Asia-Pacific Journal of Science and Technology: Volume: 29. Issue: 04. Article ID.: APST-29-04-08. Research Article

Asia-Pacific Journal of Science and Technology

https://www.tci-thaijo.org/index.php/APST/index

Published by the Research and Graduate Studies,
Khon Kaen University, Thailand

Investigating the influence of processing parameters on bimetallic catalysts for high-yield carbon nanotube synthesis

Abayomi A. Okesola[1,*], K. Mensah-Darkwa[1], Nthabiseng B. Maledi[2] and Anthony Andrews[1]

[1]Department of Materials Engineering, College of Engineering, Kwame Nkrumah University of Science and Technology, Kumasi, Ghana
[2]School of Chemical and Metallurgical Engineering, Faculty of Engineering and Built Environment, University of the Witwatersrand, South Africa
[*]Corresponding author: aaokesola@st.knust.edu.gh

Received 26 April 2023
Revised 10 July 2023
Accepted 18 June 2023

Abstract

The efficient synthesis of carbon nanotubes (CNTs) remains a challenge, and optimizing processing conditions for high-quality CNT production is a subject of ongoing research. In this study, the influence of processing parameters on the structure-property relationships of synthesized Fe-Ni bimetallic catalysts and the yield of carbon nanotubes (CNTs) was investigated. The study also aimed to optimize the synthesis conditions for the Fe-Ni bimetallic catalyst supported on $CaCO_3$ and examine the effect of CNT purification on the final product. The CNTs were synthesized using a chemical vapor deposition process with an Fe-Ni bimetallic catalyst supported on $CaCO_3$, and the effects of processing parameters such as pre-calcination temperature, stirring speed, support mass, and pre-calcination time on the yield and properties of the CNTs were analyzed. The synthesized CNTs were then characterized using SEM, FT-IR, BET, XRD, and Raman spectrometers to assess their structure and properties. The study revealed that optimizing the synthesis conditions led to increased graphitization and crystallinity of the CNTs. A maximum CNT yield of 376% was obtained under the optimal conditions of a reaction temperature of 700°C, a time of reaction of 90 min, and nitrogen and C_2H_2 flow rates of 294 mL/min and 193 mL/min, respectively. CNT purification was found to be effective in reducing impurities and functionalizing the CNTs for easy dispersion. The findings provide valuable insights for the development of efficient methods for the large-scale production of high-quality CNTs.

Keywords: Bimetallic Catalyst, $CaCO_3$, CNTs, Crystallinity, CVD, Fe-Ni, Graphitization, Purification

1. Introduction

Carbon nanotubes (CNT) are a type of carbon with a long tube structure. A thin cylinder, Multi-Walled Carbon Nanotubes (MWCNT) were composed of up to several tens of graphitic shells with adjacent shell separations of 0.34 nm, a diameter of approximately 1 nm, and a high length/diameter ratio. The CNT allotrope of carbon is the one that has been investigated the most because of its distinct hollow structure, from which they derive their unusual mechanical, thermal, and electrical properties, such as low density and high tensile strength/stiffness superior to any metal [1]. CNTs' thermal conductivity is well enhanced and exceeds what is achievable in a diamond. It is chemically and thermally stable, with extraordinary electrical conductivity and ductility. The atomic bonding and chemical composition are in their simplest form, making the material suitable for various applications [1-3].

The synthesis of CNT is an exciting field of study since no other material has such vast properties and applications cutting across diverse fields like engineering, the humanities, and the natural sciences. Because of CNT's outstanding properties, researchers have been paying close attention to synthesising huge quantities of well-defined arrays and high-crystalline CNT at a reasonable cost. However, more work is needed to improve the yield of CNT synthesized using various processing routes [4]. CNTs have been produced using a range of techniques, including laser ablation [1], arc discharge [5], plasma-enhanced chemical vapour deposition [6], electrolysis [7], and catalytic chemical vapour deposition [8].

Chemical vapour deposition (CVD) is the most extensively used technique for generating CNTs due to its simplicity, low cost, low temperature, and ambient pressure [8]. This made the process widely used in the industry. The CVD approach allows CNT development in several forms, including powder, thin and thick films, aligned, entangled, straight, coil, and even user-designed structures with distinct sites on patterned substrates [4]. Another benefit of CVD over other approaches is that it allows for temperature control of CNT development [9,10].

The choice of carbon precursor, synthesis parameters, and operation circumstances influence carbon nanotubes' quality, yield, and growth rate [11]. Selecting suitable catalyst support is one such technique that is crucial for effectively creating high-grade and large-quantity CNTs through the CVD procedure. The catalyst serves as the growth platform for CNT [10,12]. Catalyst preparation, particularly with support for the synthesis of carbon nanotubes, has piqued researchers' interest owing to the influence of the support materials on the characteristics and activities of the catalyst mixture [4]. Catalysts composed of transition metals such as Fe, Co, Ni, and Mo, either alone or in combination with support materials like SiO_2, Al_2O_3, MgO, zeolite, $CaCO_3$, TiO_2, and kaolin, have been utilized to generate carbon nanotubes (CNTs) with diverse morphologies and diameters [4]. Fe and Ni are the most frequently used transition metals because they are very soluble and have high carbon diffusion on metallic components at higher temperatures, which increases CNT production. Furthermore, when compared to other transition metals, Fe, Co, and Ni particles formed the most active and effective phase needed for CNT formation [11].

