UTILISATION OF LOCAL KAOLIN AS CATALYST SUPPORT IN THE PRODUCTION OF CARBON NANOTUBES USING CATALYTIC VAPOUR DEPOSITION METHOD

Abdulkareem A. S[1,2,*], Suleiman B[1], Kariim I[2], Onimisi I[1], Kovo A.S[1] and Mohammed I.A[2]

[1]Chemical Engineering Department, Federal University of Technology, PMB 65, Bosso, Minna, Niger State
[2]Nanotechnology Research Group, Centre for Genetic Engineering and Biotechnology, Federal University of Technology, PMB 65 Bosso, Minna, Niger State

Corresponding author: kasaka2003@futminna.edu.ng Phone: +2347068482432

ABSTRACT

The work focused on the use of kaolin as support material for the development of Fe/Kaolin monometallic catalyst for multi-walled carbon nanotubes synthesis (MWCNTs) in catalytic vapour deposition equipment. The influence of process parameters such as drying temperature, drying time, stirring speed and mass of support on the percentage yield of monometallic Fe/Kaolin catalyst using wet impregnation method was further reported using a factorial experimental approach. The optimum yield of 79.40 % was obtained at a drying temperature of 120 °C, drying time of 5 hours, stirring speed of 7 rpm, and 9 g mass of support during the optimization of the process parameters. The highest yield catalyst was then characterized for surface area, morphology, functional group, and crystallinity using BET, SEM/EDX, FTIR and XRD respectively. The well characterized catalyst was further used for the synthesis of MWCNTs in a CVD reactor and the effect of acetylene flow rate on the MWCNTs yield was recorded. It was found that the flow rate of acetylene was directly proportional to the MWCNTs yield. The synthesized MWCNTs possessed excellent morphology and surface area. Hence, the applied kaolin support showed high proficiency for possible application as catalyst support for synthesize of good quality MWCNTs in a CVD reactor.

***Keywords**: kaolin, wet impregnation, optimization, characterization, MWCNTs and CVD*

1.0 INTRODUCTION

The discovery that materials can exist in their nano scale and still maintain most of its properties stimulated many researchers around the world to begin the production of smaller, lighter, faster, and cheaper devices which possess greater functionality (Xi *et al.*, 2006). Nanoparticles, due to their smaller size and large surface to volume ratio, exhibit interesting novel properties which include nonlinear optical behavior, increased mechanical strength, enhanced diffusivity, high specific heat, magnetic behavior and electric resistivity, (Kavecký *et al.*, 2015). Though, syntheses of various nanoparticles such as gold nanoparticles, silver nanoparticles and carbon nanoparticles have been reported in literature (Afolabi et al., 2007), this present study focus on the synthesis of carbon nanotubes (CNTS).

CNTs are cylinder-shaped macromolecules having a radius as small as a few nanometers, which can be grown up to 20 cm in length. The walls of these tubes are made up of a hexagonal lattice of carbon atoms analogous to the atomic planes of graphite. They are capped at their ends by one half of a fullerene-like molecule (Guo *et al.*, 1995). It has been reported that laser ablation, arc discharge and catalytic vapour deposition methods are the three main methods of CNTs production, however catalytic vapour deposition (CVD) method has been described as the viable route of CNTs production in commercial quantities and qualities (Teo *et al.*, 2004; and Kariim *et al.*, 2015). Despite the robust nature of CVD for CNTs production, it has been reported that lack of understanding of CNT growth mechanism has caused hindrance in the production of CNT with well-defined properties (Kumar, 2012). This necessitated the need to study the several parameters such as the catalyst preparation method, type of metal and support to be used, synthesis route to be applied and type of carbon source (Kumar, 2012). Among all the factors listed, catalyst and its support play a major role in the production of CNTs which brought about the need for detail study of the effects of catalyst support on the yield and qualities of CNTs produced by CVD method. Even though several support materials such as $CaCO_3$, Al_2O_3, SiO_2 and Zeolite have been reported in literature (Afolabi et al., 2007; Iyuke et al., 2007), there is little information on the utilization of kaolin as a catalyst support for CNTs growth. It is on this basis that

this present study is focused on the development of monometallic (Fe) catalyst with Kaolin support material

2.0 MATERIAL

The chemicals and gas used in this study were of analytical grade and they include Iron (III) nitrate Nona hydrate (98.5% purity), argon gas (99.9% purity) and acetylene (99.9% purity). Kaolin used in this study was obtained in Lagos, while the distilled water was obtained from Centre for Genetic and Biotechnology, Federal University of Technology, Minna, Niger State, Nigeria.

