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SYNTHESIS OF ALIGNED CARBON NANOTUBE (ACNT) THROUGH CATALYTIC DECOMPOSITION OF METHANE BY WATER-ASSISTED CHEMICAL VAPOR DEPOSITION (WA-CVD)

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ABSTRACT

The production of Carbon Nanotubes (CNT) has a problem with the limited results of Aligned CNT (ACNT) products, due the fact that an effective and economical method has not yet been discovered. This research used catalytic decomposition of methane with the Water-Assisted Chemical Vapor Deposition (WA-CVD) method by using a bench-scale plate structured catalyst reactor and a fixed bed reactor. The Fe-Ni/Al_2O_3 Catalyst prepared by sol-gel/dip-coating and Ni-Cu-Al Catalyst prepared by co-precipitation were used to make the CNT. Transmission Electron Microscope (TEM) results show there are various types of nanocarbons produced, such as CNT, bamboo-shaped CNT and also quasi-spherical carbon onion shapes. Based on comparative results without adding the water vapor method, ACNT, which were obtained with WA-CVD, tend to grow vertically, even though they have not yet formed neat and uniform shapes. In addition, an increased number of CNT have high purity results. It shows that the role of water vapor significantly improves the quality of CNT.

Keywords: Aligned CNT; Catalytic decomposition of methane; Water-Assisted Chemical Vapor Deposition (WA-CVD)

1. INTRODUCTION

The production of Carbon Nanotubes (CNT) is now a very promising commodity. Organizations, such as World Institution Analysis, the BCC and the Royal Society, stated that the needs of CNT continue to increase every year. This is driven by the growing number of uses of this material in different sectors of life. In terms of industry, defense, health or the automotive industry, these sectors are the key to rapid demand growth of CNTs, (Purwanto, 2011). Commercial CNT applications include one of the components of nano-tech electronic equipment, such as sensors, fuel cells, semiconductors, and others (Seah et al., 2011).

The quality of a CNT can be seen from the structure and its morphology, such as the type of CNT, its diameter, structure and purity. The existence of impurities in carbon nanotubes can reduce the electrical and structural properties of CNTs (Ko et al., 2004). Structural defects can reduce the density that leads to increased electrical resistance (Endo et al., 1996). Since the successful synthesis of CNTs was arranged and aligned as being vertically straight (ACNT) in 1996 (Li et al., 1996), ACNT became one focus of nanotechnology because of its interesting characteristics, which are: identical length, uniform orientation, a very high purity, and easily shaped into macroscopic fibers. Because of its nature, the composition of ACNT is widely used

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in nanoelectronic situations or in composites as reinforcing agents (Seah et al., 2011).

Water Assisted CVD synthesis method (WA-CVD) has recently also been reported to produce ACNT, (Rong, 2009). The addition of water in the WA-CVD synthesis method is thought to enhance the purity of CNT, increase CNT yield and it can drive straight onto CNT growth. The use of catalysts Fe-Ni/Al_2O_3, where the active core is a group of Weak Metal Support Interaction (WMSI), contributes to direct the growth of CNTs with the tips-growth mechanism. Both aspects are considered effective to produce uniform ACNT growth. Nevertheless, the process typically involves a carbon source and different operating parameters. Carbon sources that are widely used to produce ACNT now are acetylene and ethylene. This research uses a carbon source, such as methane.

Methane is an alkanes compound having carbon and hydrogen bonding. Methane is used as a carbon source in the Carbon Nanotube synthesis process through decomposition reaction. Methane is normally chosen as a reactant because methane is a hydrocarbon with a high ratio of hydrogen/carbon. In addition, methane was chosen as a carbon source because of high stability at any increase in temperature, and it is able to avoid self-pyrolisis that leads to the amorphous formation, which causes deactivation of the catalyst (Wang et al., 2007). This reaction is endothermic and thus requires high operating temperatures so that decomposition reactions occur. However, it can be overcome with the addition of a catalyst to lower the activation energy, so that the maximum conversion can be achieved at lower temperatures. The reaction that occurs in the decomposition reaction of methane is as shown in Equation 1 (Grujicic, 2002).

$$CH_4 \leftrightarrow C + 2H_2 \qquad \Delta H_{298}=+75 \text{ kJ/mol} \qquad (1)$$

In addition to being economical, methane catalytic decomposition reaction is a promising nanocarbon synthesis method that produces a high product yield and is easily controlled (Wulan et al., 2011). Therefore, this study aims to synthesize ACNT through the catalytic decomposition reaction of methane with water vapor or Water-Assisted CVD methods (WA-CVD).