Calcium carbonate is a promising catalyst support for CNT synthesis due to its low cost, high catalytic activity, controllable synthesis, environmental friendliness, non-porosity, ease of handling, and favorable dominance of amorphous carbon in CNT development. Calcium carbonate has been shown to exhibit high catalytic activity for the synthesis of CNTs, resulting in high yields and high-quality CNTs [11,13,14].

In recent years, there has been significant research on optimizing catalysts for CNT synthesis via CVD to improve the yield and quality of CNTs. The optimization of catalysts involves selecting the appropriate composition, morphology, and size of the catalyst to maximize CNT growth and minimize unwanted side reactions [4,11,15].

There have been numerous studies on catalysts for carbon nanotube (CNT) synthesis via chemical vapor deposition (CVD). Some previous studies have investigated the effects of catalyst composition on CNT growth. For example, the effects of different metal catalysts, such as iron, cobalt, and nickel, on the growth of CNTs were analyzed, and it was concluded that the catalyst composition had a noteworthy effect on size, yield, and quality of the CNTs produced [5,16]. Other studies have focused on optimizing the morphology and size of the catalyst particles used in CNT synthesis. It has been shown that catalyst particle size has a significant effect on the properties of the produced CNT. The catalytic activity, lifespan, and yield of carbon nanotubes (CNTs) are significantly enhanced by combining metallic particles such as Fe, Co, Ni, and Mo due to the lower melting point of the combination. Compared to using individual metals, the incorporation of these mixed catalysts has been shown to increase CNT growth and improve their quality. Moreover, the presence of multiple metal species helps prevent the aggregation of catalyst particles. Extensive research has revealed that synthesized bimetallic catalysts exhibit superior activity and stability when compared to monometallic catalysts [14,17-19]

Despite progress in catalyst optimization for carbon nanotube (CNT) synthesis via chemical vapor deposition (CVD), research gaps still exist. These include a lack of understanding of catalyst deactivation mechanisms, limited knowledge of the relationship between catalyst properties and CNT growth, a limited understanding of the impact of impurities on catalyst performance, a lack of scalable catalyst optimization strategies, and a need for new catalyst materials. Addressing these gaps through further research will be crucial for advancing the field of CNT synthesis via CVD.

A well-designed and produced catalyst is required to successfully synthesize carbon nanotubes. The catalyst and support determine the yield of the CNT during the catalytic conversion in the Chemical Vapour Deposition (CVD) equipment. The carbon source requires a suitable surface to enable the growth of CNT, and the catalyst provides this condition. Diverse transition metals have different catalytic activities and qualities of CNT.

The catalyst known to have produced the best CNT yields includes Fe, Co, and Ni, with a bimetallic catalyst consisting of Co-Mo and Fe-Co [13]. The Fe-Co bimetallic with $CaCO_3$ support is reported to have produced clean and quality CNTs [20]. On the other hand, there is scant or no information available regarding the characteristics of CNTs made from Fe-Ni bimetallic on $CaCO_3$ support. Additionally, a synthesis period of 60 minutes and a pre-calcination temperature of up to 120°C are frequently employed in the synthesis of CNT. However, it is possible to optimize the synthesis conditions to get a high CNT yield with high crystallinity.

Optimizing catalysts for carbon nanotube (CNT) synthesis via chemical vapor deposition (CVD) is crucial but faces challenges such as catalyst deactivation, aggregation, selectivity, scale-up issues, and cost considerations. These factors can affect CNT yield and quality and make it difficult to achieve optimal catalyst performance, especially when transitioning from laboratory-scale to commercial-scale production. Addressing these challenges will require continued research and development, along with a focus on identifying new catalyst materials and refining existing catalyst optimization strategies.

This paper aims to explore the optimization of catalysts for CNT synthesis via CVD, with a focus on maximizing the yield and quality of the resulting CNTs. Through a series of experiments, we investigated the effects of different catalyst properties on CNT growth and compared the resulting CNTs in terms of quality and yield. The results of our study demonstrate the importance of catalyst optimization for efficient and cost-effective CNT synthesis via CVD.

Overall, this paper contributes to the understanding of the role of catalysts in CNT synthesis and provides valuable insights into the optimization of catalyst properties for improved CNT growth. This research can help pave the way for the large-scale production of high-quality CNTs, enabling their use in various functions.

2. Materials and methods

2.1 Materials

Chemicals employed in this work were nickel nitrate hexahydrate (Ni $(NO_3)_2{\cdot}6H_2O$), iron (III) nitrate nonahydrate ($Fe(NO_3)_3{\cdot}9H_2O$), calcium carbonate ($CaCO_3$), concentrated nitric acid (HNO_3), and concentrated hydrochloric acid (H_2SO_4), all sourced from Sigma Aldrich and are of analytical grade with 99.99% purity. Acetylene (C_2H_2) was used as a carbon source, while nitrogen was used as a carrier gas. Both gases had 99.99% purity and an analytical grade.

