Synthesis and characterization of carbon nanotubes over binary Fe-Co- CaCO₃ Catalyst

By

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Abstract

The influence of synthesis parameters such as mass of support, drying temperature and drying time on the yield of Fe-Co/CaCO₃ catalyst prepared by the wet impregnation method using 2^3 factorial design of experiment was investigated in this study. The suitability of the produced catalyst for the production of carbon nanotubes in a catalytic vapour deposition method was also investigated. Results obtained indicated that highest yield of 95.71 % of the catalyst after calcination was obtained at the synthesis conditions of 10g of catalyst, drying temperature of 120ºC and drying time of 12 hours. Particle size analysis of the catalyst revealed that the catalyst sizes are in the ranges of 96.6-10.9 nm, with specific surface area of 3.904m²/g while the HRTEM analysis shows that the catalyst is highly crystalline and well dispersed without agglomeration. Results of the characterization conducted on the carbon nanotubes produced shown that the carbon nanotubes produced is a multiwall carbon nanotube. The TGA analysis revealed that the multiwalled carbon nanotubes produced is thermally stable. While the XRD shows characteristic of graphene layers that make up the tube walls at 2θ values of 25.8736º and 44.6584 º. TEM and SEM/EDS images exhibit a clearly defined multiwall concentric tubular morphology, with 92.29 wt % C with inner diameter of 16 nm. The MWCNTs had aspect ratio of 265 with length of 4.8 µm and specific surface area of 274.06 m²/g and pore volume of 62.97 cm³ g⁻¹. It can be inferred from the various analysis conducted that the developed catalyst is suitable for multiwalled carbon nanotubes in a catalytic vapour deposition reactor.

Introduction

Since the discovery of carbon nanotubes (CNTs) accidentally, in the course of producing fullerenes by arc discharge method,[1] CNTs has continued to generate attention due of their unique fascinating electronic and mechanical properties with prospects for numerous applications in energy storage materials, polymer reinforcements, gas storage, sensors, electronics and catalysis[2]. Though, arc discharge, laser ablation, electrolysis, sono-chemical (or hydrothermal), and various forms of chemical vapour deposition (CVD) methods are the available techniques for production of CNTS. However, simplicity, low cost of operation and

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[1] Iijima, S. (1991). Helical Microtubules of Graphitic Carbon, *Nature*, 354, 56-58. doi:10.1038/354056a0. Ijima,S., Ajayan, P. M., Ichihashi, T., (1992). Growth model for carbon nanotubes, *Physical Review Letters,* 69 (21), 3100–3103

[2] Yibo, Y. J.-X. (2015). Carbon nanotube catalysts: recent advances in synthesis, characterization and applications. doi:10.1039/c4cs00492b; Zhang, Q. H. (2013). The road for nanomaterials industry: a review of carbon nanotube production, post-treatment, and bulk applications for composites and energy storage. *Small,* 9(8), 1237-1265. doi:10.1002/smll.201203252; Schnorr, J. M. (2011). Emerging Applications of Carbon Nanotubes. *Chemistry of Materials: American Chemical Society,* 23, 646–657

ease of scalability for commercial production favoured the choice of CVD methods[3]. This makes it a promising technology for the mass production of high-quality CNTs of all types[4]. Another part of CNT growth optimization in terms of yield and quality especially when using CVD is the appropriate selection and control of process parameters such as catalyst type, method of preparation and particle size.[5] Also affecting the operation of CVD are the reactor configuration,[6] choice and flow rate of inert gas and that of the carbon source, reaction temperature and time,[7],[8] amount of catalyst and its location in the reactor.

Catalyst support is adjudged to be the vehicle for the active phase with attributes of providing maximum surface area of the active phase that allow the active phase to be cast into the form of coarse particles suitable for use in carbon nanotubes production. Aside from the fact that increase in mass of support favour the yield of catalyst, it also allows the physical separation of the nanoparticles and thereby hinders their agglomeration into larger crystallites. Agglomeration leads to a decrease in the number of surface metal atoms per unit mass of metal catalyst and therefore decreases the number of active sites of the catalyst which can lead to decrease in catalyst yield. Catalyst support thus play important role in the production of catalyst and they are described as the vehicle for the active phase of the catalyst. There are many studies on the on the bi-metallic catalysts supported on different materials such as CaCO$_3$, Al$_2$O$_3$, Zeolite, MgO, CaO, SiO$_2$ through wet impregnation method that entails a suspension of the support in the salt solution for a required duration of time, followed by the oven drying of the slurry. Among the different support reported in the literature, CaCO$_3$ is becoming popular because of its advantages over other supports.[9] Calcium carbonate is relatively cheap and readily available compared to other support and decomposes easily during CNTs growth into CaO and CO$_2$ which are easily removed along with residual CaCO$_3$ from the final product by acid treatment.

Catalyst is considered to play the most important role in the growth of CNTs, it determines the morphology, type of CNTs, diameter and the growth mechanism. Catalyst not only affects the yield, but also the purity and morphology of the CNTs. Hence, the appropriate choice of catalyst is inevitable in CNTs synthesis. Common transition metals such as Fe, Co, Ni, and their combinations have been used for this purpose. These active substances of supported catalyst have effect on morphology and quality of CNTs. The use of bimetallic catalysts especially Fe-Co for CNTs growth has attracted the attention of researchers because of their

[3] Manawi, Y. M., Ihsanullah, Samara, A. Al Ansari, T. and Atieh, M. A. (2018), A Review of Carbon Nanomaterials' Synthesis via the Chemical Vapor Deposition (CVD) Method, *Matreials,* 11, 822

[4] Prasek., J., Drbohlavova, J, Chomoucka, J., Hubalek, J.,' Jasek, O, Adam V. and Kizek, R, (2011), Methods for carbon nanotubes synthesis—review, Journal of Materials Chemistry 21(40):15872-15884