The crystalline compound that formed these components was characterized using Powder X-ray diffraction (XRD) patterns with a Phillips analytical X-Ray model number BV-2500. The composition of the catalyst component was determined using a X-ray Fluorescent (XRF) of a Bruker P4 engine.

2. EXPERIMENTAL

2.1. Catalyst Preparation

Fe-Ni/Al_2O_3 catalyst was prepared by the sol-gel method. Each precursor of nitrate salts formations from Merck, namely ferric nitrate nonahydrate ($Fe(NO_3)_3.9H_2O$), nickel nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$), and aluminum nitrate nonahydrate ($Al(NO_3)_2.6H_2O$), citric acid, ($C_6H_8O_7.2H_2O$) as a chelating agent, was used. Each precursor was dissolved with ethanol, using a magnetic stirrer and hot plate at 50°C for 10 minutes. First, a solution of Ni nitrate and Al nitrate was mixed into a Fe nitrate solution. Then, a solution of the previous mixture was mixed into a solution of citric acid, using a magnetic stirrer and a hot plate at a temperature of 60^{o}C, to form a sol-gel solution of Fe-Ni/Al_2O_3.

Vapor phase growth follows a synthesis method of carbon nanotubes, directly supplying a reaction of gas and catalytic metal in the chamber with stainless steel as a substrate, (Qian, 2003). Fig.1 shows a schematic diagram of the Water-Assisted Chemical Vapor Deposition apparatus for CNT synthesis (Huan Wang, 2013).

2.2. Catalyst Coating by Dip-coating Method

Stainless steel plates were used for the substrate. First, sandpaper was used to clean the plates. Then the plates were soaked in acetone for 30 minutes. Subsequently, the plates were soaked and dipped back into 4 M nitric acid for 30 minutes. Plates were dried in a furnace at a temperature of 130^{o}C. The dry plate was weighed. Then, the plates were dipped into the catalyst solution. Dyeing was carried out for 30 minutes and then the substrate plate that had been coated with a catalyst was weighed. Plates were dried at a temperature of 130°C and calcined at a temperature of 700°C and then they were weighed to obtain the final weight data.

2.3. Catalytic Decomposition of Methane

The equipment was assembled as shown in Figure 1. The Water-Assisted CVD method is a modification of the standard CVD reactor to provide the additional bubbler and water bath. The water bath was set at a temperature of about 60°C. The bath was at the end of an argon gas pipes assembly. The reaction was performed at a temperature of 700^{o}C and 800^{o}C by comparing the presence with the addition of water (WA-CVD) and without the addition of water (non WA-CVD). Methane flowed at a rate of 101 mL/min. Before the reaction was carried out, the first catalytic reduction was conducted for 30 minutes with hydrogen gas.

