Synthesis of Carbon Nanotubes using Catalytic Chemical Vapour Decomposition of Acetylene over Co-Mo bimetallic Catalyst supported on Magnesia

***Buhari, S. A.[1]; Abdulrahman, A. S.[2]; Abdulkareem, A. S.[3]; Lawal, S. A.[1] & Akintunde, I. B.[2]**

[1]Department of Mechanical Engineering, Federal University of Technology, Minna, Nigeria.
[2]Department of Materials and Metallurgical Engineering, Federal University of Technology, Minna,
[3]Department of Chemical Engineering, Federal University of Technology, Minna, Nigeria.

E-mail address: shehubuhari32@gmail.com

Abstract

This research work investigates the utilization of acetylene as a precursor for the synthesis of multi-walled carbon nanotubes (CNTs) over bimetallic Co-Mo catalyst supported on magnesia (MgO) via catalytic chemical vapour deposition (CCVD) technique. The CCVD equipment requires the use of catalyst and support in addition to a carbon source (acetylene) and nitrogen gas for CNTs growth. The bimetallic Co-Mo catalyst supported on MgO was prepared by the wet impregnation method, which was placed in the quartz boot inside the CVD equipment. The catalyst sample with the highest yield of 93.22 % was prepared from 16 g support mass, stirring speed of 1500 rpm, stirring time of 20 minutes, drying temperature of 120℃ and drying time of 10 hours. The catalyst was characterized using high-resolution scanning electron microscopy (HRSEM) and X-Ray diffraction spectroscopy (XRD) to determine the catalyst crystallinity, morphology and elemental composition. The catalyst developed was utilized for the synthesis of CNTs by chemical vapour deposition method (CVD) with acetylene as the carbon source and nitrogen as the carrier gas while the CVD furnace was programmed to heat at 10℃ per minute. The effects of synthesis parameters (calcination temperatures, reaction time, and gasses flow rates) on the yield of the CNTs were examined with 2^4 factorial experimental design. The highest yield of 89.09 % of CNTs was obtained at a temperature of 700℃, 250 mL/min and 200 mL/min flow rate for acetylene and nitrogen, respectively. The XRD patterns of the as-synthesized CNTs revealed the development of graphitized carbon, the high-resolution scanning electron microscopy (HRSEM) micrographs indicated the formation of fairly uniform and evenly dispersed carbon nanotubes were grown on the support, while the high-resolution transmission electron microscope (HRTEM) confirm the formation of CNTs with a particle size between 31.21 and 45.03 nm. Also, the HRTEM results further revealed the increase in diameter of CNTs when the temperature is raised from 700℃-800℃. This study establishes the production of CNTs from acetylene precursor over bimetallic Co-Mo catalyst supported on MgO in a CVD reactor.

Keywords: Synthesis, Bi-metallic alloy, Catalytic Chemical Vapour Deposition, Catalyst, CNTs

Introduction

There have been rapid developments in the synthesis and characterization of nanostructured materials especially carbon nanotubes (CNTs) that lied within the nanometre scale from precursor materials since it was first discovered (Iijima, 1991). Carbon nanotubes are unique nanostructured materials with distinct tubular structures and large length to diameter ratios that have received notable attention due to their unique structural, mechanical, thermal, optical, chemical and electronic properties in the fields of science, engineering and medicine (Yang *et al*. 2016). These have drawn the attention of researchers in the field of science and technology to research in this area of study. Significant scientific studies have revealed the potential of CNT applications such as supercapacitors, reinforcements in high-performance composites, hydrogen storage, catalyst support, selective adsorption agents, field emission devices, artificial implants, biosensors, catalyst, diagnostic tools, preservative. CNTs have also been explored for biomedical applications,

lubricants, antibiotics, as well as a carrier for drug delivery (Aliyu *et al*. 2017).
Various methods have been reported to synthesis carbon nanotubes such as chemical vapour deposition (CVD), electric arc discharge, laser vaporisation, pyrolysis plasma-enhanced chemical vapour deposition (PECVD), alcohol catalytic chemical vapour deposition (ACCVD), hydrothermal or sonochemical, and high-pressure CO conversion (HiPco) (Voelskow *et al*., 2014). Thus, the catalytic chemical vapour deposition (CCVD) method has become one of the most promising, successful and versatile methods due to its potential to produce high-quality carbon nanotubes at low synthesis temperatures in large quantity at a relatively low cost (Yang *et al*., 2016). Furthermore, the use of CCVD method makes the advanced design and control of multiple physicochemical properties of the CNTs possible by selecting proper conditions, both physical (diameter, length, and shape) and chemical (graphitization) of the CNTs (Maccallini *et al*., 2010).

