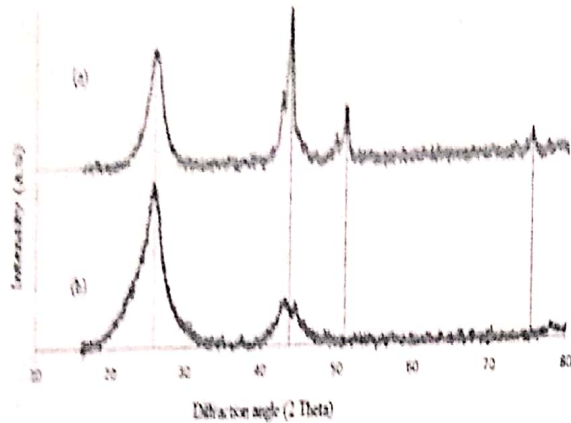


Figure 3: XRD spectral of (a) CNTs produced from Fe-Ni/Activated Carbon (b) CNTs produced from pure activated carbon.

The result as depicted in Figure 3 shows the effect of doping activated carbon with transition (catalytic enhanced metals) on the phase of the CNTs produced in a CVD technique. The phase angle at the 2 theta equals 25.67 and 43.28° depicts the formation of graphitized carbon. The formations of these peaks are observable in both the carbon nanotubes produced from Fe-Ni/Activated Carbon and pure activated carbon though at varied intensity and FWHM as shown in Table 2. The peak at around 51.00 and 75.34° are associated to the formation of Nickel ferrites crystals (NiFe<sub>2</sub>O<sub>4</sub>). This observation was observed by Abdulkareem, et al. (2017) during the process of synthesizing MWCNTs via the use of Fe-Ni-Co supported on CaCO<sub>3</sub>.

From Table 2, the formations of two distinct peaks were formed when pure activated carbon was used as a catalyst material for the synthesis of CNTs. The peaks were also observed at the same diffraction angle when the activated carbon was doped with nickel ferrites nanoparticle for CNTs synthesis. Furthermore, two pronounced peaks were formed on the CNTs produced from Fe-Ni/Activated carbon. These peaks formation might be attributed to the production of aligned and long tube carbon nanotubes.

Regarding the crystallite size of the produced CNTs, the Scherer equation was employed using (1) [Chen et al., 2006]

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

Where D represents the particle size diameter,  $\beta$  = full width at half maximum (FWHM),  $\lambda$  is the wave length of X-ray (0.1541 nm),  $\theta$  is the diffraction angle and K is the Scherrer constant (0.94).

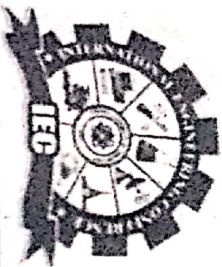
TABLE 2: CRYSTALLITE SIZES DETERMINED FROM XRD SPECTRA

S/N	Diffraction Angle	FWHM (Radian)		Crystallite Size (nm)	
		Sample B	Sample A	Sample B	Sample A
1	25.67	0.08988446	0.06047566	1.65	2.46
2	43.28	0.05270894	0.04555309	2.96	3.42
3	51.00		0.01797689		8.92
4	75.34		0.01343904		13.63

From Table 2, the average crystallite size of CNTs produced from both the pure activated carbon and the nickel ferrite doped activated carbon were determined. The Average crystallite size for sample B and A were found to be 2.31 and 7.11 nm respectively. The increment in the particle size is attributed to the formation of nickel ferrites which accompany the produced carbon nanotubes in a CVD reactor. Therefore, to maintain a low particle size of CNTs material, it's required to operate the CVD equipment with only the activated carbon without the incorporation of transition element as an active part of catalyst.