[5] Marella, C. and Tomaselli, M. (2006), Synthesis of carbon nanofibers and measurements of hydrogen storage, *Carbon*, 44(8):1404-1413

[6] Op Cit n.3

[7] Bhattacharjee, C. R. and Nath, A., (2012), Chemical Vapour Deposition (CVD) Technique and the Synthesis of Carbon Nanomaterials (CNMs), *Journal of Chemical and Pharmaceutical Research*, 4(1):706-713

[8] Manawi *et al.*, (2018), Op. Cit n. 3

[9] Mhlanga, S. D. (2009). The Effect of Synthesis Parameters on the Catalytic Synthesis of Multiwalled Carbon Nanotubes using Fe-Co/CaCO$_3$ Catalysts. *South Africa Journal Chemistry,* 62, 67-76.

effectiveness and high-quality CNTs that they produce[10],[11],[12]. For a base growth mechanism using $CaCO_3$ as the catalyst support, the conversion of acetylene into CNTs is strongly enhanced by a two-step cyclic mechanism which is as a result of the reaction taking place at the triple-point junction (Fe-Co/$CaCO_3$/C_2H_2) around the catalyst-support interface[13]. Hence, optimizing the process of CNTs production by CVD techniques will not give a good result without optimizing catalyst preparation procedure

This article presents synthesis of MWCNT from binary catalyst Fe-Co on $CaCO_3$ support based on a 2^3-factorial experimental design for optimisation of its synthesis parameters of the catalyst. Thermogravimetric analysis TGA, scanning electron microscopy (SEM), X-ray diffraction (XRD), transmission electron microscopy (TEM), dynamic light scattering, Brunauer-Emmett-Teller (BET) Analysis and X-ray photoelectron spectroscopy (XPS) characterisation techniques were used foe characterisation.

Materials and Methods

Materials
All the chemicals used in this study are of analytical grade with percentage purity in the range of 98-99.9% and used without further purification. The list of chemicals include $CaCO_3$ (kermel 99.9 %), $Co(NO_3)_2.6H_2O$ (Kem Light Lab., Mumbai India 98.5 %), $Fe(NO_3)_3.9H_2O$ (Guangdong Guanghua Chemical Factory Co., Ltd, China 98.5 %). 99.99%, tetraoxosulphate (VI) acid (H_2SO_4), 99.8%. Acetylene, argon and nitrogen gases were purchased from British Oxygen Company/Brin's Oxygen Company (BOC Gases Nigeria Plc, Lagos).

Methodology

Synthesis of catalyst

Wet impregnation method was used in this study to prepared the bimetallic catalyst Fe-Co on $CaCO_3$ support. A calculated amount of $Fe(NO_3)_3.9H_2O$ and $Co(NO_3)_2.6H_2O$, 3.62 g and 2.47 g respectively were weighed and dissolved in 50 cm^3 of distilled water. This was followed by the addition of a known weight of $CaCO_3$ under continuous stirring for 60 min. The resulting slurry was then allowed to dry at room temperature after which it was dried in an oven at 120 ^oC for 12 hrs, cooled to room temperature, ground and finally screened through a 150 µm sieve. The final powder was then calcined at 400^oC for a specified period of time. The dried catalyst was then grounded to avoid agglomeration. This procedure was repeated to investigate the influence of synthesis parameters on the yield of catalyst after calcination using 2^3 factorial design of experiment.

[10] Kumar M. and Ando Y (2010). Chemical Vapor Deposition of Carbon Nanotubes: A Review on Growth Mechanism and Mass Production Journal of Nanoscience and Nanotechnology 10(6):3739-58

[11] Prasek., J., Drbohlavova, J, Chomoucka, J., Hubalek, J.,' Jasek, O, Adam V. and Kizek, R, (2011), Methods for carbon nanotubes synthesis—review, Journal of Materials Chemistry 21(40):15872-15884

[12] Motchelaho, M. A. (2011). Effect of acid treatment on the surface of multiwalled carbon nanotubes prepared from Fe–Co supported on CaCO 3: correlation with Fischer –Tropsch catalyst activity. *Journal of Molecular Catalysis A: Chemical,* 335(1), 189-198. Retrieved from https://doi.org/10.1016/j.molcata.

[13] Afolabi, A. S. (2011). Synthesis and purification of bimetallic catalysed carbon nanotubes. *Journal of Experimental Nanoscience, 6*(3), 248–262.; Mhlanga, S. D (2009) Op. Cit n.9

The varying parameters are the mass of support, drying time and drying temperature, these factors were varied by considering the operating limit, which is referred to as lower and upper levels as shown in Table 1.

Table 1.: Levels of factors considered in 2^3 factorial of catalyst production

	Time (hr)	Temp (ºC)	Mass of support (g)
Upper (+) level	12	120	10
Lower (-) level	8	100	8

The detail of the factorial design matrix for catalyst preparation is presented in Table 2.

Table 2: 2^3 Experimental Matrix showing Yield after Dried and Calcined at 400 ºC

Run	Mass of Support (g)	Drying Temperature (°C)	Drying Time (hrs)
1	10	100	8
2	8	120	12
3	10	120	8
4	8	120	8
5	8	100	8
6	10	120	12
7	10	100	12
8	8	100	12