The most common catalysts used for the production of CNTs are transition metals (Aliyu *et al*., 2017) supported on silica, magnesium oxide, zeolite, alumina, calcium carbonate and SBA-15 (Hoyos-Palacio *et al*., 2014). Earlier studies on the synthesis of CNTs were carried out using different metallic catalysts particularly Fe, Co, Ni, and their alloys (Aliyu *et al*., 2017). These active transition metals can exist alone (Fe, Co, Mo, and Ni) or as a bimetallic (Fe-Co, Ni-Fe, and Co-Ni), tri-metallic (Fe-Co-Ni, Co-Mo-Fe), or sometimes ternary (Fe-CoNi-Mo) catalyst (Dervishi *et al*., 2009). Allaedini *et al*. (2015) reported the synthesis of carbon nanotubes by the decomposition of methane over the tri-metallic Ni–Co–Fe catalyst. The main advantage of using bimetallic and tri-metallic catalysts is that CNTs could be grown at significantly lower temperatures (Kumar & Ando, 2010). Moreover, alloys are known to be better catalysts than pure metals, as well, it has been shown that the mixing of two or three metals can enhance the catalytic activity (Kumar & Ando, 2010).

The choice of Molybdenum (Mo) as the catalyst promoter to enhance the performance of the catalyst is due to its suitability to be paired with Co to form a bimetallic catalyst which is efficient for synthesis of high-quality CNTs (Tang *et al*., 2001; Ni *et al*., 2006; Niu & Fang, 2007). It has been reported to be a good support for bimetallic Co-Mo catalyst for the synthesis of high-quality CNTs and improved yield (Tang *et al*., 2001; Colomer *et al*., 2000; Yeoh *et al*., 2010). In the synthesis of CNTs, several materials such as Al_2O_3, SiO_2, MgO, $CaCO_3$, zeolite and kaolin have been employed as supports for catalyst synthesis, among the catalyst; MgO possesses the advantage of being removed easily from the CNT products by acids (Ezekiel *et al*., 2014).

Numerous researches have been conducted in the production of CNTs from precursors. Yeoh *et al*. (2010) reported an effective synthesis of carbon nanotubes via catalytic decomposition of methane on support interaction of Co-Mo/MgO catalyst. Also, Lee *et al.* (2010) researched the optimization of carbon nanotubes synthesis via methane decomposition over alumina-based catalyst. While Chai *et al*. (2006) reported the preparation of carbon nanotubes over cobalt-containing catalysts via catalytic decomposition of methane. Abdulkareem *et al*. (2016) investigated the process parameters on the yield of monometallic (Fe) catalyst on Al_2O_3 for possible application in cabon nanotubes growth. The analyses of the study indicated that operating parameters such as mass of support, stirring speed, drying time and drying temperature influenced the yield of catalyst. Aliyu *et al*. (2017) studied the synthesis of multi-walled carbon nanotubes via catalytic chemical

vapour deposition method on Fe-Ni bimetallic catalyst supported on kaolin. Furthermore, Medupin *et al*. (2019) investigated the synthesis and characterization of monometallic cobalt catalyst supported on kaolin for the production of carbon nanotubes. Chiwaye *et al*. (2014) reported the use of $CaCO_3$ supported on a Fe-Co catalyst for effective MWCNTs production using acetylene as the carbon source. The authors observed the presence of CaO in the synthesized MWCNTs due to the partial decomposition of $CaCO_3$.

This study investigated the combined effect of bimetallic support interaction of Co-Mo/MgO catalyst on the synthesis of carbon nanotubes via catalytic decomposition of acetylene in a catalytic vapour deposition (CVD) reactor.

Materials and Methods

Materials

The materials used in this study include; Cobalt (II) nitrate hexahydrate $Co(NO_3)_2.6H_2O$ and Molybdenum (III) nitrate hexahydrate $Mo(NO_3)_3.6H_2O$ sourced from Kem light laboratory, Mumbai India, Sulphuric acid (H_2SO_4) sourced from Guangdong Guanghua Sci-Tech Co. Ltd (JHD) China, MgO obtained from Kermel China, all the chemicals were of analytical grade with 99.9% purity. Acetylene and nitrogen gases of analytical grade with the percentage of 99.99 % purity were supplied by BOC Gases Nigeria Plc and distilled water was sourced from Dana Pharmaceuticals Co. Ltd Minna.

Preparation of Co-Mo/MgO Catalyst

The bimetallic Co-Mo catalyst on MgO support was prepared by wet impregnation method. A 2^4 factorial experimental design was used to investigate the influence of (mass of support, stirring speed, drying time and drying temperature) with a central composite design method (Abdulkareem *et al*. 2016). 19.4 g of $Co(NO_3)_2.6H_2O$ and 1.2g of $Mo(NO_3)_3.6H_2O$ salts were weighed and dissolved in 50 cm^3 of distilled water. The mixture was allowed to dissolve completely and 15 g of magnesium oxide was added to it then stirred for 1 hour using a magnetic stirrer at a stirring speed of 1500 rpm. The obtained slurry was then dried in an oven for 10 hours at 120^OC. The dried catalyst was grinded then sieved through a 150 μm sieve aperture to obtain a uniform particle size. The uniformly sieved catalyst was then calcined in an electric furnace at an optimized temperature of 500^OC and 600^OC at time of 2 and 4 hrs. The obtained catalyst was then analysed for surface morphology and crystallinity. The percentage yield of the obtained catalyst was then calculated using the relationship as shown in Equation (1).