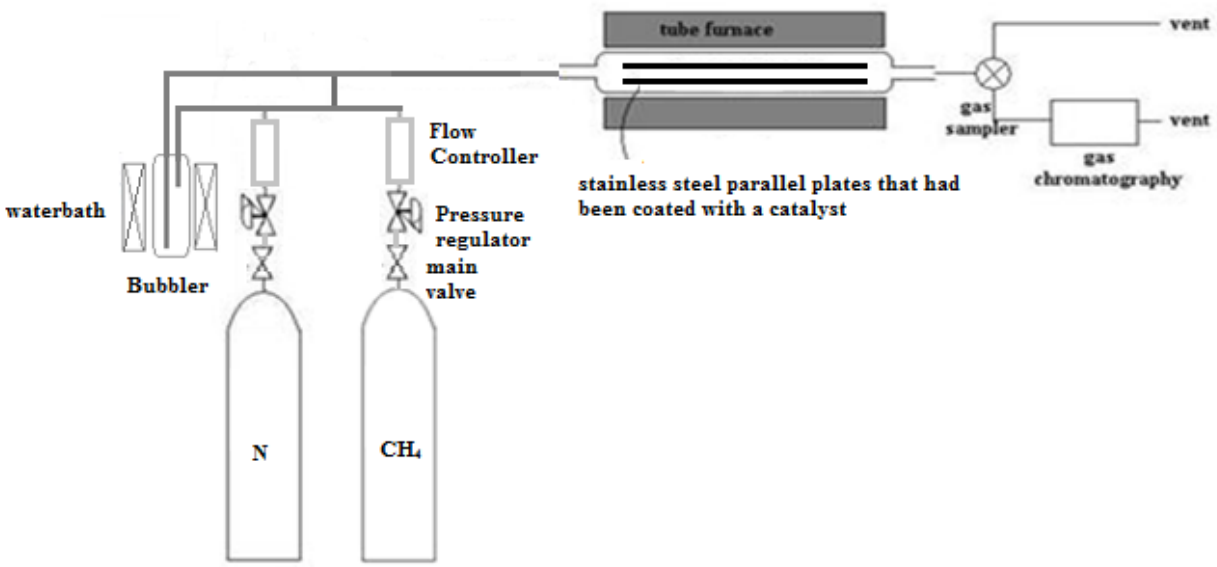

Figure 1 Schematic diagram of the Water-Assisted Chemical Vapor Deposition apparatus for CNT synthesis

GC data was processed to determine the production performance, which was observed in the conversion of methane. Methane conversion is defined as the percentage of methane that reacts to the methane initially inserted into the reactor. Using Equation 2, we obtained the methane conversion.

$$X_{CH_4} = \frac{\left|(CH_4)_{in} - (CH_4)_{out}\right|}{(CH_4)_{in}} x100\% \quad (2)$$

CNT product characterization is needed to determine the nature and morphology of CNTs produced, such as the diameter and height of the CNT. Characterization is done by using two microscopes, namely a TEM (Transmission Electron Microscope) and a FE-SEM (Field Emission-Scanning Electron Microscope).

3. RESULTS AND DISCUSSION

Preparation, Characterizations and Catalyst Coating at this stage, ethanol is used as a solvent because ethanol has small dielectric constant values that can lead to the solution of the low solubility values. Notably, the degree of saturation is high in inorganic solvents.

Table 1 Concentration Component as XRF Results

Elements	Concentration (%)
Fe	51
Ni	22
Al	27

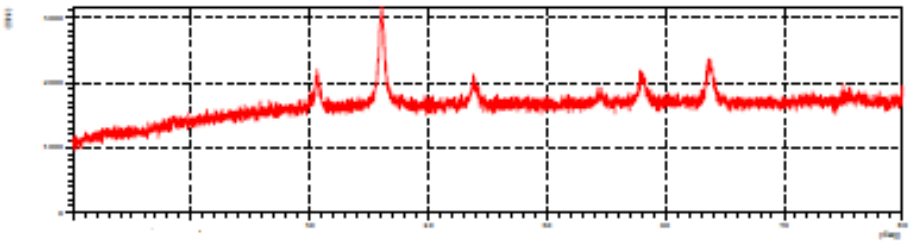

Figure 2 XRD result of Fe-Ni/Al_2O_3

These properties are made in order to form little colloidal particles so that the sol-gel solution can be formed (Yang, 2010). XRF characterization results are shown in Table 1. The composition is stated as the mole ratio of 2.3: 1: 1.2. These XRD results are shown in Figure 2.