2.2 Optimization of Fe/Ni bimetallic catalyst supported on $CaCO_3$

To produce a suitable catalyst for the production of CNT, a 2^4 (2 levels, 4 factors) design experiment was conducted on Minitab to determine the optimal set-up for the best yield of catalyst. The parameters considered in the design are pre-calcination temperature, pre-calcination time, stirring speed, and support mass. These parameters are considered essential for successful catalyst production [11], and the effect of the individual parameters and a combination of the parameters on the catalyst yield were studied. The Pareto chart analysis (Figure 1 A) show that the temperature affects the yield of the catalyst more than any of the other parameters considered.

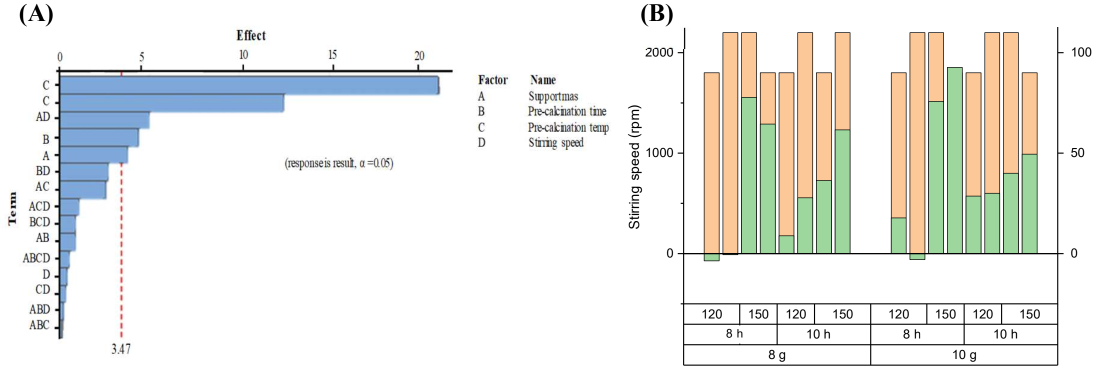

Figure 1 (A) Pareto Effect analysis of the optimized catalyst, and (B) Catalyst optimization graph showing the yield in percentages.

Figure 1 B shows a graph of the optimized runs for the catalyst preparation from the results generated on Minitab. The support mass ranges from 8-10 grams with a temperature of 120-150°C and speed of stirring of 1800-2200 rpm, and yield is expressed in percentage. The highest yield was obtained at the highest pre-calcination temperature of 150°C corroborating the Pareto analysis. The optimization effectively reduced the number of trial runs to 16, thereby saving both time and money.

2.3 Preparation of a Fe/Ni bimetallic catalyst supported on $CaCO_3$

The bi-metallic catalyst of Fe/Ni supported on $CaCO_3$ was prepared according to the optimum formulation generated on Minitab, which produced the best yield of the catalyst.

A 10 wt.% of the metallic salt (nickel nitrate hexahydrate (Ni $(NO_3)_2$ $6H_2O$) and iron (III) nitrate nonahydrate (Fe $(NO_3)_3$. $9H_2O$) in a ratio of 1:1 was added to 10 g of the $CaCO_3$ in a beaker holding 50 mL of distilled water. The beaker content was stirred at 1800 rev/min for 60 min using a magnetic stirrer. The equivalent weight of the bimetallic salt was calculated by multiplying the molecular weight of each of the metallic salts by 0.05. The stirred mixture dried for 60 min at room temperature before drying at 150°C for 8 h in the oven, based on the optimization analysis. Before CNT synthesis, the Fe-Ni/$CaCO_3$ catalyst was calcined at 500°C for 16 h.

2.4 Synthesis of CNT by CVD

The CVD was conducted in a tubular furnace (Vacutec XD-1200NT). A quartz boat containing 2.8 g of the catalyst was placed in the furnace after pre-heating the furnace to 700°C. Nitrogen gas was allowed to flow through the furnace at 190 mL/min and acetylene at 294 mL/min for 90 min to produce the CNTs. The furnace was cooled to room temperature in a nitrogen atmosphere after reaching a reaction time of 90 min. The weight of the CNT produced was measured at 13.34 g, and the CNT yield was calculated using Equation (1): [21].

$$\text{CNTs Yield}(\%) = \frac{\text{Wproduct} - \text{Wcatalyst}}{\text{Wcatalyst}} \text{ X } 100\% \tag{1}$$

where $W_{product}$ is the total mass of the final catalyst and carbon products after CVD reaction process and $W_{catalyst}$ is the initial mass of Fe-Ni/$CaCO_3$ catalyst.

The as-synthesised CNTs were purified using a combination of both physical and chemical processes. Purification was carried out to remove residual Fe, Ni, and CO_3 used as catalysts. The as-synthesized CNT was treated with concentrated H_2SO_4 and HNO_3 at a ratio of 3:1, which is a liquid-phase oxidation process [22]. 100 mL of the acid mixture was used to purify 5 g of the as-synthesized CNT in an ultrasonicator at 60°C for 1 h. Distilled water was added to the contents of the beaker and allowed to settle. The content was decanted every 4 hours and topped up with fresh distilled water till a pH of 7 was obtained. The slurry was then collected in a beaker and oven dried at 150°C for 10 h to obtain purified carbon nanotubes, which were then pulverized and sieved through a 150-micron sieve and stored. The various samples, their preparation conditions, and average pore surface area are provided in Table 1.