$$\text{Catalyst Yield (\%)} = \frac{\text{Final weight of catalyst after drying(g)}}{\text{Initial weight of catalyst before drying (g)}} \times 100 \qquad (1)$$

Synthesis of Carbon Nanotubes

CNTs were synthesized in a horizontal CVD reactor following the methods of (Abdulkareem *et al*., 2016; Medupin *et al*., 2019; Oyewemi *et al*., 2019). 0.5 g of the produced Co-Mo/MgO catalyst was measured and placed in a boat at the centre of the quartz reactor. The reactor was purged using nitrogen gas at a flow rate of 50 mL/min until the reaction temperature reaches 700^OC. At this temperature, the nitrogen flow rate was increased to 200 ml/min while the acetylene flow rate was released for carbon nucleation process to take place for a reaction period of 1 hour. Immediately the reaction time was attained, the flow of acetylene was truncated and nitrogen gas was reduced to 50 mL/min until the system cools to room temperature. The boat contained the synthesized carbon nanotubes were removed, weighed and the percentage carbon nanotubes synthesized was determined using Equation 2.

$$\text{CNTs Yield (\%)} = \frac{\text{Final weight of CNTs after reaction(g)}}{\text{Initial weight of catalyst before reaction(g)}} \times 100 \quad (2)$$

Purification of Carbon Nanotubes

The purification was done in accordance with (Oyewemi *et al*., 2019). The as-synthesized CNT was treated with 30 % wt. concentrated nitric acid, heated and stirred at a temperature of 50^{O}C for 30 minutes using sonicator to remove residual portions of magnesium oxide and other catalysts materials including impurities. The sample was washed with distilled water until the pH was approximately 7.0 and later dried at 100^{O}C for 8 hours.

Characterization of Catalyst and Synthesised Carbon Nanotubes

The catalyst produced and purified CNTs were characterised by X-ray diffraction (XRD) Bruker AXS D8 X-ray diffractometer system coupled with Cu-Kα radiation of 40 kV and a current of 40 mA. (Panalytical X'Pert Pro, Cu-Kα radiation = 0.1789, nm scanning rate was 1.5ºC/min, while a step width of 0.05° was used over the 2θ range value of 20-80º) at 40 kV and 30 mA. High-Resolution Scanning Electron Microscopy (HRSEM) images in SE mode were taken with a Zeiss Supra 35 field emission equipped with energy dispersive X-ray (EDX) analyser. Also, samples for transmission electron microscopy were prepared by dispersing powder and High-resolution Transmission Electron Microscopy (HRTEM) images were obtained using a 200 kV JEOL JEM-2100F transmission electron microscope (TEM), equipped with a field emission gun and EDX analyser (Medupin *et al*., 2019; Oyewemi *et al*., 2019).

Results and Discussion

The study examined the effects of catalysts synthesis parameters such as the mass of support, drying temperature and drying time on the yield of the bimetallic catalyst via central composite design techniques. The results obtained as shown in Table 1 indicated the highest yield of 93.22% at drying time of 10 hours, drying temperature of 120 ^{O}C and mass of support of 16 g.