Synthesis of carbon nanotubes

The Carbon nanotubes were produced by catalytic chemical vapour (CCVD) deposition through the decomposition of acetylene in a CCVD reactor. The reactor had a quartz tube, of 52 mm internal diameter, and of 1010 mm length, placed in a furnace that can reach a temperature of 1200 °C, the schematic of the various segments of the reactor for the synthesis procedure is shown in Figure 1.
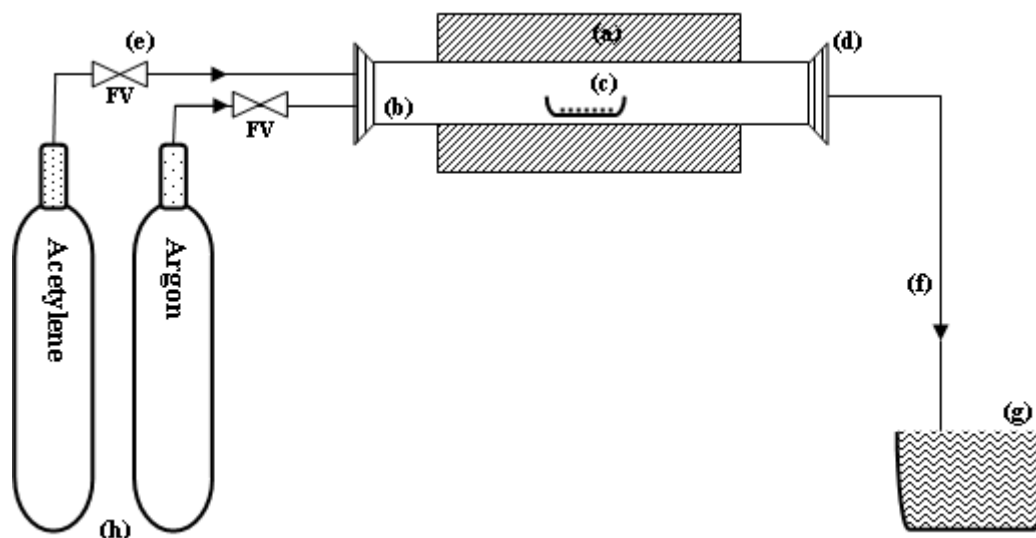
Figure 1: Scheme of set-up for CNT synthesis in CVD, (a) Furnace, (b) Quartz tube, (c) Ceramic boat with catalyst, (d) Cork, (e) Flow controller, (f) Gas outlet, (g) Gas collector with water, (h) Acetylene and Argon gas cylinders.

A ceramic tube containing bi-metallic Fe-Co catalyst on $CaCO_3$ support was place at the middle of the quartz tube. The reactor quartz tube was heated by the furnace at rate of 10 °C min^{-1}, under argon flow rate of 30 ml min^{-1} into the reactor purge the system of air and as carrier gas. At 700 °C, the argon flow was adjusted to a flow rate of 190 ml/min, and acetylene as reducer gas was introduced into the quartz tube at flow rate of 290 ml min^{-1} for 60 min and the process was then terminated. The furnace was subsequently turned off and left to cool to room temperature at an argon flow rate 30 ml min^{-1}.

The as-synthesis carbon nanotubes (CNT) were purified by acid treatment with concentrated HNO_3 and H_2SO_4 in 1:3 by volume ratio. The CNT was vigorously stirred in the acid mixture for 3 hours at 45 °C in a sonicator subsequently washed thoroughly in distilled water to a pH of 7 dried in air and later in oven for 12 hours at 120 °C. The purified carbon nanotubes synthesised was characterised to determine their morphology, structures, crystallinity, purity using TEM, SEM/EDX, XRD, BET, TGA and Particle size by DLS analysis

Results and Discussion

The focus of this study is to develop a suitable catalyst for the production of carbon nanotubes by catalytic vapour deposition method. This was achieved through investigation of process parameters as mass of support, drying temperature and drying time on the yield of the catalyst using factorial design of experiment.

Characterization of catalyst

Different parameters have been reported to influence the catalytic yield and performance while using the wet impregnation method, among which are mass of support, oven drying time, oven drying temperature and stirring[14]. The result on the influence of the mass of support on the

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[14]Munnik, P., De Jongh, P. E., & De Jong, K. P. (2015). Recent developments in the synthesis of supported catalysts. *Chemical reviews*, *115*(14), 6687-6718.

percentage yield of catalyst after calcination at temperature of 400 ⁰C, is presented in Table 2. It reveals increase mass of support resulted to increment in the yield of catalyst. For instance, at constant drying temperature of 100 ⁰C and drying time of 12 hours, the catalyst yield increases from 84.60 % to 86.45%.

Table 2: 2³ Yield Experimental result after Drying and Calcined at 400 ⁰C

Run	Catalyst Support Mass (g)	Temperature of Drying (°C)	Time of Drying (hrs)	Yield (%) After Calcination at 400 ⁰C
1	10	100	8	86.69
2	8	120	12	76.79
3	10	120	8	85.31
4	8	120	8	78.00
5	8	100	8	85.10
6	10	120	12	95.71
7	10	100	12	86.45
8	8	100	12	84.60

Also investigated is the influence of drying temperature on the yield of catalyst, for the purpose of optimization the two-level temperature of 100 ⁰C and 120 ⁰C was considered and the results as presented indicate that the higher the oven drying temperature while keeping other parameters constant, the higher the yield of the catalyst. It was reported that drying temperature is responsible for the onset of several deactivation mechanisms. As the temperature increase, the interactions between support and active material takes which will result into accelerated sintering and result in the formation of less active species.[15] At a low oven drying temperature, the interaction between the active metals and the support is reported to decelerate the sintering, thus, catalyst yield decreases

The influence of drying time on the yield of catalyst is considered as one of the major factors that influence the yield and quality of catalyst produced by wet impregnation method. The drying rate strongly influence the dispersion of the active metals on supported material and the rate of elimination of water from the pores which leads to the increase of precursor concentration up to saturation and consequent crystallization, preferably on the seeds resulting from the interaction with the support. Though it has been reported that increase in oven drying time may resulted to increase or decrease in catalyst yield pending on the rate of dispersion of active metals on the support. However, the results obtained in this study reveals that increase in drying time favoured the yield of catalyst which implies that the rate of dispersion of the active metal on the support during wet impregnation increases. Thus, as observed, a 10 g mass of support, drying temperature of 120⁰C and dying time of 12 hours were the optimum parameters that gave the highest yield of 95.71% of catalyst

