

# OPTIMIZED PARAMETERS FOR CARBON NANOTUBES SYNTHESIS OVER Fe AND Ni CATALYSTS VIA METHANE CVD

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**Abstract.** Multi walled carbon nanotubes (MWNTs) were synthesized via methane chemical vapor decomposition using low-cost activated carbon (AC) as support for Fe and Ni catalyst. Maximum methane conversions of 98% and 42% were observed on Fe and Ni catalysts respectively at reaction temperature of 750 °C by on-line gas chromatography. Bundles of MWNTs with an average internal dia ~ 20nm at 850 °C over Ni catalyst and thin-walled CNTs (dia ~ 8 nm) formed over Fe catalysts were confirmed by morphological studies by transmission electron microscopy. CNTs formed over Fe catalyst illustrated a typical *tip-growth phenomenon*. The formation of MWNTs was further supported with the data obtained from thermogravimetric analysis. The ideal condition for CNTs growth was noticed under N<sub>2</sub>/CH<sub>4</sub> gasflow ratio of 2:1 rather than H<sub>2</sub>/CH<sub>4</sub> atmosphere.

## 1. INTRODUCTION

Carbon nanotubes (CNTs) are a new form of carbon molecules with many outstanding properties which makes them potentially useful in various applications such as electronic, mechanical, composite, medical, etc., [1-5]. In general, CNTs has been classified either as metallic or semi-conducting that depends strongly on their chirality and diameter. Among CNTs synthesis methods, chemical vapour decomposition (CVD) is the most suitable method at low temperatures when compared with other techniques [6]. In this process, various inorganic porous materials such as alumina [7], silica [8], magnesium oxide [9] and Zeolites [10] were investigated as support materials by numerous researchers in producing various diameter ranges of single-walled carbon nanotubes (SWNTs) and MWNTs [11]. How-

ever, while considering high quantity and lower production cost of CNTs, it is necessary to trace a new support material to overcome current drawbacks like higher production cost and purification issues. In recent years, carbon itself finds more importance in catalytic reactions either as a catalyst or as supports owing to its fascinating physical and chemical characteristics. The potential use of carbon as catalyst support has not yet been fully exploited, even though there is considerable volume of literature devoted to this field in last 20 years [12-14]. Since Malaysia being the leading producer of activated carbon from its palm industry, there is abundant resource for its cheaper availability. Hence, our present study was focused on using low-cost AC (derived from wood base material) as support for Fe and Ni catalysts with the aim to grow CNTs of different morphologies.

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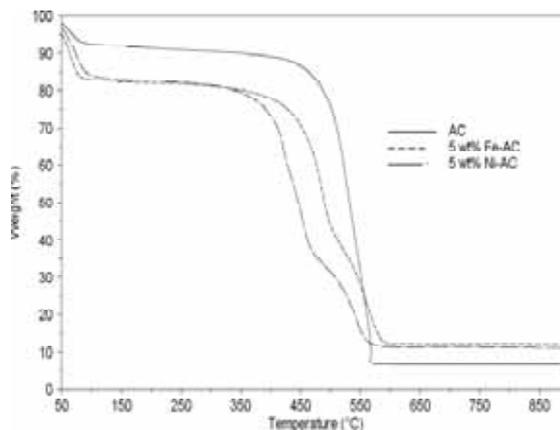
**Table 1.** Proximate and ultimate analysis of AC (catalyst support) sample.

| Samples | Proximate Analysis(dry basis), % |                 |          |         |        |
|---------|----------------------------------|-----------------|----------|---------|--------|
|         | Fixed Carbon                     | Volatile Matter | Ash      |         |        |
| AC      | 85.3                             | 7.4             | 7.3      |         |        |
|         | Ultimate Analysis(dry basis), %  |                 |          |         |        |
|         | Carbon                           | Hydrogen        | Nitrogen | Sulphur | Oxygen |
|         | 71.0                             | 0.5             | 0.66     | 0.75    | 27.07  |