2.1 Catalyst Preparation

Preparation of catalyst involves wet impregnation of iron salt on kaolin support and the influence of the process of impregnation on the yield of the catalyst was investigated using 2^4 factorial experimental designs. This implies that four factors were studied at two (low and upper) levels as shown in Table 1. A calculated amount (4.65g) of Iron (III) nitrate Nona hydrate salt was dissolved in 50ml of distilled water and shaken to form homogeneous solution. A given quantity of kaolin (lower level - 8g and upper level - 9g) was added to the mixture and stirred at a known stirring speed of 400 rpm and 700rpm respectively for lower and upper level for a period of twenty minutes. The slurry obtained was then oven-dried at a selected temperature of 110°Cand 120°C respectively for lower and upper level. The drying of the sample obtained was done in an oven for a pe riod of 5 hours and 7 hours respectively for the lower and upper level. The sample obtained was then allowed to cool at room temperature, grinded to avoid particle agglomeration and screened through 50 µm. The screened sample was then calcined at temperature of 500°C for a period of 14 hours. The yield of the catalyst obtained was then calculated using the Equation 1. The detailed experimental combination obtained from the design expert with the yield of catalyst as the output is as presented in Table 2.

$$yield(\%) = \frac{mass\ of\ catalyst\ after\ calcination}{mass\ after\ oven\ drying} \times 100 \quad (1)$$

The sample that gave the best yield was analyzed using TGA, SEM/EDX, XRD, FTIR and BET to respectively determine the thermal stability, morphology, crystallinity and surface area. FTIR was also used to determine the type of bond present in the catalyst developed.

Table 1: Level of Factors for Catalyst Synthesis

	Mass of support (g)	Stirring speed (rpm)	Drying temp. (°C)	Drying time (hr)
Upper (+) Level	9	700	120	7
Lower (-) level	8	400	110	5

2.2 Carbon Nanotubes Synthesis

The Fe/Kaolin composite catalyst developed was then utilized in the production of Carbon Nanotubes in Catalytic Vapour Deposition (CVD) Reactor with acetylene as the carbon source. The CVD reactor used in this study was made of a quartz tube (52 mm internal diameter, 4 mm thickness and 1010 mm length), placed in a furnace that has heating capacity of 1200°C. Gas cylinders for the carbon source (acetylene) and the carrier gas (Argon) were connected to the inlet of the reactor which had flow meters to control the gas flow. The control system of the CVD allows for an appropriate temperature program in maintaining consistent and appropriate heating rate, reaction temperature, and cooling rate. The exhaust gases through an exhaust pump at the reactor outlet were collected by bubbling in water. A known weight (1.0 g) of the monometallic Fe catalyst on kaolin support was placed in the ceramic boat, which was inserted in the horizontal quartz tube of the CVD furnace. The production temperature was kept constant at 750°C while the production time was varied between 20 to 60 minutes with step increment of 10 minutes. The furnace was set to the required temperature of 750°C during which argon was allowed to flow over the catalyst at a flow rate of 30ml/min this is for the purpose of purging the system of the air that might have been trapped in the reactor during the process of placing the catalyst inside the reactor. When the system attained the set temperature of 750°C, the argon flow rate was adjusted to 100 ml/min and acetylene was introduced into the system at the required flow rate of 20, 30, 40, 50, 60 ml/min for a period of 40 minutes. After which the flow of acetylene was stopped and the flow rate of argon was reduced to 30ml/min to cool the furnace to room temperature. The boat that contained the black soot was then removed and weighed to determine the quantity of CNTs produced. Percentage of CNTs produced was determined using Equation 2 (Lee *et al.*, 2009).

$$\frac{MTotal - MCatalyst}{MCatalyst} \times 100\ \%$$

Where, MTotal = the total mass of the catalyst and carbon products after CVD reaction process;
MCatalyst = initial mass of Fe/kaolin catalyst

The CNTs produced were characterized with SEM-EDX, TEM, XRD and BET to determine their morphology, nature, crystallinity/crystallite size and surface area respectively.