The catalyst obtained at the optimum production conditions was characterized and the results obtained are hereby presented in Figure 2. It shows the surface area and pore volume analysis of CaCO₃ support and synthesised catalyst measured using Brunauer, Emmett and Teller (BET) method. The BET analysis of the optimized catalyst reveals a specific surface area of 3.904 m²/ g, while that of CaCO₃ used as support possessed specific surface area of 3.842 m²/ g. The

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[15] Munnik, *et al*., 2015. Ibid

little increase in surface area for catalyst could be attributed to the dispersion of Fe and Co nanoparticles in the support matrix. The catalyst has specific pore volume of about 0.002 cm^3/g, and pore radius of between 0.184 and 1.4 nm.
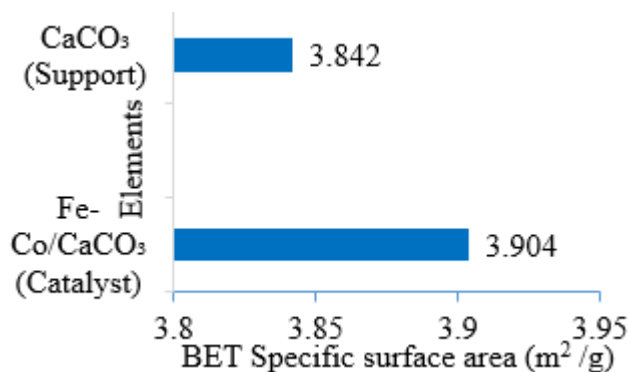

Figure 2. Surface area of CaCO$_3$ and Fe-Co/CaCO$_3$ catalyst

Dynamic Light Scattering (DLS) was used to determine the particles sizes of all samples (catalyst) from the 2^3 experimental run post-calcinated at 400 ºC for 16 hours. The catalyst particles sizes ranged from 96.6-109.0 nm as shown in Figure 3. Results obtained as presented in Figure 3 clearly shown that the synthesis parameters not only affect the yields of catalyst but also the catalyst particle size.
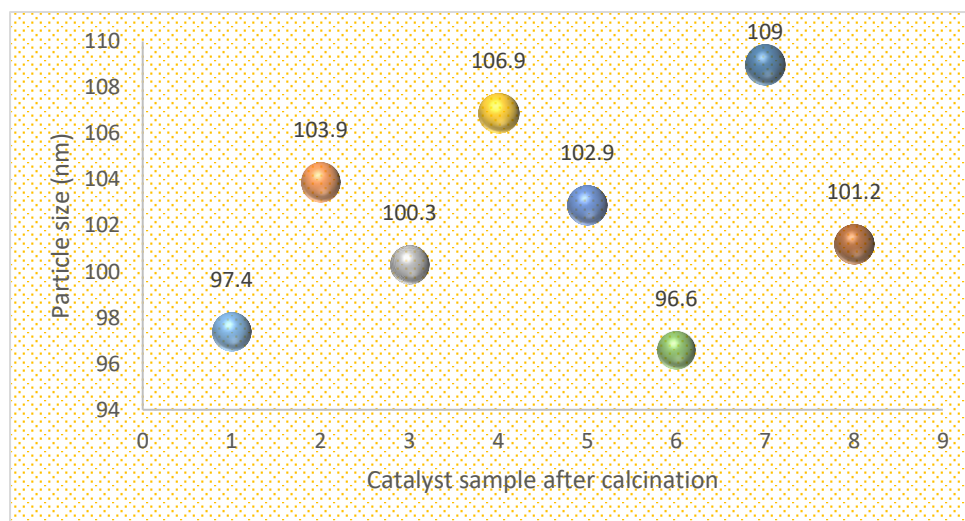
Figure 3: Catalyst particle sizes after calcination at 400 ºC and grinding

Morphology of the catalyst produced was studied using high resolution transmission electron microscopy (HRTEM) Figure 4 represent HRTEM of the catalyst and shows that the catalyst produced is in highly crystalline phases and dispersed in the whitish CaCO$_3$ support matrix.
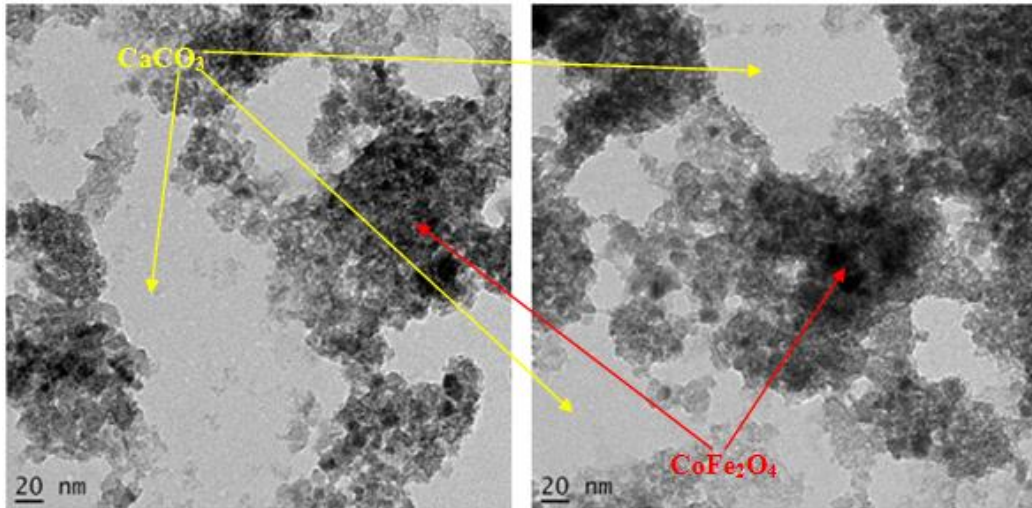
Figure 4: HRTEM of the catalyst

Characterization of carbon nanotubes

The carbon nanotubes were characterised using TGA, XRD, SEM, HRTEM and XPS to determine the thermal stability, crystallinity, morphology and oxidation state respectively and the results obtained presented.