Table 1: Central Composite Design for Co-Mo/MgO Catalyst

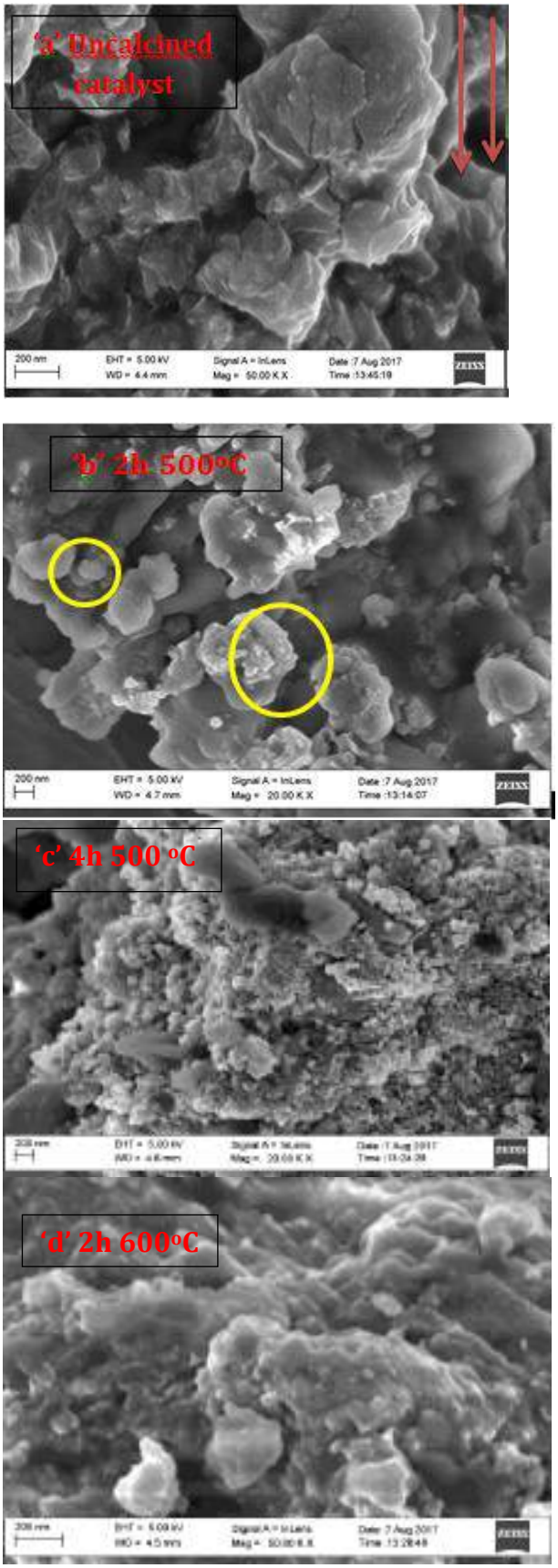
Run	Drying Time (h)	Drying temp. (^{O}C)	Mass of support (g)	Yield (%)
1	12.00	110.00	14.00	77.45
2	11.00	115.00	13.32	71.23
3	10.00	120.00	14.00	75.76
4	11.00	115.00	15.00	84.65
5	12.00	110.00	16.00	71.32
6	12.68	115.00	15.00	89.90
7	11.00	115.00	15.00	87.87
8	11.00	123.41	15.00	86.76
9	9.32	115.00	15.00	87.95
10	10.00	110.00	16.00	91.14
11	11.00	115.00	15.00	84.67
12	11.00	115.00	16.68	78.89
13	12.00	120.00	14.00	59.23
14	10.00	120.00	16.00	**93.22**
15	12.00	120.00	16.00	91.44
16	11.00	115.00	15.00	86.34
17	10.00	110.00	14.00	83.45
18	11.00	115.00	15.00	89.99
19	11.00	106.59	15.00	81.29
20	11.00	115.00	15.00	86.78

Furthermore, the morphology and mineralogical phases of the Co-Mo/MgO Catalyst are presented as follows:

Scanning Electron Microscopy Analysis

Figure 1 shows the HRSEM of the catalyst supported on MgO. The results give the surface morphology of the developed catalyst materials. The surface morphology of the synthesized bimetallic catalysts as depicted in Fig. 1 (a-e) indicates the presence of crystal-like nanomaterial formation. Fig. 1 (a) shows the presence of plate-like nature of the active part of the catalyst on the support material, which revealed that the support material was completely covered by the Co-Mo oxides formed during the impregnation method. There was also the presence of hollow

cavity formation on the surfaces of the catalyst as indicated in Fig. 1a, though the active part of the catalyst was not crystalline; flakes-like. The calcination process degrades the nitrate to nitrogen hence, improves the surface morphology and then lead to a crystalline particle formation as depicted in Fig. 1 (b-e). At the calcination temperature of 500 ^{O}C for a period of 2h, an improved morphological make-up of the catalyst is observed with a distinct crystallite material indicated in Fig. 1 b. The observed particles sizes were fairly distributed. As the reaction time was increased to 4 hours at 500^{O}C, the particles sizes were also decreased and the rate of particle compartments also become appreciated as indicated in Fig. 1c. The observable particle sizes reduction at the calcination time of 4 hours could increase the surface areas, the pore sizes and the pore volume of the catalyst material thereby, improve its suitability for use in carbon nanotubes nucleation process. Furthermore, as the calcination temperature increases to 600^{O}C for 2 hours, there are continuously connected particles of catalysts deposited on the surfaces of the support material with a smaller particle size to that of Figure 1a. Therefore, an increase in temperature from 500^{O}C to 600^{O}C at constant calcination time of 2h resulted in the production of a more finely catalyst material. As the calcination time increases to 4 hours at 600℃, the particle sizes become smaller due to attrition of catalyst particles in the mix due to mechanical grinding and collision. The finding is in accordance with the investigation reported in the work of Abdulkareem *et al*. (2016), Oyewemi *et al*. (2019) and Karim *et al*. (2015).



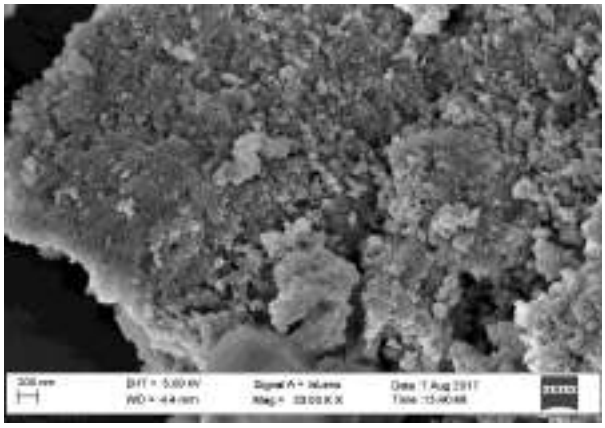


Fig. 1: HRSEM Micrographs of (a) uncalcined (b) calcined at 2h at 500ºC (c) calcined at 4h at 500ºC (d) calcined at 2h at 600ºC and (e) calcined at 4h at 600ºC of Co-Mo/MgO bimetallic catalyst.