3.0 RESULTS AND DISCUSSION

3.1 Kaolin Characterization

Results obtained showed that the raw kaolin had a specific surface area of 98.79 m^2/g, pore volume of 0.0885 cc/g and a pore size of 0.3102 nm. These properties showed that raw kaolin is a micro-porous material with an order of a few molecular diameter of the inter-molar distance (Hendrik *et al.* 2011). Thermal stability analysis of the raw kaolin was also conducted; the results obtained revealed that the kaolin sample was thermally stable up to a temperature of 800°C with less than 15% lost in weight as shown in Figure 1. This is an indication that the kaolin sample will be thermally suitable as catalyst support for the production of CNTs.

Presented in Figure 2 is the SEM micrograph of kaolin, which showed that it was plate-like in nature with irregular particle shapes containing compartments of aluminosilicate. The micrograph also showed that the particles of raw kaolin were well defined with porosity that were related to the spaces between agglomerates, the presence of this agglomerates as well as large particle size defined the density of this material.

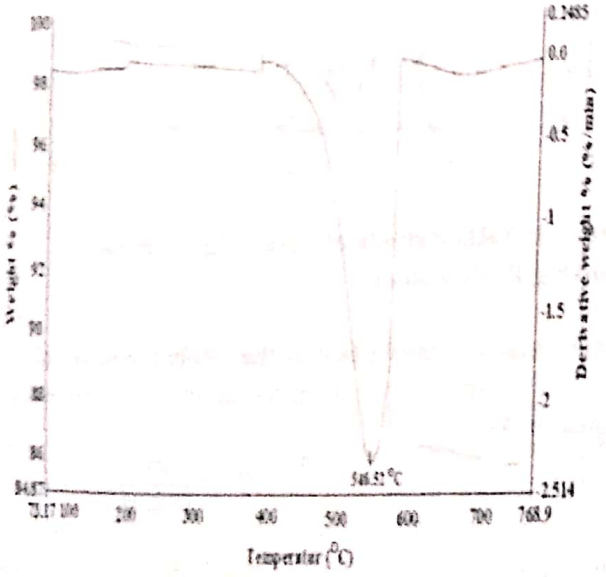

Figure 1: TGA/DTG Thermograph of Kaolin support

Figure 2: HRSEM Micrograph of kaolin sample

3.2 Catalyst Preparation

The effects of operating condition such as mass of support (kaolin), stirring speed, drying time and drying temperature on the yield of monometallic Fe/kaolin were presented in Table 2 using 2^4 factorial design of experiments. The optimum catalyst yield of 79.4 % was obtained at a drying temperature of 120°C, drying time of 5 hours, stirring speed of 7 rpm, and 9 g mass of support.

Table 2: Influence of Operating Parameters on the Yield of Catalyst

Run order	Mass of support (g)	Stirring Speed (rpm)	Drying Time (hrs)	Drying Temperature (°C)	Yield (%)
1.	8	400	5	110	77.8
2.	9	400	5	110	77.21
3.	8	700	5	110	76.74
4.	9	700	5	110	77.23
5.	8	400	7	110	77.69
6.	9	400	7	110	76.61
7.	8	700	7	110	77.84
8.	9	700	7	110	78.01
9.	8	400	5	120	75.47
10.	9	400	5	120	77.23
11.	8	700	5	120	77.28
12.	9	700	5	120	77.43
13.	8	400	7	120	77.62
14.	9	400	7	120	78.49
15.	8	700	7	120	78.60
16.	9	700	7	120	79.46

The yields of catalyst were used to carry out factorial design analysis, this involved the analysis of variance (ANOVA) to create theoretical model for the main and combined effect on yield after calcination. The equation for estimating yield in terms of significant factors is presented as follows (Equation 3):

$$\%\,Yield = +77.47 + 0.53(mass\ of\ support) + 0.33(stirring\ speed) + 0.35(drying\ time) - 0.37(stirring\ speed \times drying\ time \times drying\ temperature) \quad (3)$$

The highest yield of Fe/Kaolin produced at the optimum yield was characterized for surface morphology, elemental analysis, surface area, surface functional group and crystallinity. Figure 3 depicts the HRSEM micrograph of the catalyst sample.