Figure 3 is the TGA profile of purified CNTs sample. It shows an onset temperature at 490 ⁰C and peak temperature at 533 ⁰C with the weight loss of about 34.87% indicating 34.87% of pristine MWCNTs decomposed. This represents the characteristic of a crystalline graphitic carbon confirming very little or no presence of both metallic impurities and amorphous carbon.
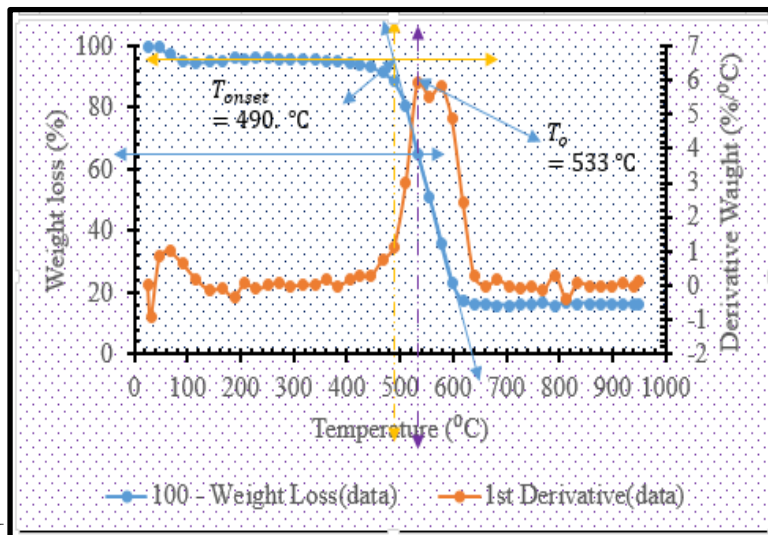
Figure 5: TGA-DTG Curves of Purified MWCNTs

The crystal structure of the as deposited and purified CNTs was determined by, Bruker AXS D8 X-ray diffractometer machine Kα radiation and λ of 0.1541 set and scanning rate at 1.5 ⁰/min, while a step width of 0.05° was used over the 2θ range value of 20 – 90 ° as shown in Figure 4.
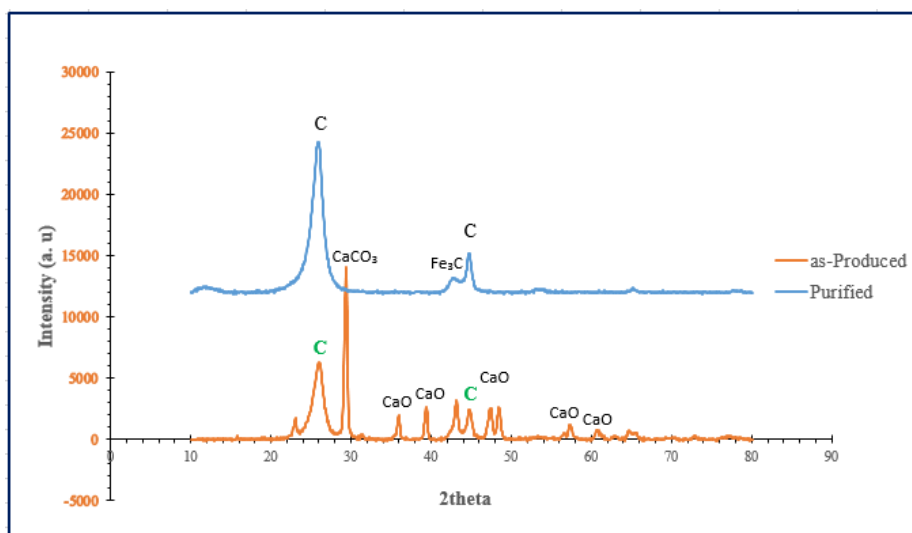
Figure 4: XRD pattern of combined plots of as-produced and purified MWCNTs

The figure revealed the diffraction of X-rays characteristic of graphene layers that make up the tube walls at 2θ values of 25.8736 º and 44.6584 º for the purified CNT. The diffraction peaks at $2\Theta \approx 25.87$ º and $2\Theta \approx 44.66$ º corresponding to the crystal planes (002) and (101) respectively with the hexagonal lattice parameters "a = 2.47 and c = 6.80". These corresponds to an interplanar distance, of 0.3354 nm (3.354 Å) and 0.20312 nm (2.0312 Å) characteristic planes of graphitised carbon of the CNTs[16]. The Fe_3C peak indicate presence of metallic impurities inside the tube shielded from the acid during the purification process.[17]

The CNT produced was analysed for surface morphological and alignment test of tube bundles. Figure 5(a) and (b) are the SEM micrograph of the as-produced and purified CNTs respectively.
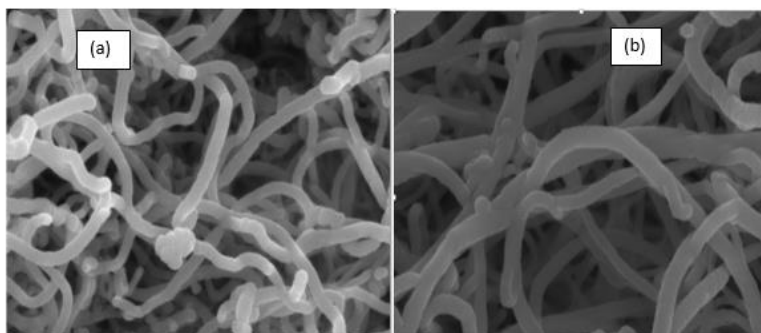

Figure 5: SEM micrograph of the (a) as-produced and (b) purified MWCNTs

SEM images exhibit a clearly defined tubular morphology (nodules-like structure). The SEM micrograph shows that the nodules-like structure is well arranged, smooths and not entangled.