As can be seen from Table 1, there is an increase in the surface area of the material from the dried catalyst phase up to the purified state of the CNT. This is characteristic of the change from micro to nanoscale in the material.

Table 1 Catalyst and CNT samples prepared at varying conditions with average surface area.

Sample ID	Conditions	Avg. surface area (m^2/g)	Avg. pore diameter (nm)
C	Fe-Ni/$CaCO_3$ catalyst dried and pulverised	2	2
C500-16	Fe-Ni/$CaCO_3$ catalyst calcined at 500°C for 16 h	2	1
CNT500-16	As-synthesized CNT using sample C500-16	15	1
PCNT500-16	Purified CNT500-16	46	1

2.5 Characterization methods

The catalyst, the as-synthesized CNTs, and the purified CNTs were characterized to determine their structure and purity. Fourier transform infrared (FT-IR) was carried out using Perkin Elmer's FT-IR Spectrometer Spectrum on transmittance mode settings. Microstructures and grain morphologies were obtained through scanning electron microscopy using VEGA3 TESCAN. Brunauer-Emmett-Teller (BET) analysis was performed using Quantachrome® ASiQwin™- Instruments version 5.21. The XRD patterns were obtained through X-ray diffraction analysis using an XRD Bruker D2 phaser with a copper anode ($K\alpha1 = \lambda = 1.54$ Å) as the source. The 2-theta range was from 5° to 80° at 0.026° step size and a scan rate of 8.5° per min. The radiation source had a current of 10 mA and a voltage of 30 kV. The purity was obtained by Raman spectroscopy.

3. Results and discussion

Several researchers who are working on the process of viable CNT production have reported various synthesis parameters, catalyst combinations, and yields. A list of some of the mentioned works is presented in Table 2. The yield obtained in the current work has been added for comparison.

Table 2 Comparison of CNT yields obtained in the current work and other researchers.

S/N	Catalyst	Synthesis parameters	Yield (%)	References
1	Co-Ni/SiO_2	Reaction temperature: 700°C Time of reaction: 60 min Hydrogen rate of flow: 110 mL/min C_2H_2/N_2 rate of flow: 220 mL/min	9	[15]
2	Fe-Ni/SiO_2	Reaction temperature: 700°C Time of reaction: 60 min Hydrogen rate of flow: 110 mL/min C_2H_2/N_2 rate of flow: 220 mL/min	47	[15]
3	Fe-Co/SiO_2	Reaction temperature: 700°C Time of reaction: 60 min Hydrogen rate of flow: 110 mL/min C_2H_2/N_2 rate of flow: 220 mL/min	61	[15]
4	Co-Ni/γ-Al_2O_3	Reaction temperature: 700°C Time of reaction: 60 min Hydrogen rate of flow: 110 mL/min C_2H_2/N_2 rate of flow: 220 mL/min	76	[15]
5	Fe-Ni/γ-Al_2O_3	Reaction temperature: 700°C Time of reaction: 60 min Hydrogen rate of flow: 110 mL/min C_2H_2/N_2 rate of flow: 220 mL/min	239	[15]
6	Fe-Co/γ-Al_2O_3	Reaction temperature: 700°C Time of reaction: 60 min Hydrogen rate of flow: 110 mL/min C_2H_2/N_2 rate of flow: 220 mL/min	263	[15]
7	Fe-Ni/Kaolin	Reaction temperature: 750°C Time of reaction: 60 min Argon rate of flow: 230 mL/min C_2H_2 rate of flow: 200 mL/min	306	[4]
8	Fe-Co/$CaCO_3$	Reaction temperature: 700°C Time of reaction: 60 min Argon rate of flow: 190 mL/min C_2H_2 rate of flow: 230 mL/min	92	[11]
9	Fe-Ni/$CaCO_3$	Reaction temperature: 700°C Time of reaction: 90 min Nitrogen rate of flow: 294 mL/min C_2H_2 rate of flow: 193 mL/min	376	This study

From Table 2, Fe-Ni catalyst has better performance than Fe-Co catalyst. Even for the same catalyst, differences in the type and mass of support affect the yield of the CNT produced. For instance, the yield obtained in the current work is four (4) times higher than that obtained by [11] and 1.2 times higher than that reported by [4]. Both reports used similar catalysts and supports, but with different masses. From Table 2, calcining the catalyst for 16 h resulted in a higher yield of 376%. It is worth noting that previous studies used a reaction time of 60 minutes, whereas the present study extended the reaction time to 90 min. This possibly contributed to the higher yield recorded in the current work. This prolonged reaction time facilitated the complete reaction between the catalyst and the carbon source, resulting in an improved yield and better crystalline carbon nanotubes, as evidenced by the characterization of the synthesized material.