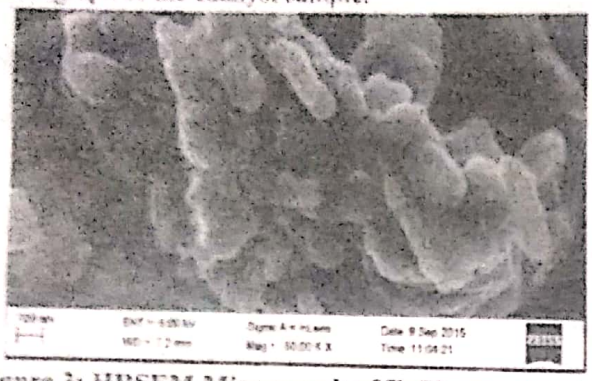

Figure 3: HRSEM Micrograph of Fe/Kaolin Catalyst

Results presented in Figure 3 showed that the catalyst is nearly spherical in geometry with the formation of agglomerate which can be linked to the formation of oxide on the surface and pores of the kaolin sample. Also, proper dispersion of the metal on the support material was achieved as shown by the presence of small pores within the composite as seen from Figure 3 compared to the starting kaolinite clay. Figure 4 showed the EDS spectral of the catalyst sample.

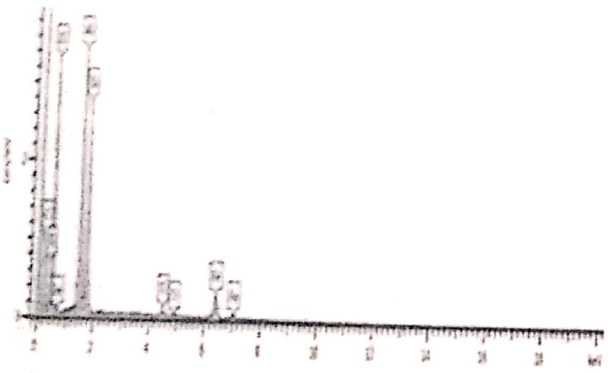

Figure 4: EDS Spectral of Fe/Kaolin Catalyst

Figure 4 showed the EDS spectrum which confirmed the presence of Fe, C, O, Al, Si and Ti chemical components in different proportions in the catalyst matrix. The observation of element such as Fe at lower energy level showed that it could be present in the oxide form.

Brunauer-Emmett-Teller (BET) analysis was used to determine the surface area, pore radius, pore volume and pore size of the catalyst. Table 3 showed the summary of the BET data of the catalyst sample obtained in a Nitrogen environment. The obtained characteristics depicted in Table 3 showed that the developed catalyst was of high and good crystallinity with pores classified as nicropores according to IUPAC nomenclature. This revealed that the catalyst produced possessed adequate textural properties that will allow the diffusion of carbon sources into the catalyst pores for CNTs growth

Table 3: Summary of BET Results of Developed Fe/Kaolin

Properties	Catalyst
Surface area (single point) (m^2/g)	119.2
Pore volume (DR method micropore volume) (cc/g)	0.07407
Pore size (DR method micropore half pore width) (nm)	0.3091

The X-ray diffraction method was used to analyze the crystalline size and texture of the catalyst sample (Figure 5). The detailed identification of the phase presence in the bulk of the Fe/Kaolin catalyst was shown in Figure 5. The estimated particle size showed that Fe/kaolin catalyst with particles in nanometer range can be produced under appropriate synthesis conditions (Kariim et al., 2015 and Iyuke et al., 2007).