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[16] Abdulkareem, A. S., Suleiman, B., Abdulazeez, A. T., Kariim, I., Abubakre, O. K. and Afolabi, A. S., (2016). Synthesis and Characterisation of Carbon nanotubes on Fe/Al$_2$O$_3$ Composite Catalyst by Chemical Vapour deposition Method. *Proceedings of the World Congress on Engineering and Computer Science, San Francisco, USA,* 11.; Afolabi *etal.,* (2011) Op. Cit n.13

[17] Chiwaye, N. J. (2014). Insitu powder XRD and Mössbauer study of Fe-Co supported on CaCO$_3$. *Materials Research Bulletin,* 56, 98.

The EDS analysis of the as-produced and purified CNTs is presented in Figures 6 (a) and (b) respectively.
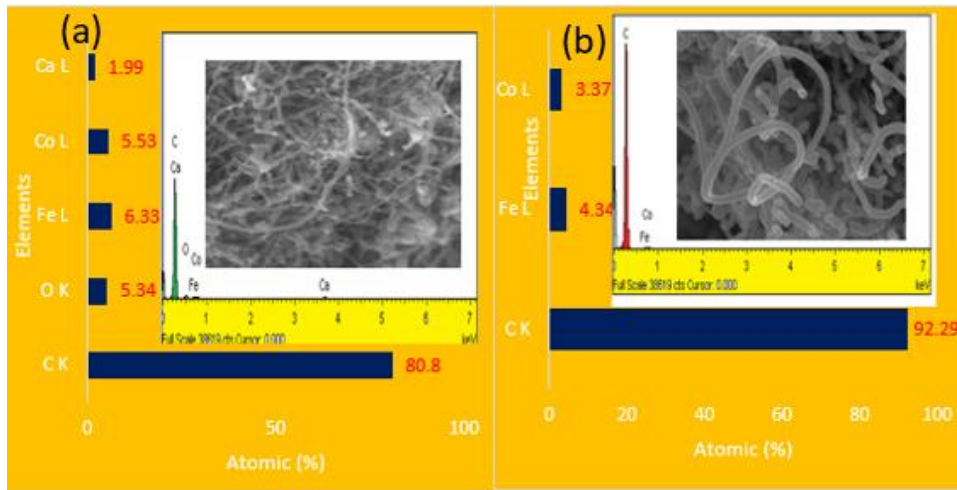

Figure 6: SEM/EDS of (a) as-produced and (b) purified MWCNTs showing the atomic % composition of each element in the samples

The results reveal that the as-produced nanotubes have purity of about 80.8 wt % C, while the purified samples had a higher percentage of 92.29 wt % C. The EDS also revealed that CaO, $CaCO_3$, and amorphous carbon in the as-produced CNTs were effectively removed by the acid purification process. Though the EDS results shows that the purified CNTs still contains metallic particle of Fe and Co after purification. The purity of CNTs depends on the techniques used in production of CNTs and purification methods.[18]

TEM micrograph of as-produced and purified CNTs presented in Figure 7(a) and (b) respectively shows that both the wall structures diameter distribution varied. Result also show that the CNTs produced is cylindrical in shape with many walls Figure 7(c) and (d). Confirming the CNTs produced are multiwalled carbon nanotubes with concentric tubes from the tip. Encapsulated metal nanoparticles are observed along the inner diameter of the nanotubes.

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[18] Mohammed, I. A., (2016). Response Surface Approach to Formulation of Bimetallic (Fe/Co) Catalyst on CaCo₃ Support for Carbon Nanotube Growth. *Unpublished MTech Theses, Federal University of Technology, Minna, Nigeria.* 97-180
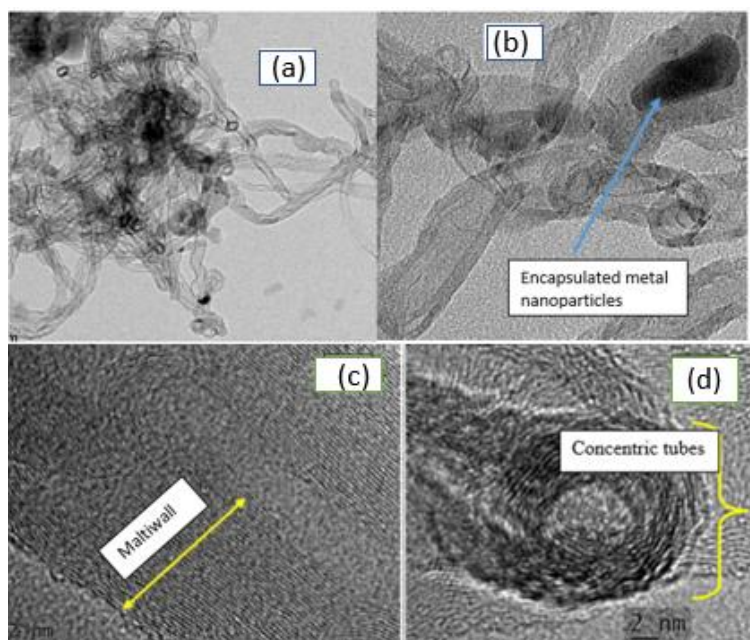
Figure 7: TEM image of (a) as-produced MWCNTs (b) purified MWCNTs with encapsulated metal nanoparticles (c) image showing multiple walls, and (d) concentric tubes

The particle sizes of purified MWCNTs were determined by the method of cumulants in a nano Zetasizer machine. The result shows that samples have Z-average (Z_h) of 810.7 nm and poly dispersity of 0.456. This Z-average result obtained from DLS cannot be regarded as the actual particle size of the sample because DLS measurement is based on spherical shape, however CNTs, is rather cylindrical. In looking for the size of CNTs, aspect ratio plays an important role. It is a factor that determine what the CNTs are to be used for based on its length. The length of CNTs determines its application in various fields.