## 2. EXPERIMENTAL

### 2.1. Preparation of supported catalysts

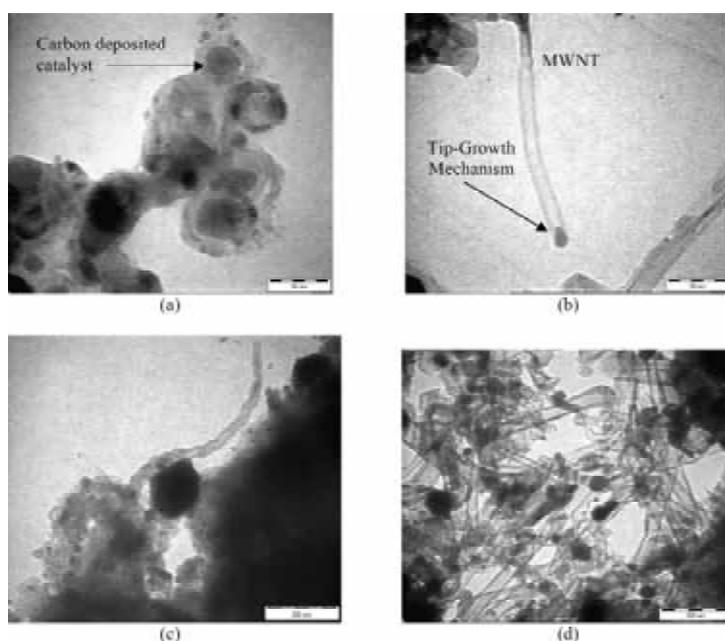
Iron(III)nitrate nanohydrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) was supplied by Sigma-Aldrich and Nickel(II)nitrate hexahydrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) was obtained from Merck. The metal nitrates were supported on AC (supplied by Century chemicals Sdn. Bhd.). Catalysts were prepared by dissolving the right amount of respective metal nitrates in acetone and followed by impregnation onto the AC supports. The catalyst samples were prepared with 5 wt.% of metal oxide over AC support. Metal impregnated catalysts samples were dried at 105 °C for 12 h and calcined in air at 350 °C for 3 h. The catalysts were then

**Fig.1.** TGA curves of Raw Support and Catalysts (a) AC (b) 5 wt.% Fe /AC (c) 5wt% Ni /AC.

sieved to a size of <math><50 \mu\text{m}</math>. The calcined samples were further reduced at 450 °C for 3 h under  $\text{H}_2$  atmosphere in tubular quartz reactor.

### 2.2. Preparation of carbon nanotubes

The synthesis of CNTs was carried out in a horizontal quartz tube fixed-bed reactor (length and diameter of the reactor were 1050 and 60 mm, respectively) via catalytic decomposition of methane at standard pressure of 1 atm. High purity methane (99.99%) was mixed with either nitrogen or hydro-

**Fig.2.** TEM images of CNTs formed over Fe / AC catalyst (a) 750 °C (b) 850 °C and over Ni / AC catalyst (c) 750 °C (d) 850 °C for  $\text{N}_2/\text{CH}_4 = 2:1$ .