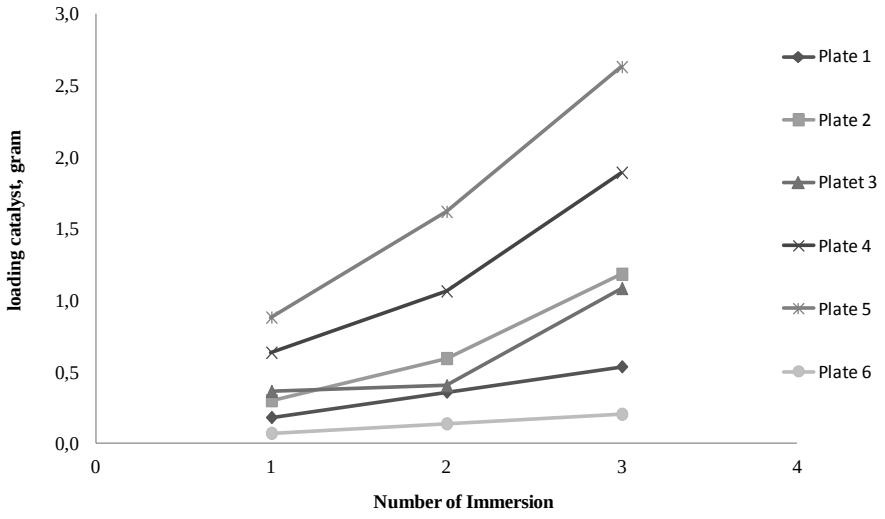

Figure 3 Loading catalyst of plates

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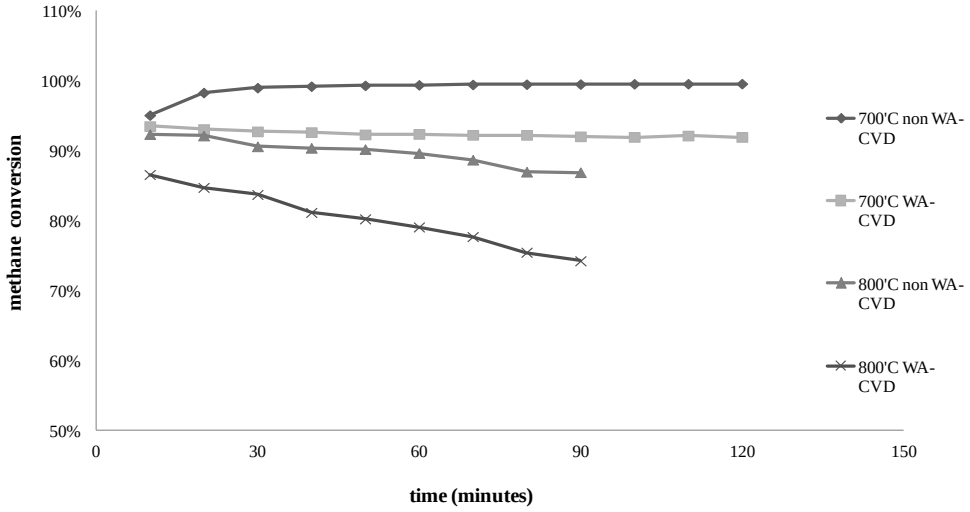
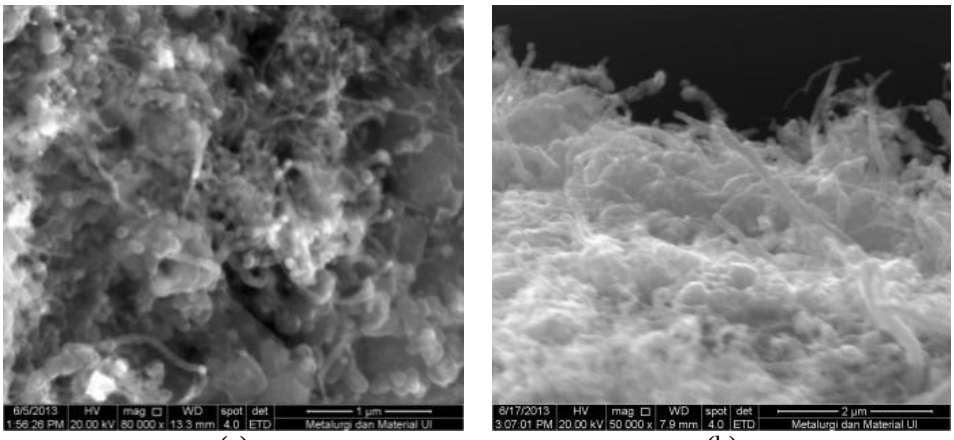


Figure 4 Methane conversion in the variation of temperature on WA-CVD and non-WA-CVD

A peak was generated for the Fe-Ni/Al_2O_3 catalyst in the range of 2θ = 30 to 2θ = 70.5. These results are in line with the results that have been conducted in previous studies (Qian, 2003). This catalyst coating was performed three times in order to obtain an optimum catalyst loading on the plate. As seen in Figure 3, the increased loading of the catalyst increased the number of immersions.