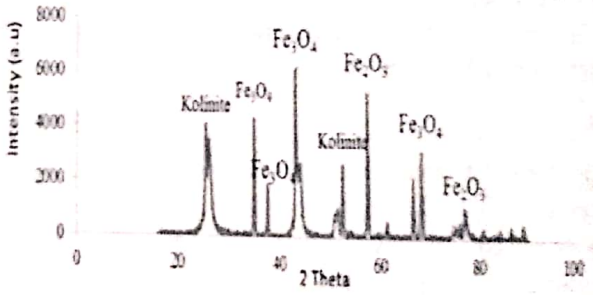

Figure 5: XRD Pattern of Fe/kaolin Catalyst Showing Peak Values

The average crystallite size of the catalyst was found to be 35.27 nm using DeBye-Scherrer Relationship (Equation 4).

$$D = \frac{K\lambda}{\beta COS\theta} \quad (4)$$

Where D is the particle size diameter, β is the full width at half maximum, θ is the diffraction angle, λ is wave length of X-ray (0.1541 nm) and K is Scherer constant (0.94). Fourier Transform Infrared Spectroscopy Analysis, FTIR (Figure 6) was used for identifying the surface functional group present on the prepared Fe/kaolin monometallic catalyst.

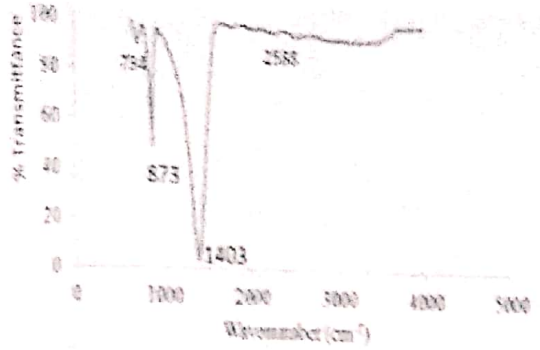

Figure 6: FTIR Spectral of Fe/Kaolin Catalyst

Figure 6 revealed the presence of several peaks with different functional groups; the observed wavenumber at 734 cm^{-1} corresponded to the O-Al-O symmetric bending vibration, the band wavelength at 873 cm^{-1} was assigned to the region of OH with Fe, while the adsorption band at 2588 cm^{-1} was attributed to OH bending hydration (Aliyu, 2016).

3.3 CNTs Production

The well characterized Fe/Kaolin was used for the synthesis of carbon nanotubes in a CVD reactor. During the latter process, the effect of acetylene flow on the percentage yield of CNTs was examined at constant argon flow rate (100mL/min), reaction temperature (750 °C) and deposition time (40 mins). Table 4 showed the results of the effect of acetylene flow rate.

Table 4: Effect of Acetylene Flow Rate on the Percentage Yield of CNTs

Runs	Acetylene flow rate (ml/min)	Mass of CNT produced (g)
1	20	0.02
2	30	0.19
3	40	0.37
4	50	0.43
5	60	0.53

From Table 4, the effect of acetylene flow rate on the percentage yield of CNTs has been observed to exhibit direct proportionality relationship. This shows that as the flow rate of the carbon source increases, more of the carbon from the source is introduced into the reactor for deposition on the catalyst surface (Kariim et al., 2015). The highest yield CNTs obtained at the flow rate of 60 mL/min was characterized for surface area, functional group, crystallinity, morphology, and EDS for elemental composition.

The BET results of the produced CNTs were as follows: specific surface area = 299.167 m^2/g, specific pore volume = 0.01106 cc/g and pore size = 0.3171 nm. These characteristics showed that the CNTs have potential as adsorbent materials for wastewater purification and in catalysis (Afolabi et al., 2007). Figure 7 showed the surface morphology of the synthesized carbon nanotubes.