**Table 2.** Surface characteristics of AC (support) materials.

|  |                           |
|--|---------------------------|
| <i>Dubinin-Astakhov method:</i>  |                           |
| Micropore surface area:  | 824.31 m <sup>2</sup> /g  |
| Limiting micropore volume:   | 0.3070 cm <sup>3</sup> /g |
| <i>Surface Area</i>  |                           |
| Single point surface area at $P/P_0 = 0.242221660$ :   | 646.56 m <sup>2</sup> /g  |
| BET Surface Area:  | 626.49 m <sup>2</sup> /g  |
| Langmuir Surface Area:   | 847.97 m <sup>2</sup> /g  |
| <i>Pore Volume</i>   |                           |
| Single point adsorption total pore volume of pores less than 1276.026 Å width at $P/P_0 = 0.984593561$ : | 0.3274 cm <sup>3</sup> /g |
| Single point desorption total pore volume of pores less than 738.008 Å width at $P/P_0 = 0.973058159$ :  | 0.3259 cm <sup>3</sup> /g |
| <i>t-Plot micropore volume:</i>  | 0.2641 cm <sup>3</sup> /g |
| BJH Adsorption cumulative volume of pores between 17.000 Å and 3000.000 Å width:                         | 0.0328 cm <sup>3</sup> /g |
| BJH Desorption cumulative volume of pores between 17.000 Å and 3000.000 Å width:                         | 0.0387 cm <sup>3</sup> /g |
| <i>Pore Size</i>   |                           |
| Adsorption average pore width (4V/A by BET):   | 20.90 Å                   |
| Desorption average pore width (4V/A by BET):   | 20.81 Å                   |
| BJH Adsorption average pore width (4V/A):  | 92.68 Å                   |
| BJH Desorption average pore width (4V/A):  | 58.45 Å                   |
| <i>Horvath-Kawazoe</i>   |                           |
| Maximum pore volume at $P/P_0 = 0.011776870$ :   | 0.2687 cm <sup>3</sup> /g |
| Median pore width:   | 5.31 Å                    |

gen gas (99.99%) with ratios of 1:1 (120:120 ml/min) and 1:2 (120:240 ml/min) before entering the reactor. The flow of gases was controlled using respective mass flow controllers. For synthesizing nanotubes, 0.2 g of synthesized catalyst was placed in the middle part of the reactor using a small quartz boat for each run. The reactor was then mounted in an electrical furnace and heated under N<sub>2</sub> flow to the desired temperatures of 750 °C and 850 °C re-

spectively. The schematic diagram of the experimental apparatus has been shown elsewhere [15].

### 2.3. Characterization

The surface characterization studies of the AC support was done using Micrometrics with ASAP 2020 V3.02 H software. AC materials were analyzed for its chemical composition using Perkin Elmer Series II(2400) CHNS analyzer. The product gases were analyzed using an on-line gas chromatograph (Agilent Technologies 7890, USA). The gas chromatograph was controlled on-line, using ChemStation B.02.01 software. The carbons deposited on the catalyst were analyzed using a Philips, model CM12 transmission electron microscope. Thermal stability analysis of product samples was carried out using TA Instruments, SDT Q600 thermogravimetry analyzer with Universal Analysis 2000 software. A mixture of N<sub>2</sub> gas and purified air were used in TGA instrument for thermal stability test.

## 3. RESULT AND DISCUSSION

It is known that support material plays a vital role in metal-support interaction as well as in CNTs formation during CVD reactions. Surface properties and characteristic of AC were studied to know its composition both by proximate and ultimate analysis. The results of ultimate analysis, proximate analysis were shown in Table 1. The surface characteristics like surface area, pore size and pore volume has been studied and the results of raw AC sample were shown in Table 2.

### 3.1. Thermal stability of prepared catalysts

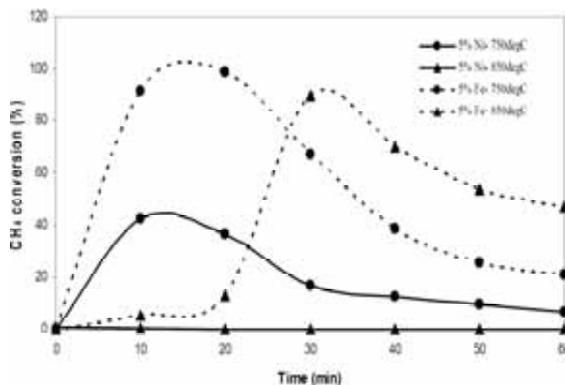
Thermal stability of the raw AC support materials and metal loaded catalysts were studied for a temperature range of 30-900 °C in a mixture of N<sub>2</sub> and purified air atmosphere. The TGA curves in Fig. 1 show that an initial weight loss of around 10-15% with in the temperature range of 60-80 °C, which may be due to the removal of volatile organic impurities inherited with the base support material. Raw AC samples showed much higher thermal stability than that of Fe and Ni -metal loaded catalysts. Fig.1(a) showed that thermal degradation of raw AC started at 416 °C and was completely decomposed around 570 °C. It was noted that both Fe and Ni-loaded catalysts started its initial decomposition with in 400 °C and a small bump in their profile appeared

at temperature around 525 °C. The second stage degradation > 475 °C corresponds to the decomposition of respective metal oxides. Ermakova et al. [16] also reported the similar decomposition behavior of metal oxides at lower temperatures. Complete thermal oxidation of 5 wt.% Fe and Ni catalyst were found to occur at 585 °C and 560 °C. This showed that FeO was much stable as compared to NiO catalysts.