Fig. 2: shows HRSEM image of the as-synthesised CNTs in the catalytic chemical decomposition reaction of Co-Mo/MgO. The obtained carbon nanotubes are formed as a network of rope-like structure with different densities and this may be attributed to calcination temperature of the catalyst. CNTs diameters can be estimated as between 10 and120 nm and their lengths are up to 10 µm. The figure shows a SEM image of the CNT surface, fairly homogeneously distributed and the formation of spherical shape material might be to the formation of intermediate like MgO.

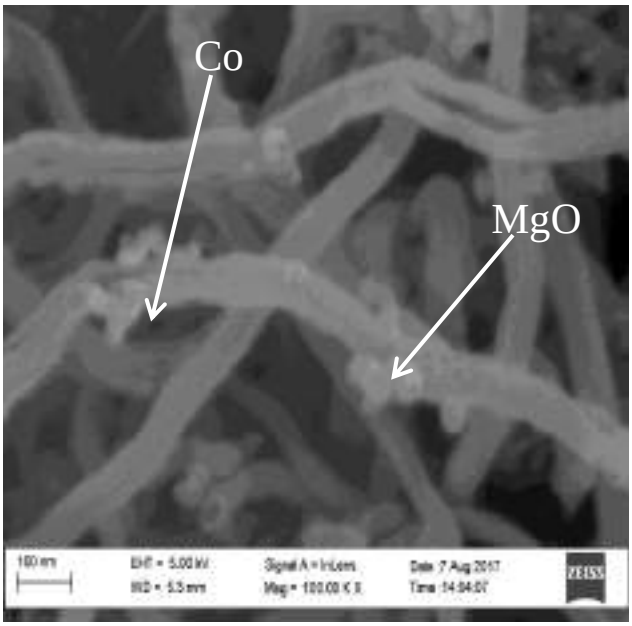


Fig. 2: HRSEM image of the as-synthesized CNTs showing Co and MgO Catalytic support

X-Ray Diffraction Analysis of the Developed Co-Mo/MgO Catalyst

Fig. 3 shows the XRD spectral of the developed catalyst at varied temperature and time. Several diffraction peaks were obtained at the diffraction angles of 36.55, 42.83, 58.09, 62.17 and 78.60º. The uncalcined catalyst depicts no formation of molybdenum oxide, MoO_3 crystal as formed in the remaining calcined catalysts. The calcination process resulted in the formation of crystallite materials which possibly might have been encapsulated in the bulk of the catalyst.

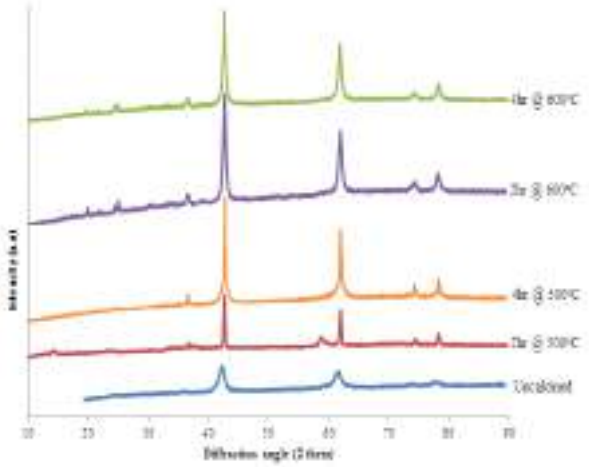


Fig. 3: XRD spectral of the developed catalyst

The presence of $MgMoO_4$ formation at the diffraction angle of 58.09º is observed for the catalyst calcined at the temperature of 500ºC for 2h. The observation of $MgMoO_4$ formed at this operating condition suggests its favourable formation at lower temperature and less calcination time. Furthermore, the diffraction angles at 42.83, 62.17 and 78.60º are associated with the presence of $CoMoO_4$ and CoMo oxides nano-crystals. These peaks formation are present throughout the catalyst produced. This is in agreement with the report of Ezekiel *et al*. (2014).