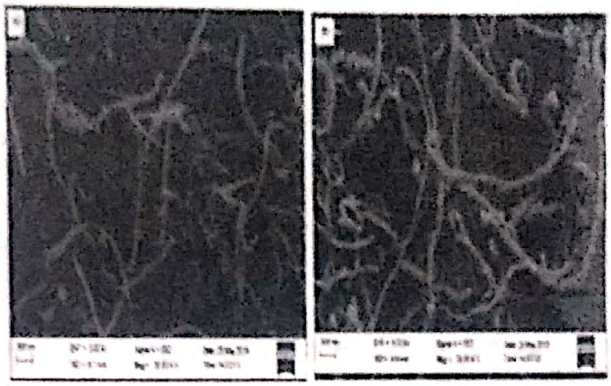

Figure 7: HRSEM of CNTs for (a) High Yield and (b) Low Yield CNTs

Figure 7 a and b showed clearly that the structural morphology of the synthesized CNTs varied. In Figure 7a high yield CNTs depicted densely populated strands of CNTs with little or low level of branched tubes compared to the low yield carbon nanotubes. Thus, it was revealed that low flow rate favored the synthesis of branched and irregular CNTs formation. The EDS analysis resulted in useful information on the elements present in the CNTs in terms of percentage composition. The results of the EDS analysis were shown in Figure 8.

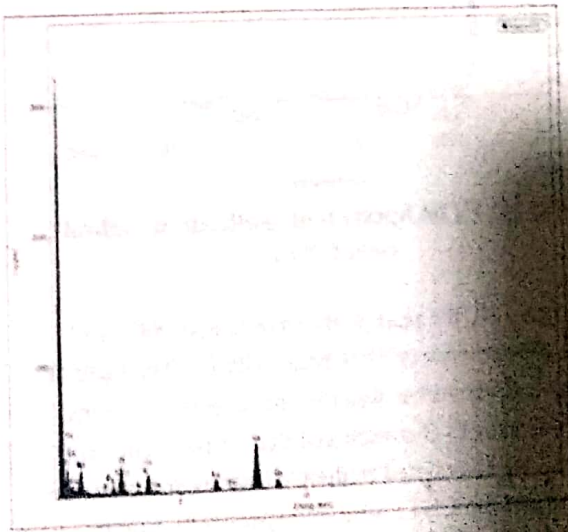

Figure 8: EDS Spectral of theSynthesized CNTs of the Highest Yield of Produced CNTs

The EDS data showed the presence of high amount of C and other impurities resulting from the kaolinite clay used as support material.

The X-Ray diffraction technique was used to investigate the crystallinity of the CNTs produced. Figure 9 showed the XRD pattern of the produced CNTs for varying conditions for runs 1-5(Acetylene flow rate of 20-60ml/min with step increment of 10ml/min) as depicted in Table 4. The characteristics peaks of the graphitized carbon were depicted in Figure 9 at 2 theta of 25.14 and 44.73 ° in all the CNTs samples produced. The presence of diffraction peaks was an indication of the iron oxides introduced by the catalyst material as an impurity, which must be removed to promotes the utilization of CNTs for various industrial applications (Karnim et al., 2015).

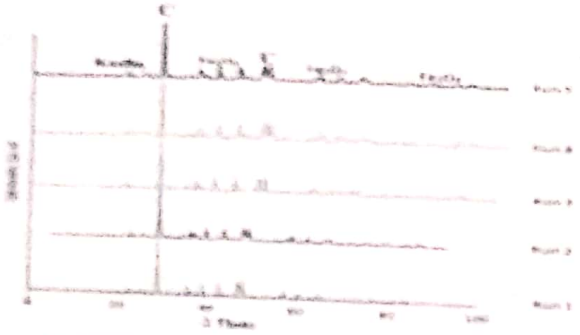

Figure 9: XRD Spectral of the Synthesized CNTs at Various Acetylene Flow Rates.

Furthermore, the surface functional group present in the synthesized CNTs was further characterized using the FTIR technique (Figure 10).

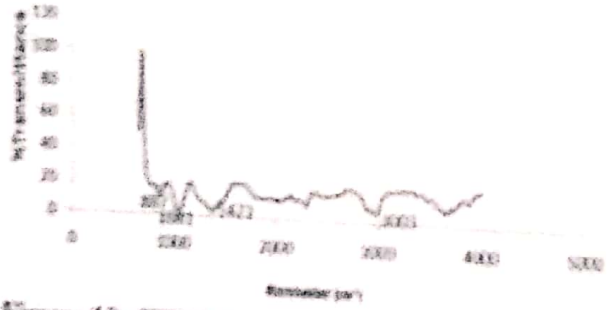

Figure 10: FTIR Spectral of synthesized highest yield CNTs

From Figure 10, the peak with wavenumber 887 cm^{-1} showed the presence of O-H bond with Fe. The peak of 1081 cm^{-1} wavenumber was the characteristic regions representing the C-O stretch and that of 1423 cm^{-1} and 3003 cm^{-1} were assigned to the C-H bends and stretches in the bulk of the CNTs sample respectively. Figure 11 represented the internal morphology of the highest yield of the synthesized CNTs.