### 3.2. Effect of gas atmosphere

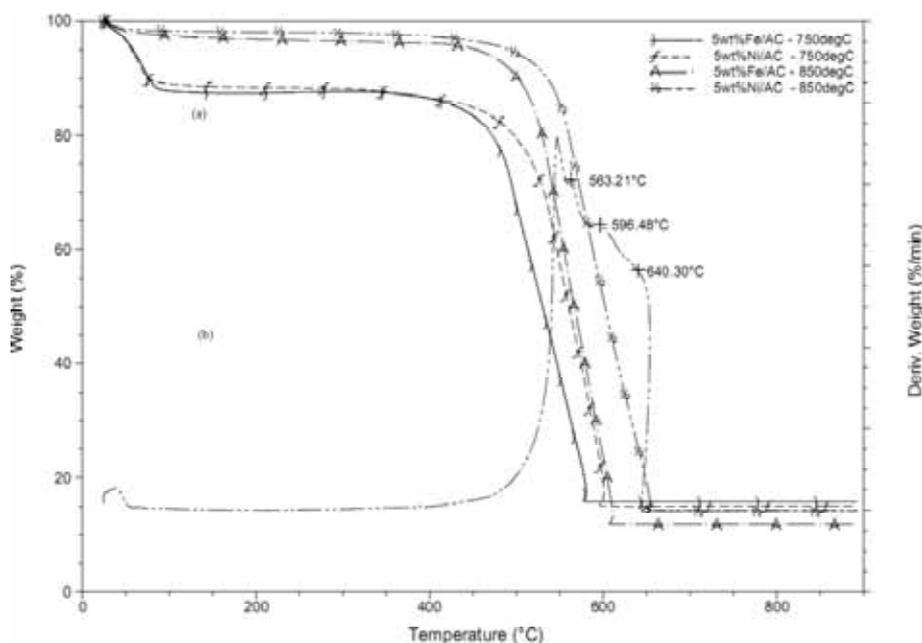
The CVD reaction over Fe and Ni catalysts was carried out to investigate the methane decomposition. The mixture of gases ( $N_2/CH_4$  and  $H_2/CH_4$ ) in the ratio of 1:1 and 2:1 was used in our decomposition studies. Highly populated and fully developed growth of CNTs was obtained when  $N_2$  was used as carrier gases as shown in Figs. 2a – 2d. However there was no formation of CNTs under  $H_2/CH_4$  conditions. This may be due to the rapid reduction of metal oxides by  $H_2$  gas, which in turn makes  $CH_4$  to decompose at a faster rate. This would deposit pyrolytic carbons on to the active catalytic sites, thereby reducing the catalyst activity.

Higher volume of MWNTs was formed in product obtained from  $N_2/CH_4$  environment. This can be attributed to the presence of inert  $N_2$  gas that could be helpful in maintaining the catalytic activity for a longer duration and thereby resisting the reduction



**Fig.3.** Plot of methane conversion with respect to time using Ni (—) and Fe (---) catalyst at temperature 750 °C (•) and 850 °C (▲).

of metal oxides. Furthermore, the flow rate ratio of  $N_2:CH_4$  (2:1) tends to form abundant CNTs population than that of 1:1 ratios. When the concentration of  $N_2$  was higher, the probability of  $CH_4$  molecules decomposition over the active metal sites may be in a slow manner that could enhance the formation of carbon nuclei to produce high yield of MWNTs. Similar kind of observations was earlier reported by Zhan et al. [17]. It was noticed in Fig. 2a that only circular shaped carbon rings were formed at 750 °C over Fe catalyst. However at 850 °C, thin and elongated CNTs having internal dia ~ 8 nm were formed