Characterization of Carbon Nanotubes

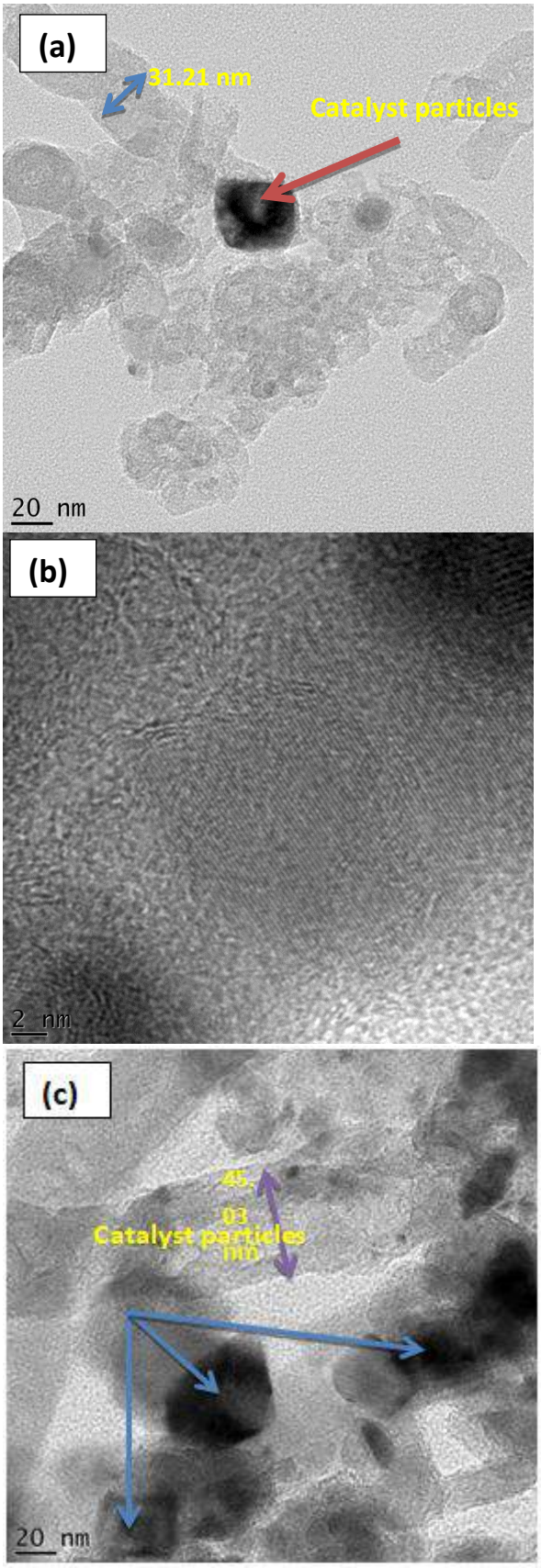
Synthesis temperature has been reported as an important parameter that affects the yield, purity, growth rate and morphology of CNTs produced by the CVD method, by varying the operating parameters in a 2^4 factorial design (Oyewemi *et al.*, 2019). The carbon nanotubes produced was characterized to determine its internal structure, surface morphology, crystallinity and elemental composition. The result of the effects of operating parameters on the yield of the carbon nanotubes is shown in Table 2.

Table 2: 2^4 Factorial Design of the experiment for CNT synthesis

Factor 1 Time (T)	Factor 2 Temp (^OC)	Factor 3 N_2 flow (ml/min)	Factor 4 C_2H_2 flow (ml/min)	Response wt. (g)
60.00	700.00	250.00	200.00	1.14
60.00	800.00	200.00	250.00	0.92
60.00	700.00	200.00	200.00	0.87
45.00	800.00	200.00	250.00	0.94
60.00	700.00	200.00	250.00	0.94
60.00	800.00	250.00	250.00	0.96
60.00	800.00	250.00	200.00	0.99
45.00	700.00	200.00	250.00	1.04
45.00	800.00	200.00	200.00	1.09
60.00	800.00	200.00	200.00	1.55
60.00	700.00	250.00	250.00	0.66
45.00	800.00	250.00	250.00	0.99
45.00	700.00	200.00	200.00	0.74
45.00	800.00	250.00	200.00	0.98
45.00	**700.00**	**250.00**	**250.00**	**1.59**
45.00	700.00	250.00	200.00	1.17

Transmission Electron Microscopy Analysis of Carbon Nanotube Developed

The internal structure of the developed MWCNTs having the highest and the lowest yield was examined via HRTEM techniques and the results were presented in Fig. 4 (a-d).