Figure 11: HRTEM Micrograph of the Synthesized CNTs.

The Figure 11 showed the internal structural makeup of the developed CNTs. It was found that the CNTs produced MWCNTs with series of concentric tubes of varied diameter. The presence of encapsulated catalyst particles in the tubes of the CNTs was depicted by the blackishly dense spots in Figure 11.

5.0 CONCLUSION

The study addressed the suitability of locally sourced kaolin as a support material for the development of monometallic catalyst for the synthesis of high quality MWCNTs in a CVD reactor. The optimum yield of 79.40 % was obtained at a drying temperature of 120 °C, drying time of 5 hours, stirring speed of 7 rpm, and 9 g mass of support during the optimization of the process parameters. Wet impregnation methods employed showed a high level of catalyst dispersion for high efficiency. Thus, the TEM images of the synthesized CNTs showed that the nanomaterial produced was MWCNTs with irregular diameter. The study further showed that the flow rate of acetylene was directly proportional to the percentage yield of the MWCNTs in a CVD reactor. Hence, the application of kaolin as a support material showed high suitability level for the development of monometallic Fe/kaolin for the synthesis of MWCNTs.

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REFERENCES

Afolabi, A. S., Abdulkareem, A. S. & Iyuke, S. E. (2007). Synthesis of carbon nanotubes and nanoballs by swirled floating catalyst chemical vapour deposition method, Journal of Experimental Nanoscience 2(4): 269-277.

Guo, T., Nikolaev, P., Rinzler, A. G., Tomanek, D., Colbert, D. E., and Smalley, R. E. "Self-Assembly of Tubular Fullerenes", J. Phys. Chem., 99 (1995) 10694-10697.

Iyuke, S.E., Abdulkareem, A. S., Afolabi, A. S. & Piennar, C. H. vZ. (2007). Catalytic production of carbon nanotubes in a swirled fluid chemical vapour deposition reactor, International Journal of Chemical Reactor Engineering 5(Note S5):1-9

.

Kariim 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. International Engineering Conference (IEC2015); 09/2015 .

Kavecký S., Valúchova J., Čaplovičová M., Heissler S., Šajgalík P., Janek M. (2015). Nontronites as catalyst for synthesis of carbon nanotubes by catalytic chemical vapour deposition. Applied Clay Science, 114: 170-178.

Kumar, M. and Ando, Y., (2012) "Chemical Vapor Deposition of Carbon Nanotubes: A Review on Growth Mechanism and Mass Production", Journal of Nanoscience and Nanotechnology Vol. 10, 3739–3758.

Motchelaho A.M.M. 2011. Iron And Cobalt Catalysts Supported on Carbon Nanotubes For Use In The FischerTropsch Synthesis. A thesis submitted to the Faculty of Engineering and the Built Environment, University of the Witwatersrand, Johannesburg, in fulfillment of the requirements for the degree of Doctor of Philosophy, Johannesburg,:http://wiredspace.wits.ac.za/bitstream/handle/10539/11208/PhD%20Thesis-2011-Anne%20Myriam%20Megne%20Motchelaho.pdf?sequence=2

Teo, K.B.K.; Singh, Ch.; Chhowalla, M.; Milne, W.I. Catalytic synthesis of carbon nanotubes and nanofibers. In Encyclopedia of Nanoscience and Nanotechnology; Nalwa, H.S., Ed.; American Scientific Publisher: Valencia, CA, USA; Volume 1, pp. 665–668, 2003.

Xi S, Ci L, Tang D, Yan X, Li Y, Liu Z, Zou X, Zhou W and Wang G (2006), Chem. Phys. Lett. 349, 191–195.