Therefore, Z-average (D_h) obtained from DLS, is used to estimate values of length (L) of the purified MWCNTs. The associated equation used for the estimation of length (L) and thus the aspect ratio (L/d). as stated in the literature[19] is:

$$D_h = \frac{L}{\left\{ ln\left(L/d\right) + 0.32 \right\}}$$

Value of diameter (d) is obtained from the TEM Figure 8 shows the correlation chart between the aspect ratio, length and diameter of the purified MWCNTs.

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[19] Horiba Scientific Ltd (2023). Dynamic Light Scattering (DLS) Particle Size Distribution Analysis https://www.horiba.com/int/scientific/technologies/dynamic-light-scattering-dls-particle-size-distribution-analysis/dynamic-light-scattering-dls-particle-size-distribution-analysis Retrieved May, 2023; Nair, N., Kim, W. J., Braatz, R. D., & Strano, M. S, (2008). Dynamics of Surfactant Suspended Single-Walled Carbon Nanotubes in a Centrifugal Field. *Langmuir*, 24(5), 1790 – 1795
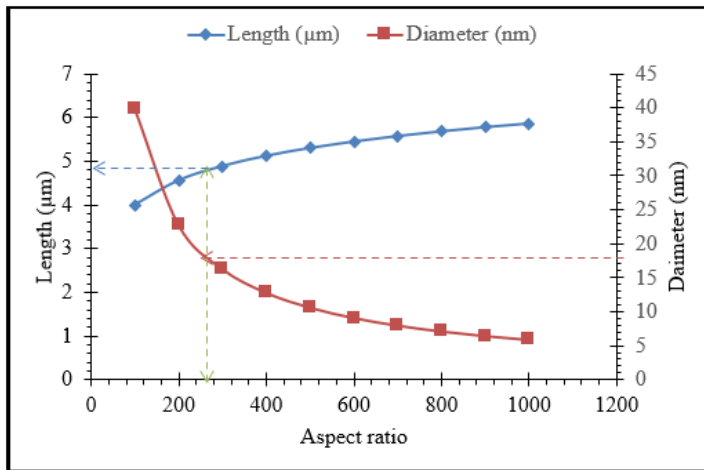
Figure 8: Aspect ratio correlation of length and diameter of purified CNTs

The results indicate that the aspect ratio of CNTs is 265 with length of 4.8 μm, this result agreed with Rashid *et al*.[20] which states that the aspect ratio of MWCNTs synthesised by CVD process could range from 157 to 3750.

Specific surface area (m^2/g) of as-produced and pristine MWCNTs are presented in Table 3. The result show that there is no much significant deference in the pore volume of both as-produced and the purified MWCNTs but their specific surface area varies. The variation in specific surface area of the two CNTs (as-produced and purified) is attributed to removal of impurities from as-produced after purification. Also, purification process involves ultrasound procedure that breaks the CNT agglomerates which result in more separate CNT in the same mass and volume, thus more surface area[21],[22],[23].

Table 3: BET analysis of as-produced and pristine MWCNTs samples

MWCNTs.	Surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})
As-produced	272.98	62.72
Purified	274.06	62.97

The wide XPS scan of the purified MWCNTs sample is shown in Figure 9 (a), and shows the presence of C, O, Ca, N and S. The N and S are at very low concentration, from the purification

[20] Rashid, K., Abu, A. R., Ahmad I. A. and M.T. Bryan, (2012). On the aspect ratio effect of multi-walled carbon nanotube reinforcements on the mechanical properties of cementitious nanocomposites. *Journal of Construction and Building Materials*. 35, 647-655

[21] Naseh, M., Khodadadi, A. and Mortazavi, Y., (2009). Functionalization of carbon nanotubes using nitric acid oxidation and DBD plasma. *International Journal of Chemical Engineering,* 37, 177–179

[22] Chakraborty, S., Chattopadhyay, J., Peng, H., (2006). Surface area measurement of functionalized single-walled carbon nanotubes. *Journal of Physical Chemistry B*. 110, 24812–24815.

[23] Peigney, A., Laurent, C., Flahaut, E., (2001). Specific surface area of carbon nanotubes and bundles of carbon nanotubes. *Carbon*. 39, 507–14.