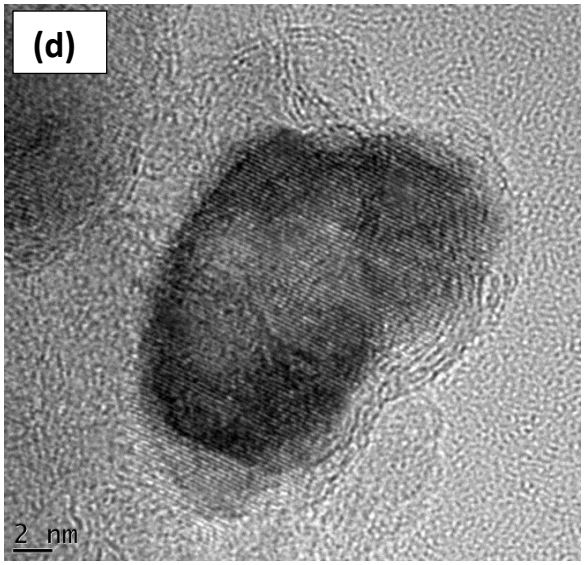
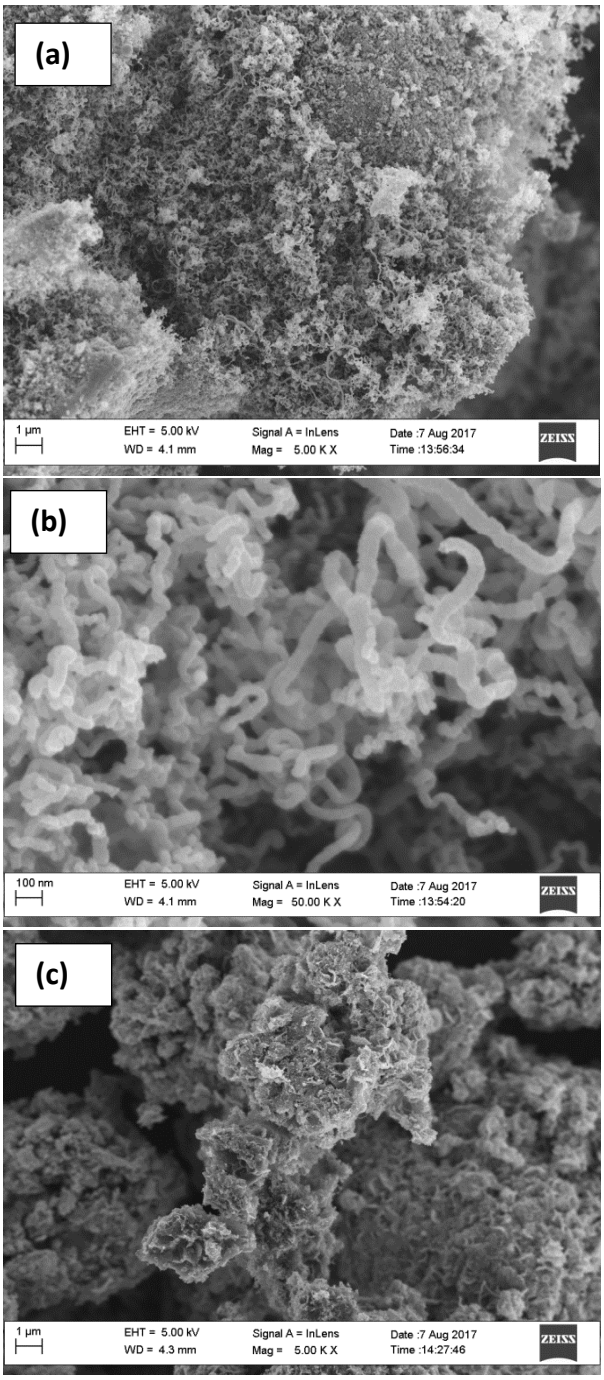


Fig. 4: HRTEM micrographs of CNTs; (a and b) represented the highest yield while (c and d) depicted the lowest yield CNTs at different magnification.

Fig. 4 represented the tubes compartment of the produced carbon nanotubes at varied synthesis condition. Fig. 4 (a) shows the presence of a minute quantity of blackish-like materials which could be linked to the possible presence of catalyst constituents and amorphous carbon materials formed during the synthesis process compared to that of Fig. 4 (c). This observation implies that the higher the flow rate of acetylene over a catalyst material during a carbon nanotubes nucleation process, the lower the level of impurities accompanied. The diameter of the produced carbon nanotubes was observed to depend on the flow rate of acetylene and nitrogen gas. From Figure 3 c, the diameter of CNTs was found to be 31.21 nm at 250 mL/min and 100 mL/min for both acetylene and nitrogen flow rate, respectively. The diameter of the carbon nanotubes produced at lower acetylene flow of 200 mL/min and a constant nitrogen flow rate resulted in the production of higher diameter carbon nanotubes. Fig. 4 (b) and (d) shows that the produced carbon nanotubes are multi-walled carbon nanotubes with several tubes walls.

Scanning Electron Microscopy Analysis of Carbon Nanotube Developed

The surface morphology of the produced CNTs was investigated via high-resolution scanning electron microscope. The result of the HRSEM is as depicted in Fig. 5 (a-d).



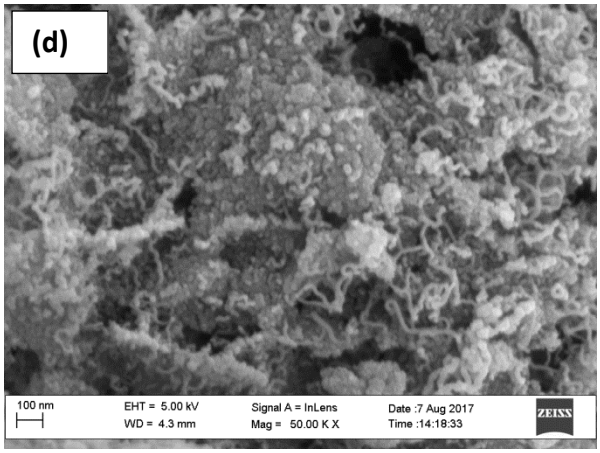


Fig. 5: HRSEM Micrograph of CNTs (a and b) represented the highest yield while (c and d) depicted the lowest yield CNTs at different magnification.