**Fig.4.** (a) TGA plot of synthesized CNTs over Fe & Ni catalysts at 750 °C & 850 °C, (b) DTA plot of Ni catalyst at 850 °C showing different CNTs synthesized.

with Fe catalyst embedded at its tip. In case of Ni catalyst, not much CNTs were formed at 750 °C as witnessed in Fig. 2c. Bunch of MWNTs with thick walls having internal dia ~ 20 nm were developed on Ni catalyst at 850 °C as noticed in Fig. 2d. At higher temperature i.e. 850 °C, both exhibit a typical *Tip-growth mechanism* which indicated that the interaction between AC support and metal catalyst were weak. Hence the nano-sized catalysts particles were carried from the support surface during the growth process.

### 3.3. Methane conversion and CNT formation

Methane CVD experiment was performed at temperatures of 750 and 850 °C, during which CH<sub>4</sub> was converted to C and H<sub>2</sub>. The deposited carbon over the catalyst surface tends to form carbon nanotubes. The structure and morphology of CNTs depends on factors such as catalyst pretreatments and reaction atmospheric conditions. Fe catalysts were found to be more active in CH<sub>4</sub> conversion than Ni catalyst as noticed in Fig. 3. It was observed from the methane conversion plots that at 750°C, higher CH<sub>4</sub> conversion over Fe (98.6%) and Ni (42.4%) catalysts were achieved. This was due to the fact that oxides of Fe were much stable and active than NiO particles. Furthermore, Fe catalyst active sites were available in plenty for a longer duration showing that methane decomposition at 750 °C was very slow. Even though there was a slow decomposition rate of CH<sub>4</sub>, nanotubes could not be formed as seen in Figs. 2a and 2c. Though the methane conversion becomes low at elevated temperature, MWNTs were formed predominantly as shown in Fig. 2b and 2d. This showed that the conversion of methane and its decomposition rate has no direct dependence on CNT growth.

At higher CVD temperature of 850 °C, both catalytic activity and methane conversion were found to decrease drastically. Fe and Ni catalysts reported 40% and <10% conversions respectively. In this case, rate of CH<sub>4</sub> decomposition was little bit faster, which showed that NiO and FeO were much active and readily decomposed the reactant CH<sub>4</sub> gas. It was noticed that Fe catalyst maintained its activity even after 60 min of reaction time at both temperatures.

Fig. 4a showed the TGA thermograms for synthesized CNTs over Ni and Fe catalyst at 750 and 850 °C. It was observed that MWNTs synthesized from Ni catalyst showed higher thermal stability than that of Fe catalyst. This may be due to the fact that

CNTs with varying wall structures possess different thermal stability. From Fig. 4b, we can notice that the thermal decomposition of activated carbon supports occurred around 560 °C and after that MWNTs started to degrade thermally at 596 °C. As-synthesized MWNTs were completely decomposed at 640 °C. The final weight retained (10-15 wt.%) was mainly due to the presence of inbound mineral content of activated carbon support and the deposited metal.

## 4. CONCLUSIONS

MWNTs were synthesized on low-cost activated carbon supports with Ni and Fe catalysts by methane CVD method. N<sub>2</sub>/CH<sub>4</sub> with gas ratio 2:1 gave more CNTs yield than 1:1 and H<sub>2</sub>/CH<sub>4</sub> combinations. Maximum methane conversions of 98% and 42% over Fe and Ni catalyst were reported at 750 °C. High yield of MWNTs were formed at 850 °C. TGA showed that MWNTs formed over Ni exhibited higher thermal stability as compared to Fe catalyst. Parameters like gas mixtures, N<sub>2</sub>/CH<sub>4</sub> ratio, reaction temperature contributes a vital role in methane decomposition, catalytic activity and CNTs formation. Further study is being conducted to know the in-depth role of metal catalysts, reaction and growth kinetics.

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