of the MWCNT using HNO_3 and H_2SO_4, while O and Ca are from the $CaCo_3$ catalyst substrate the presence of Argon (Ar) is the Ar gas used in the CVD reactor.
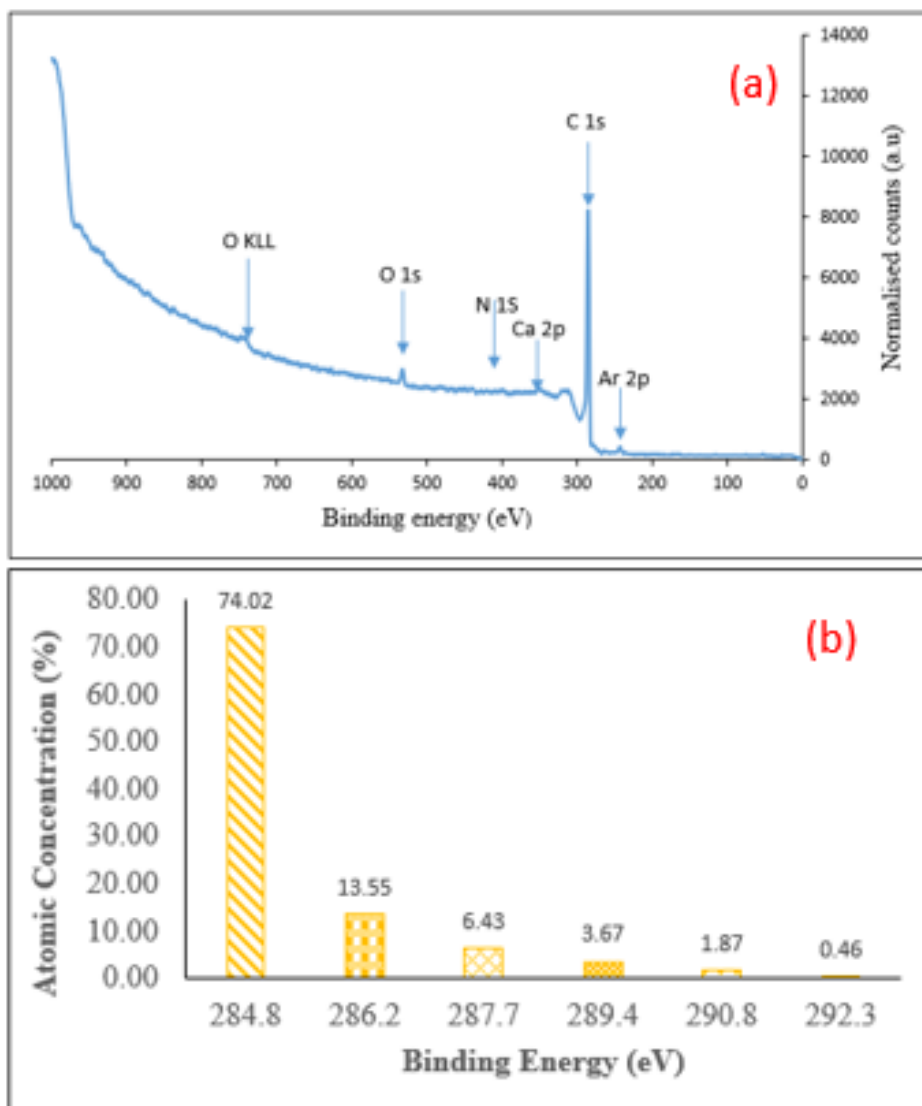

Figure 9: (a) XPS Scan of purified MWCNTs (b) Atomic % concentration of C 1s region for purified MWCNTs

The scan revealed that C 1s is major part of the sample with the binding energy of 284.8 eV and atomic percentage (at %) of 74 %, and O 1s of binding energy of 532.5 eV, while Ca 2p is the remnants of the catalyst support ($CaCO_3$) used in the production of the CNTs

Deconvolution of the C1s peak of sample (Figure. 10.) shows that the peak at 284.8 eV, is attributed to the graphitic structure of carbon atoms in poly-aromatic structures ($C(sp^2)$) and carbon atoms in aliphatic structures ($C(sp^3)$).
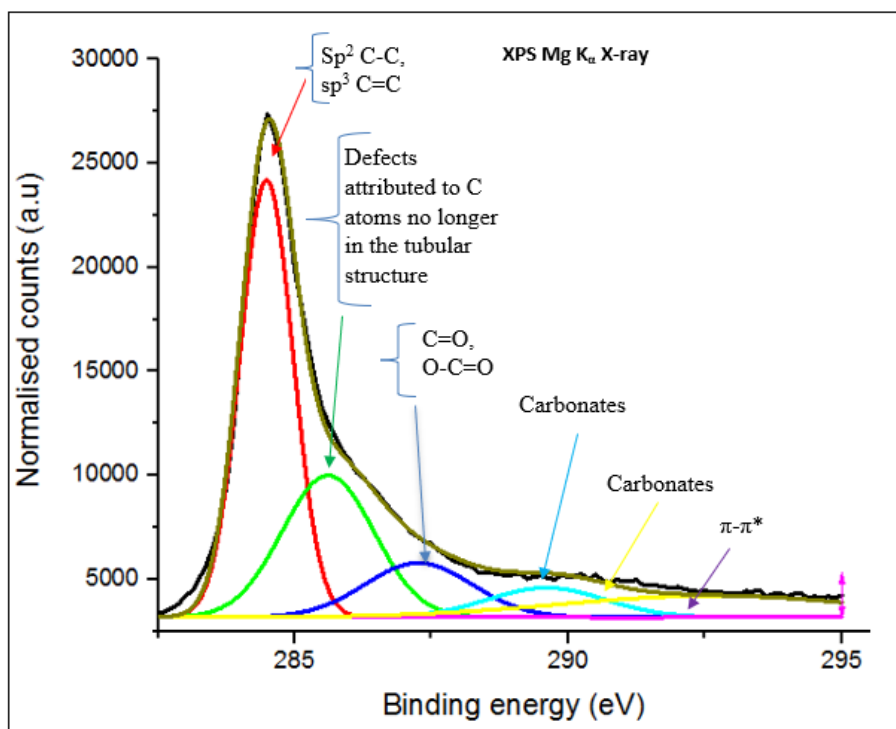
Figure 10: High resolution curve of C 1s on pristine MWCNTs

The observations agree with the literature on photoemission studies on MWCNTs.[24] Also, peak at 286.21 eV indicate defects on the structure of nanotube[25] whereas the peaks at 287.71, 289.41 and 290.81 eV, attributed to attachment of different oxygen-containing moieties, this agrees with studies on functionalisation of carbon nanotubes.[26] Lastly, the π-π* transition loss peak was also detected at 292.31 eV, denote the attractive force on surface of the CNTs.

Conclusion

This work is focussed on the optimization of catalyst production by wet impregnation through 2^3 factorial designs of experiment for multiwalled carbon nanotubes production. The optimum conditions for the catalyst production were established when the mass of catalyst used was 10g, drying temperature of 120°C and drying time of 12 hours. The developed catalyst was suitable for the production of multiwalled carbon nanotubes that is thermally at temperature slightly higher than 500°C. The purification techniques adopted in this study is effective and able to remove the impurities present in the carbon nanotubes includes the amorphous carbon with causing any defect on the carbon nanotubes. It can be concluded based on the various analysis conducted that Fe-Co/CaCO₃ catalyst developed by the wet impregnation method is suitable

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for the production of multiwalled carbon nanotubes in a catalytic vapour deposition (CVD) reactor.