Fig. 5 (a-d) depicts a typical form of MWCNTs surface morphology having a densely populated strand of tubes; spongy-like with varied diameter architecture. Fig. 5 b shows that the carbon nanotubes are completely formed with distinct tubes having lesser impurities as compared to Fig. 5(d). The variation in the surface structural make-up could be attributed to the differences in the flow rate of acetylene gas. Therefore, for the synthesis of completely formed CNTs, it's recommended that the flow of acetylene gas increases over the catalyst material. The elemental composition of the produced MWCNTs was examined via EDS analysis. The result of the analysis for both the low yield CNTs and high yield CNTs are shown in Fig. 6(a) and Fig. 6(b) respectively.

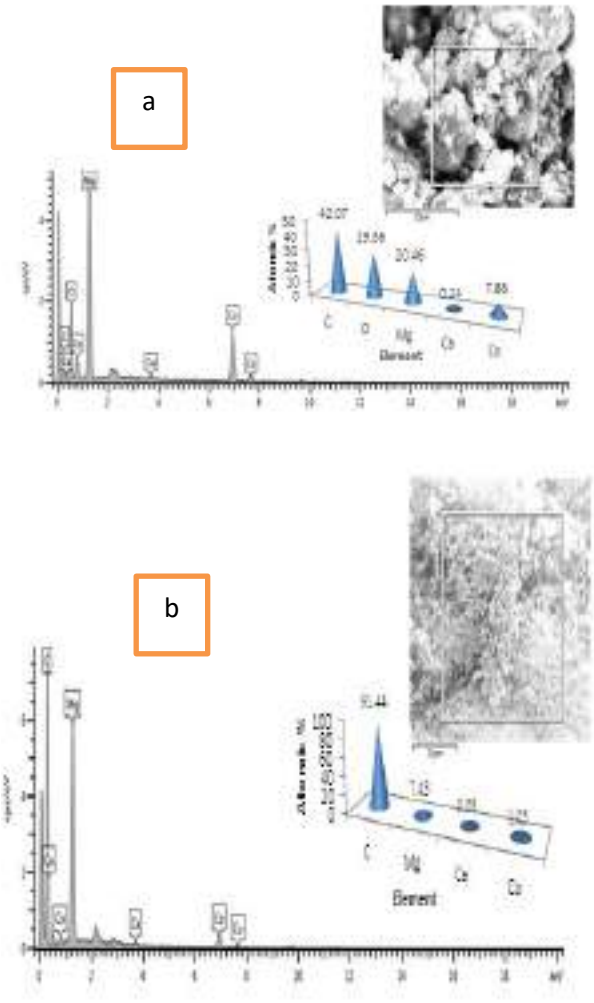


Fig 6: EDX spectral of CNTs Yield (a) Low yield CNTs (b) High yield CNTs

From Fig. 6 (a) and (b), several elements were detected in the bulk of the carbon nanotubes. These include carbon, magnesium, calcium, and cobalt with percentage composition of 42.07, 20.46, 0.24, 7.86 and 91.44, 7.43, 0.08, 1.05 % for the low yield and high yield CNTs, respectively. The percentage composition of carbon in the high yield CNTs was higher than that of the low yield CNTs. This is an indication of higher carbon conversion observable during the nucleation process leading to the formation of the CNTs at the operating condition. The presence of Molybdenum was not noticeable in the EDS results presented in Fig. 6a and b. These could be as a result of the small ionic radius exhibited by

molybdenum which could not be detected by the EDX equipment during the analysis.

Conclusions

This research work investigates acetylene as a precursor for the synthesis of carbon nanotubes (CNTs) over bimetallic Co-Mo catalyst supported on MgO via catalytic chemical vapour deposition (CCVD) technique. The effects of catalyst production parameters on the yield of the as-prepared catalyst were evaluated. Also, the effects of synthesis temperature and gas flow were examined on the yield of CNTs. The optimum catalyst yield of 93.22 % was prepared from 16 g support mass, stirring speed of 1500 rpm, stirring time of 20 minutes, drying temperature of 120℃ and drying time of 10 hours the optimum parameters. The prepared catalyst exhibited high metal-support interactions between Co-Mo and the MgO support, which promotes the catalytic properties for the subsequent growth of the MWCNTs. The optimum yield of 89.09 % of CNTs was obtained at a temperature of 700℃, 250 mL/min and 200 mL/min flow rate for acetylene and nitrogen respectively. The synthesis parameters; temperature, time, argon flow rate, acetylene contributed significantly to the physicochemical process in the production of the CNTs. The HRTEM, HRSEM/EDX and XRD of the as-grown CNTs revealed that the prepared sample was a high-quality CNT containing fewer defects. This study established that CNTs can be successfully prepared from Co-Mo bimetallic catalyst supported on magnesia.

Acknowledgements

The authors wish to recognise and appreciate the support of the Petroleum Technology Development Fund (PTDF). The opportunity granted by The Centre for Genetic Engineering and Biotechnology (CGEB) FUT Minna for permitting direct access to the centre facilities is appreciated.

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