Production of Multi-walled Carbon Nanotubes via Catalytic Decomposition of Methane in the Chemical Vapor Decomposition process

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Abstract: In this paper, carbon nanotubes (CNTs) were synthesized via vapor deposition of methane as a carbon source in the presence of Ni/MgO catalyst. The catalyst crystallinity and morphology was examined by XRD and SEM and its superior size distribution and crystallinity was confirmed. The catalytic methane decomposition was conducted in a chemical vapor deposition reactor at 900 °C. Methane, with the flow rate of 600 ml/min, was used as a carbonous gas and hydrogen and nitrogen were used at the flow rate of 500 ml/min. The obtained carbon was characterized by transmission electron microscopy (TEM) and recognized to be multi-walled carbon nanotubes with an average diameter of ~8.6 nm. The Raman spectrum confirmed a high graphitization degree of the obtained CNTs with an I_D/I_G ratio of 2.05, indicative of high crystallinity with few structural defects. Moreover, the thermal analysis showed the high oxidation stability of the multi-walled carbon nanotubes.

Keywords: Ni/MgO catalyst, methane decomposition, multi-walled carbon nanotubes.

I. INTRODUCTION

Multi-walled carbon nanotubes (MWCNT) were discovered by Iijima in 1991[1]. Later in 1993, single-walled carbon nanotubes (SWCNT) were discovered by the same researcher[2]. Carbon nanotubes with form of Bamboo shaped has been reported as well.[3] Since the discovery, research about the different methods of production, properties and applications of carbon nanotubes has been continued. Although all carbon nanostructures, including fullerenes, graphene and nanotubes are of great interest, CNTs have many unique physical and electrical properties [4] which make them an ideal candidate for numerous applications from field emission sources[5] to anti-cancer agent[6].

There are a number of methods to produce carbon nanotubes, including arc discharge, chemical vapor deposition, plasma enhanced chemical vapor deposition, laser ablation, and high-pressure CO conversion production[7] and CO2 conversion [8]. However, chemical vapor deposition (CVD) is still the most dominant method of high-volume carbon nanostructures production [9] which typically utilizes a fluidized bed reactor that enables a uniform gas diffusion and heat transfer to the metallic catalyst nanoparticles employed in the CNT production[10]. In a CVD process, CNTs are produced via the decomposition of a gaseous carbon-containing hydrocarbon source at an elevated temperature in the presence of a transition metal catalyst [11]. A high nanotubes production yield can be achieved using this method. In addition, the product obtained using this approach tends to possess high purity and the growth of the carbon nanotubes requires a lower temperature in the range of 550-1000 °C when compared to other methods. This renders the process cheap, easy for lab scale production, and suitable as production for commercial applications[12]. Finally, when catalyst is supported with a substrate, the growth of nanotubes can be controlled in a desired direction with respect to the substrate[13, 14].

As mentioned earlier common transition metals such as Ni, Co, Fe have been used in the production of carbon nanotubes. Despite the fact that MgO has been shown to be a superior support in the production of carbon nanotubes [15], there are no comprehensive reports which examines the utilization of such materials in the production of carbon nanotubes via chemical vapor deposition of methane gas. In this work MgO supported nickel was used as a novel catalyst in the production of
carbon nanotubes. Additionally, the prepared CNTs were examined in order to identify the potentials of MgO as a support material in the carbon nanotube synthesis.

II. METHODOLOGY
Magnesium Oxide (MgO), M=40.3 g/mol was purchased from R&M chemicals, Malaysia. Hydrochloric acid (HCl), 37 wt% was purchased from Fisher Chemicals. Nickel (II) nitrate hexahydrate Ni(NO₃)₂, 99.99% trace metal basis and oleic acid 99% CH₃(CH₂)₇CH=CH(CH₂)₇COOH were purchased from Sigma Aldrich, U.S.

The employed catalyst synthesis process was a modification of a study by Budiredla et al. [16]. To synthesize Mg-doped NiO nano particle catalyst, magnesium nitrate hexahydrate (Mg(NO₃)₂·6H₂O), nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O), and Oleic Acid (C₁₈H₃₄O₂) were used as precursors with ethanol as a solvent. 20 g of magnesium nitrate hexahydrate was added slowly to 100 ml of ethyl alcohol and stirred at 100 °C until the complete dissolution. Similarly, 10g of nickel nitrate hexahydrate was dissolved in 100 mL of ethyl alcohol. The obtained solutions were then mixed and oleic acid was added slowly to the obtained mixture at a constant stirring to produce a thick white gel. The product was dried at 100 °C for 24 hr to achieve Ni-doped magnesium. The result was then calcined for 4 hr at 600 °C.