#### 4 CONCLUSION

In summary, a wet impregnation method was used for the preparation of catalysts via the used of activated carbon and alumina as support. The effects of pure activated carbon, nickel ferrites doping on the activated carbon and alumina on the morphological characteristic of CNTs were investigated. Base on this study, the SEM revealed the formation of tailored morphology resulting to a dense and long strand of CNTs when activated carbon and alumina support were doped with nickel ferrite compared to the CNTs produced with pure activated carbon. While, the XRD results revealed formation of graphitic carbon at 2 theta angles of 25.67 and 43.28° for both the CNTs produced from pure activated carbon and



that of Fe-Ni/activated carbon and the presence of nickel ferrites were also observed in the spectrum. This study demonstrated for the first time the potential characteristic properties of activated carbon as an excellent support material for the synthesis of good quality and aligned CNTs and also the important roles of incorporating active metals into the support materials for CNT's production.

#### ACKNOWLEDGEMENTS

The financial support from the senate research based fund of Federal University of Technology, Minna with grant number (SENATE/FUTMINNA/2015/06) is much appreciated. Support received for the use of facilities at Centre for Genetic Engineering and Biotechnology, CGEB, Federal University of Technology, Minna, Nigeria is also acknowledged.

#### REFERENCES

- Karim I., Abdulkareem A. S., Abubakre O. K., Aliyu A., Garba M. U., & Mohammed I. A. (2015). Optimization of lead (II) ions adsorption on to chemically activated carbon from sugarcane bagasse, *Nigeria Journal of Technology Research*, 10( 2), 27-33.
- Krusenbergt, I., Alexeyeva, N., Tannevski, K., Kozlova, J., Matusen, L., Sammelsejg, V., Solha-Gullón, J., & Felhu, J. M., (2011). Effect of purification of carbon nanotubes on their electrocatalytic properties for oxygenreduction in acid solution, *Carbon*, 49 (12), 4031-4039.
- Lee C. J., Park J., & Yu J. A. (2002). Catalyst effect on carbon nanotubes synthesized by thermal chemical vapor deposition. *Chem. Phys. Letts.*, 360: 250-255.
- Pelech I., Narkiewicz U., Kaczmarek A., & Jedrzyewska A.(2009). Preparation and characterization of multi-walled carbon nanotubes grown on transition metal catalysts. *Polish Journal of Chemical Technology*, 16: 117-122.
- Quian W., Liu T., Wang Z., Yu H., Li Z., Wei F., & Luo G. (2003). Effect of adding nickel to iron-alumina catalysts on the morphology of as-grown carbon nanotubes. *Carbon*, 41:2487-2493.
- Terrado E., Redrado M., Munoz E., Maser W. K., Benito A. M., & Martinez M. T. (2006). Carbon nanotube growth on cobalt-sprayed substrates by thermal CVD. *Mater. Sci. Eng., C* (26), 1185.
- Yeoh W. M., Lee K. Y., Chai S. P., Lee K. T., & 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*, 24: 60041-60044
- Abdulkareem A. S., Karim I., Bankole M. T., Tijani J. O., Abodunrin T. F., & Olu S. C. (2017). Synthesis and characterization of tri-metallic Fe-Co-Ni catalyst supported on CaCO<sub>3</sub> for Multi-Walled Carbon Nanotubes growth via Chemical Vapor Deposition Technique. *Arabian Journal for Science and Engineering*. DOI 10.1007/s13369-017-2476-2
- Almad S. N., Hakeem S., Alvi R. A., Farooq K., Farooq N., Yasmin F., & Saeed S. (2013). Synthesis of multi-walled carbon nanotubes and their application in resin based nanocomposites. *Journal of Physics: Conference Series*, 439: 1-8.
- Aliyu A. (2016). Synthesis and characterization of carbon nanotubes (CNTs) via novel support in catalytic chemical vapour deposition (CCVD) method. MEng. Thesis, Department of chemical Engineering, Federal University of Technology Minna, Nigeria.
- Chen Y., Zhang Y. Q., Zhang T. H., Gan C. H., Zheng C. Y., & Yu G. (2006). Carbon nanotube reinforced hydroxyapatite composite coatings produced through laser surface alloying. *Carbon*, 44:37-45.
- Karim I., Abdulkareem A.S., Abubakre, O.K., Mohammed, I.A., Bankole, M.T., & Jimoh, T.O. (2015). Studies on the suitability of alumina as bimetallic catalyst support for MWCNTs growth in a CVD reactor. *Proceedings of the International Engineering Conference (IEC2015)*, 296-305