The Fe-Ni/$CaCO_3$ catalyst (sample C) had a surface area of 2 m^2/g. This falls within the range of 3m^2/g reported by [12] but differs from the 13.2 m^2/g reported by [13]. Both studies employed $CaCO_3$ as a support, and the variation in surface area could be attributed to differences in the particle size of the $CaCO_3$ used. Before CNT synthesis, the Fe-Ni/$CaCO_3$ catalyst support was calcined at 500°C for 16 h, resulting in an increased surface area of 2 m^2/g for sample C500-16.

The increase in surface area after calcination suggests successful conversion of metal salts to oxides, leading to adequate openings on the support material, that allowed the metallic particles to penetrate the catalyst support pores [14]. The calcination time appears to affect the bi-metal-support reaction, which in turn influences the yield. McCarthy [23] studied the supported metal and supported metal oxide catalysts stability and reported that high-temperature interactions between metals and their support materials could increase catalyst yield. The surface area of the CNT powder produced, specifically the as-synthesized CNT sample CNT500-16, was found to be 15 m^2/g. This indicates that the duration of calcination has an impact on catalyst yield due to increased metal-support interactions during longer holding times, allowing for the burn-off of impurities in the sample [24]. Therefore, the reaction time plays a crucial role in the conversion of Fe-Ni/$CaCO_3$ catalyst support to CNT using the CVD process.

The synthesized CNT was purified by removing the catalyst residue that could block the pores of the as-synthesized CNT. After purification and acid functionalization, the average surface area of CNT500-16 increased from 15 m^2/g to 46 m^2/g (PCNT500-16).

Scanning electron microscopy with EDS was used to analyze the microstructures and grain morphologies of the as-synthesized Fe-Ni/$CaCO_3$ catalyst prepared under optimal conditions. The SEM images of the samples are shown in Figure 2. The SEM image of the as-synthesized metal-carbonate support (sample C) revealed the presence of spherical and agglomerated grains with a mean particle diameter of 28 µm.

After calcination (sample C500-16), the mean particle diameter decreased to 1 µm. The reduction in grain size indicates that the catalyst was well-impregnated in the pores of the support material and not just on the surface, which also leads to less agglomeration [12]. The grains exhibited an irregular shape with flaky boundaries, indicating good dispersion of the metal catalyst in the support. The porous nature of the material was confirmed by SEM images at high magnifications, as well as previous research [3,5]

Upon calcination, the average pore diameter of the Fe-Ni/$CaCO_3$ catalyst decreased from 2 nm to 1 nm (Table 1). This reduction in pore diameter indicated the introduction of micropores in the catalyst. The average pore diameter of the catalyst affected the pore diameter of the CNTs produced, as evidenced in Table 1.

EDS analysis, (Figure 3 A), confirmed the dispersion of Fe-Ni on the $CaCO_3$ support material, with Ca, Ni, Fe, and O being the dominant elements present in sample C500-16. The presence of oxygen was attributed to the oxidation of the metals after calcination and the CaO formed from the calcination of $CaCo_3$.

The purified sample (PCNT500-16) exhibited an irregular spherical shape with a distinct sphere, indicating improved crystallinity. EDS analysis, (Figure 3 B), of the sample indicated a reduction in the concentration of Ca, Fe, and Ni, which were the principal elements in the catalyst material. This result suggests the effectiveness of the acids used in the purification process in dissolving residues, leaving majorly pure CNT.

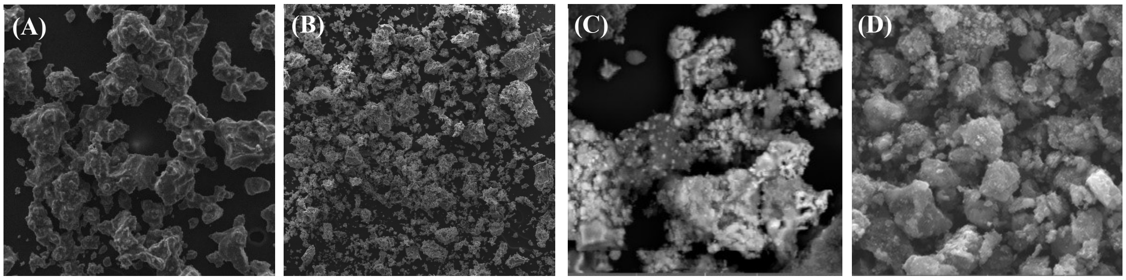

Figure 2 SEM images of (A) as-synthesize catalyst support, (B) calcined catalyst support (C500-16), (C) as-synthesized CNT (CNT500-16) and (D) purified CNTs (PCNT500-16).