For the CNT production, 5 g of the obtained catalysts were placed in the CVD reactor and heated in the presence of N₂ to 600 °C for 1 hr. The CVD reactor was then purged with H₂ and maintained for 2 hr at 600 °C. The temperature of the reactor was then increased to 1000 °C in the presence of N₂. Once the temperature was stabilized at 1000 °C, the methane gas was introduced to the reactor with a flow rate of 600 ml/min for 3 hr. The reactor was then cooled to ambient temperature while passing N₂ gas for 30 minutes. The schematic representation of the CVD process is shown in Figure 1. The obtained powder was collected and purified using 50 ml concentrated HCl for further characterization. XRD analysis was performed in a Bruker D8 Focus advanced powder diffractometer with a Cu Ka radiation of wavelength 0.15406 nm. Field emission scanning electron microscopy (FESEM) (Zeiss SUPRA55) micrographs were obtained to visualize the prepared catalyst as well as CNTs and determine their surface morphology at an operating voltage of 3 kV. Raman spectrophotometer with a laser of 532.230 nm wavelength (WITec, Model: Alpha 300R) was used to confirm the formation of CNTs. Transmission electron microscopy (TEM) (Hitachi47700m) at an operating voltage of 10 Kv to investigate the nanotubes’ diameter. Thermo gravimetric analysis (TGA) was performed (Mettler Toledo Model: TGA/DSC1) at the resolution of 10 °C per 5 min to examine the CNTs’ thermal properties.

III. RESULT AND DISCUSSION
The SEM images of Ni/MgO catalyst are shown in Figure 2. Large surface area of the catalyst particles can be observed in this figure. As can be noted in the SEM micrographs, Ni-MgO particles, served as the catalyst and support for the CNTs production, exhibits flower/star like morphology.
Figure 2-SEM micrographs of the flower-like Ni/MgO catalyst

XRD diffraction pattern of the Ni/MgO catalysts is presented in Figure 3. XRD analysis was carried out to examine the crystalline structure of the catalyst. The peaks at 2θ = 26°, 38°, 52°, 58°, and 68° are assigned to the planes of (111), (200), (220), (311), and (322) of Ni/MgO respectively. The volume-averaged crystalline size was calculated using Debye-Scherer’s formula:

\[ D = \frac{K\lambda}{\beta \cos \theta}, \]

Where \( D \) is the crystalline size (nm), \( K \) is the Scherer constant equal to 0.89, \( \lambda \) is the radiation wavelength (nm), \( \beta \) is the observed peak width, and \( \theta \) is the diffraction angle. The average particle size was calculated to be 32 nm.

Figure 3-XRD diffraction pattern of the Ni/MgO catalyst with the calculated average particle size of 32 nm

The SEM micrographs of the grown carbon nanotubes are shown in Figure 4. The tubes grown amid the Ni/MgO flower-like catalysts are shown by arrows in Figure 4 (a). Carbon has been grown over the surface of the catalyst, suggesting that the catalytic methane decomposition has followed the tip growth mechanism to produce CNTs. Figure 4 (b) shows the high quality SEM images of the carbon nanotubes after the purification.

Figure 4-(a) SEM images of the grown carbon nanotubes in the presence of the prepared catalyst and (b) carbon nanotubes after the purification

Figure 5 shows the TEM images of multi-walled carbon nanotubes with an average diameter of 8.6 nm.

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Figure 5- TEM image of a multi-walled carbon nanotube with an average diameter of 8.6 nm

Figure 6 shows the Raman spectrum of purified CNTs. Graphite-like carbon materials exhibit a Raman band at around 1580 cm⁻¹ assigned to the G band, and a peak at 1350 cm⁻¹ assigned to the D band. The D-band is known to depend on the disorder features of the hexagonal graphitic layers as well as the presence of small crystalline grains [17-19]. Since the G band is attributed to the tangential stretching mode of the graphite C=C bond, which is assigned to the vibration of sp²-bonded carbon atoms in a two-dimensional hexagonal lattice, we can justly conclude the formation of graphitic nanotubes. The intensity of the D-band is inversely proportional to the effective crystallite size ($L_a$) in the direction of the graphite plane:

\[ \frac{I_D}{I_G} = C \left( \frac{\lambda}{L_a} \right) \]  

(2)

where $I_D$ and $I_G$ are the integrated intensities of the D and G bands, respectively, and $C$ ($\lambda$) is the wavelength dependent pre-factor with the value of 4.36[20]. The $I_D/I_G$ ratio is an indication of the level of defects. The average value of $I_D/I_G$ is determined to be 2.05 which is indicative of an satisfactory graphitization degree[21].

Figure 7 shows the TGA curve of the obtained carbon nanotubes grown on the surface of the Ni/MgO catalyst, showing the $I_D/I_G$ ratio of 2.05.

Figure 7 shows the TGA curve of the obtained nanocarbons. This figure shows the amount of weight loss as a function of temperature. Oxidative temperatures are reported to be around 330°C for amorphous carbon, and 500-700°C for MWCNTs, respectively [22, 23]. As is observed in Figure 7, no weight loss was noted for the temperatures below 550°C. However, about 80% weight loss is noted in temperatures between 550 and 700°C for the obtained CNTs which confirm the formation of MWCNTs.

VI. CONCLUSION

Ni/MgO catalyst was prepared, characterized and employed for the production of carbon nanotubes in a vapor deposition reaction. Multi-walled carbon nanotubes were synthesized successfully by the
decomposition of methane over the surface of the prepared catalyst. TEM micrographs confirmed the formation of the multi-walled carbon nanotubes with the diameter of 8.6 nm. Raman spectroscopy results suggested a low degree of defects for the obtained CNTs. Moreover, high oxidation stability was observed from the TGA results. It can be concluded that Ni/MgO can be successfully used in the production of carbon nanotubes.

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