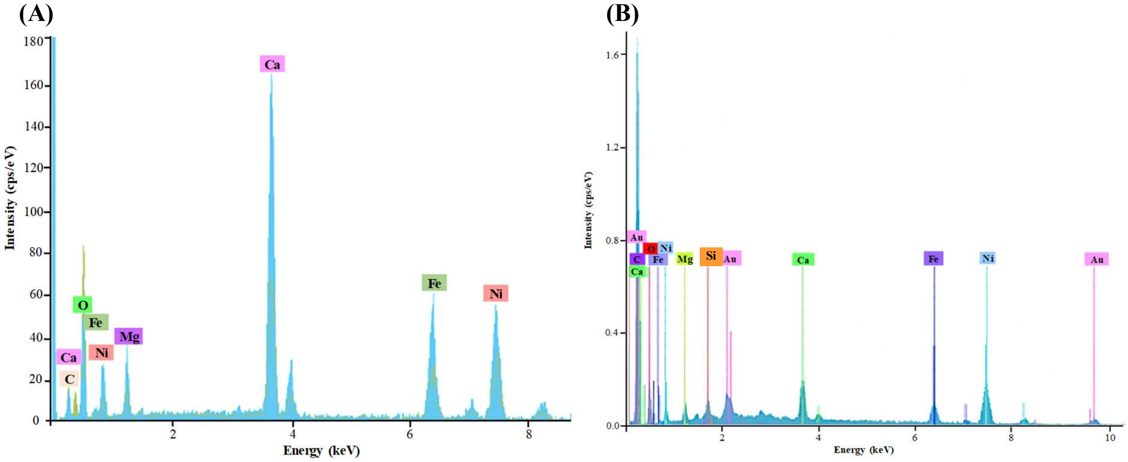

Figure 3 EDS Spectra for (A) C500 -16 and (B) PCNT500-16.

In this study, Fe-Ni/$CaCO_3$ catalysts were analyzed using X-ray diffraction (XRD) to determine the phases present in both the as-synthesized and calcined samples. Figure 4 (A) illustrates the crystalline phases identified at room temperature for the different catalyst samples prepared under varying conditions. The as-synthesized catalyst displayed mainly amorphous characteristics, with weak peaks attributed to Ni/Fe compounds, iron carbide, and calcium carbonate. Samples C500-16 exhibited similar diffraction peaks, and after calcination, the crystallinity increased. The decomposition of the salts resulted in the formation of Ni-Fe oxides, $CaCO_3$, and $Ca_2Fe_2O_5$ during calcination, indicating good impregnation on the support material. These identified phases in the catalysts suggest that a well-impregnated bimetallic was formed in the support to create a porous material. However, not all $CaCO_3$ decomposed due to the low calcination temperature of 500°C.

Additionally, Figure 4 (B) displays the XRD patterns of both purified and unpurified, carbon nanotubes (CNTs). The purified and unpurified CNTs showed similar diffraction peaks, with the two most dominant graphitized CNT peaks occurring at 2θ values of 26.5° and 44.3°, as widely reported by other authors [1,4,24]. However, the intensities of the graphite peaks were low in the unpurified sample (CNT500-16). Other low-intensity phases such as $CaCO_3$, Fe_3O_4, Fe_3C, and NiO were observed in the unpurified samples. The graphitized peaks became more pronounced after purification, indicating some degree of success in the purification process, although some impurities like NiO, Fe_3C, and Fe_3O_4 are still present after purification. This observation is consistent with other works involving similar catalysts or support [4,11].

Overall, the results suggest that the purification process had a positive effect on the CNT, increasing the intensities of the graphitized peaks and reducing the amount of impurities present.

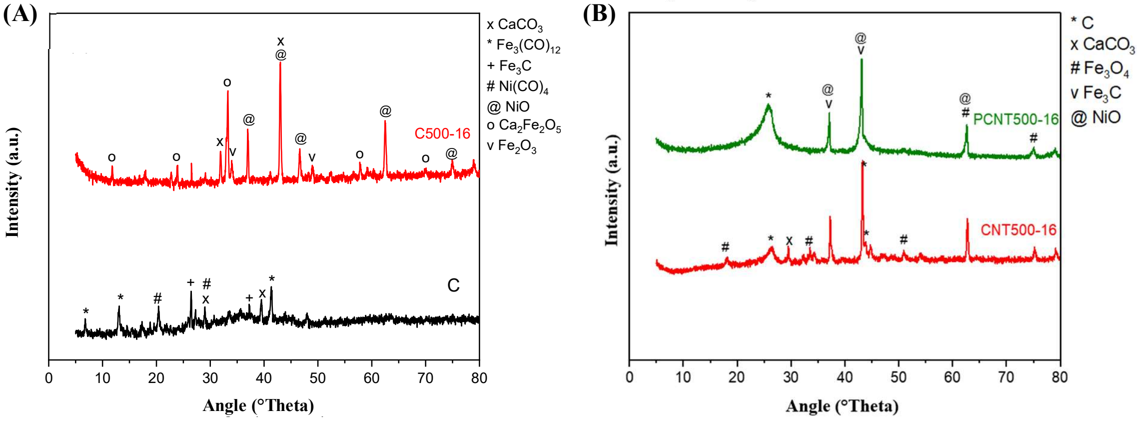

Figure 4 XRD patterns of (A) calcined catalyst and (B) synthesized CNT samples at different conditions.

Figure 5 shows FTIR results for the synthesized catalyst and CNT. After calcination at 500°C for 16 h, Sample C500-16 displays functional groups belonging to alcohol and aromatic compounds. Sample CNT500-16 exhibited O-H stretching group. Sample PCNT500-16 showed a different functional group, indicating successful functionalization.

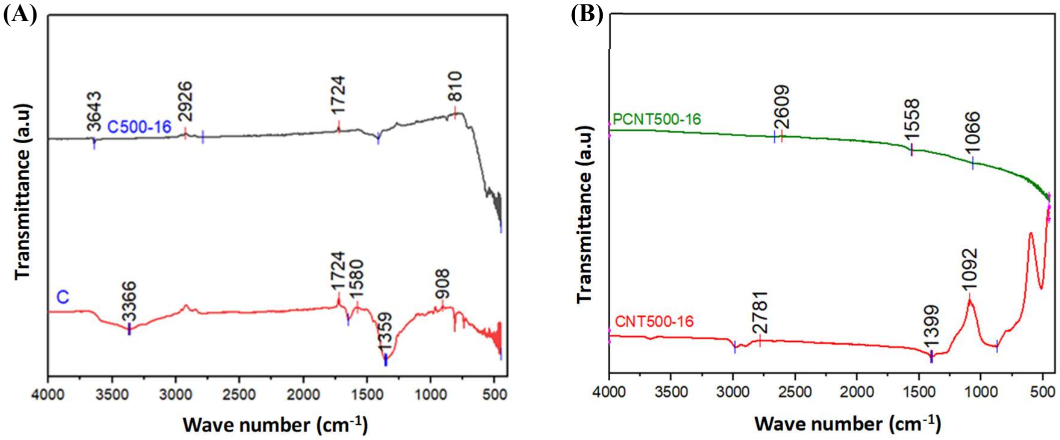

Figure 5 Fourier Transform Infrared (FTIR) of synthesized (A) bimetallic catalyst and (B) CNTs

Figure 6 shows the Raman shift for the unpurified and purified CNT samples. The two main graphite bands are present in both the purified and unpurified CNT bundles. The D-band, present at 1345 cm^{-1}, is activated by the presence of disorderliness in the carbon system. The G-band, present at 1613 cm^{-1}, is assigned to the in-plane vibration of the C-C bond, which is typical of defective graphite-like materials [9]. The Raman spectrum also exhibits a band around 2704 cm^{-1} called the G' or 2D band, which is attributed to the overtone of the D band. The

G' band was more pronounced in the unpurified samples but significantly reduced after the purification process. The calculated ratio, IG/ID, of the intensity of the D-band (ID) and G-band (IG) is 1.04. The closer the IG/ID ratio is to unity, the more crystalline the material [8]. The XRD patterns shown in Figure 4 (B) confirm the crystallinity of sample PCNT500-16. It is also worth noting that the IG/ID ratio of the purified CNT (PCNT) is slightly higher than what was obtained before purification. This suggest that the impurities blocked the surface of CNT and did not allow the instrument probes to get direct contact with the materials under test. Once the impurities are removed, the probe is able to get direct access to the material under test.

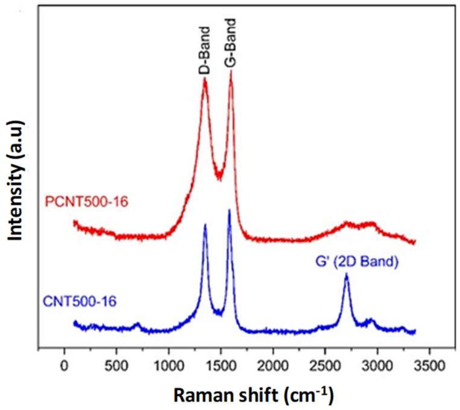

Figure 6 Raman peaks before and after purification process.

4. Conclusion

In conclusion, the efficient synthesis of high-quality carbon nanotubes (CNTs) remains a challenge, and identifying optimal processing conditions is crucial for large-scale production. This study investigated the effects of various processing parameters on the yield and properties of carbon nanotubes (CNTs) synthesized using a chemical vapor deposition process with an Fe-Ni bimetallic catalyst supported on $CaCO_3$. The study found that optimizing the synthesis conditions increased the graphitization and crystallinity of the CNTs produced, resulting in a maximum CNT yield of 376% under the optimal conditions of a reaction temperature of 700°C, a time of reaction of 90 minutes, and nitrogen and C_2H_2 flow rates of 294 mL/min and 193 mL/min, respectively. CNT purification was effective in reducing impurities and functionalizing the CNTs for easy dispersion. These findings demonstrate that processing parameters play a significant role in the yield and quality of synthesized CNTs, and optimizing the synthesis conditions and purifying the CNTs can enhance the quality of the final product. These results could inform the development of efficient and cost-effective methods for large-scale production of high-quality CNTs for numerous applications.

5. References

[1] Gupta N, Gupta SM, Sharma SK. Carbon nanotubes: synthesis, properties and engineering applications. Carbon Lett. 2019;29:419-447.

[2] Maślana K, Kaleńczuk RJ, Zielińska B, Mijowska E. Synthesis and characterization of nitrogen-doped carbon nanotubes derived from g-C_3N_4. Materials. 2020;16(6):1-12.

[3] Ali E, Hadis D, Hamzeh K, Kouhi M, Zarghami N, Akbarzadeh A, et al. Carbon nanotubes: properties, synthesis, purification, and medical applications. Nanoscale Res Lett. 2014;9:393:1-13.

[4] Aliyu A, Abdulkareem AS, Kovo AS, Abubakre OK, Oladejo JT, Kariim I. Synthesize multi-walled carbon nanotubes via catalytic chemical vapour deposition method on fe-ni bimetallic catalyst supported on kaolin. Carbon Lett. 2017;21:33-50.

[5] Arora N, Sharma NN. Arc discharge synthesis of carbon nanotubes: comprehensive review. Diam Relat Mater. 2014;50:135-150.

[6] Prasek J, Drbohlavova J, Chomoucka J, Hubalek J, Jasek O, Adam V, et al. Methods for carbon nanotubes synthesis - review. J Mater Chem. 2011;21:15872-15884.

[7] Cheng Y, Jiang SP. Advances in electrocatalysts for oxygen evolution reaction of water electrolysis-from metal oxides to carbon nanotubes. Prog Nat Sci Mater Int. 2015;25(6):545-553.

[8] Kavecký Š, Valúchová J, Čaplovičová M, Heissler S, Šajgalík P, Janek M. Nontronites as catalyst for synthesis of carbon nanotubes by catalytic chemical vapor deposition. Appl Clay Sci. 2015;114:170-178.

[9] Kumar U, Yadav BC. Synthesis of carbon nanotubes by direct liquid injection chemical vapor deposition method and its relevance for developing an ultra-sensitive room temperature based CO 2 sensor. J Taiwan Inst Chem Eng. 2019;96:652-663.

[10] Arunkumar T, Karthikeyan R, Subramani RR, Viswanathan K, Anish M. Synthesis and characterisation of multi-walled carbon nanotubes (MWCNTs). Int J Ambient Energy. 2020;41:452-456.

[11] Bankole MT, Mohammed IA, Abdulkareem AS, Tijani JO, Ochigbo SS, Abubakre OK, et al. Optimization of supported bimetallic (Fe-Co/CaCO3) catalyst synthesis parameters for carbon nanotubes growth using factorial experimental design. J Alloys Compd. 2018;749:85-102.

[12] Purohit R, Purohit K, Rana S, Rana RS, Patel V. Carbon nanotubes and their growth methods. Procedia Mater Sci. 2014;6:716-728.

[13] Chiwaye N, Jewell LL, Billing DG, Naidoo D, Ncube M, Coville NJ. *In situ* powder XRD and Mössbauer study of Fe-Co supported on $CaCO_3$. Mater Res Bull. 2014;56:98-106.

[14] Abdulkareem AS, Kariim I, Temitope BM, Oladejo JT, Abodunrin T, Olu SC. Synthesis and characterization of tri-metallic Fe-Co-Ni catalyst Supported on $CaCO_3$ for multi-walled carbon nanotubes growth via chemical vapor deposition technique. Arab J Sci Eng. 2017;42(6):4365-4381.

[15] Ratković S, Kiss E, Bošković G. Synthesis of high-purity carbon nanotubes over alumina and silica supported bimetallic catalysts. Chem Ind Chem Eng Q. 2009;15:263-270.

[16] Shah KA, Tali BA. Synthesis of carbon nanotubes by catalytic chemical vapour deposition: A review on carbon sources, catalysts and substrates. Mater Sci Semicond Process. 2016;41:67-82.

[17] Bajad G, Guguloth V, Vijayakumar RP, Bose S. Conversion of plastic waste into CNTs using Ni/Mo/MgO catalyst - an optimization approach by mixture experiment. Fuller Nanotub Carbon Nanostructures.2016; 24(2):162-169.

[18] Liu H, Zhang Y, Li R, Sun XL, Rachid HA. Effects of bimetallic catalysts on synthesis of nitrogen-doped carbon nanotubes as nanoscale energetic materials. Particuology 2011;9(5):465-470.

[19] Ayillath Kutteri D, Wang IW, Samanta A, Li L, Hu JL. Methane decomposition to tip and base grown carbon nanotubes and CO_x-free H_2 over mono- and bimetallic 3d transition metal catalysts. Catal Sci Technol. 2018;8(3):858-869.

[20] Magrez A, Seo JW, Smajda R, Mioni M, Forró L. Catalytic CVD synthesis of carbon nanotubes: towards high yield and low temperature growth. Materials. 2010;3(11):4871-4891.

[21] Voelskow K, Becker MJ, Xia W, Muhler M, Turek T. The influence of kinetics, mass transfer and catalyst deactivation on the growth rate of multiwalled carbon nanotubes from ethene on a cobalt-based catalyst. Chem Eng J. 2014;244:68-74.

[22] Ismail AF, Goh PS, Tee JC, Sanip SM, Aziz M. A review of purification techniques for carbon nanotubes. Nano. 2008;3:127-143.

[23] McCarty JG, Gusman M, Lowe DM, Hildenbrand DL, Lau KN. Stability of supported metal and supported metal oxide combustion catalysts. Catal Today. 1999;47(1-4):5-17.

[24] Kumar R, Singh RK, Singh DP, Vaz AR, Yadav RR, Rout CS, et al. Synthesis of self-assembled and hierarchical palladium-CNTs-reduced graphene oxide composites for enhanced field emission properties. Mater Des. 2017;122:110-117.