Methane Conversion for WA-CVD and non-WA-CVD results of the methane conversion at 700°C showed higher values than the reaction with 800^{o}C temperature. This is due to the reaction temperature used in the catalytic methane decomposition reaction, which is at an optimum temperature (Purwanto et al., 2011).

The highest conversion rates in the conversion profile are at the reaction temperature of 800^{o}C. Figure 4 shows the ability of the catalyst is optimum at the start of the reaction, when the entire surface of the catalyst has direct contact with the methane to obtain the highest conversion. Then a downward trend occurs, which is caused by reduced ability of the catalyst due to its deactivation.



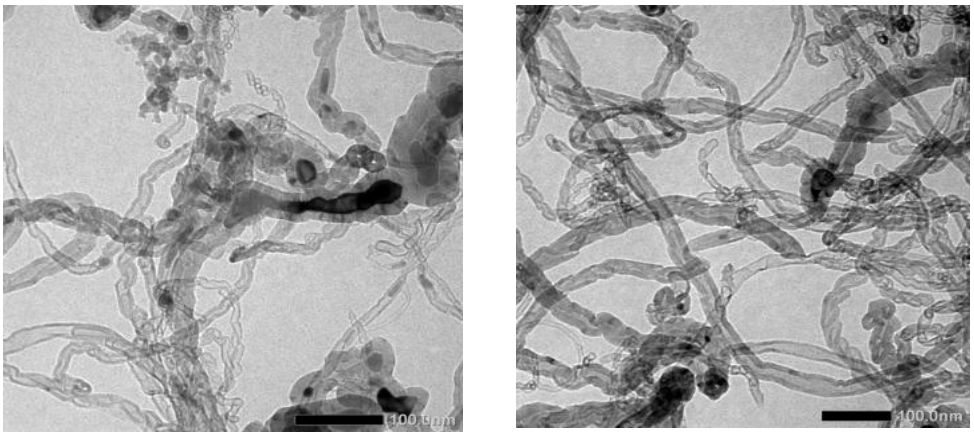
(a) (b)

Figure 5 FE SEM Result of CNT on the Plate at 800^{o}C: (a) Non-WA-CVD; (b) WA-CVD

Deactivation of the catalyst occurs because of carbon deposits in the graphite layer on the catalyst surface. Reaction time goes on continuously and this will causes a reduction in the catalyst lifetime. This condition can be overcome by the addition of water in the WA-CVD method. The addition of water can clean up carbon deposits formed on the catalyst surface (Hata, 2004). After a reaction time of more than 90 minutes, it is predicted a reduction in catalyst lifetime will possibly occur. Higher conversion values in non-WA-CVD method showed more carbon products were produced, in comparison with the WA-CVD method.

3.1. Characterization of CNT product

The CNT morphology produced at a temperature of 800^{o}C reaction is characterized by FE SEM (Figure 5) and TEM (Figure 6). Although it has not grown uniformly on the surface of the plate, there is a tendency to straighten out CNT growth as shown by the reaction with the WA-CVD method. The resulting CNT will grow longer and a good purity reading is predictable as shown in Figure 5(b). The role of water in the WA-CVD method looks to be quite significant in shaping the growth of CNT which tends to straighten out the morphology, in contrast to Figure 5(a) which shows that the generated CNT tends to be broken. These results, clarified by TEM characterization, are shown in Figure 6(a). CNT is formed as a jointed carbon nanofilament. Nanocarbon products produce varied shapes, namely hollow core carbon onions, quasi-spherical carbon onions, carbon nanofilament, as well as carbon nanotubes.



(a) (b)

Figure 6 TEM result of CNT on the plates at 800^{o}C scale 100 nm: (a) Non-WA-CVD; (b) WA-CVD

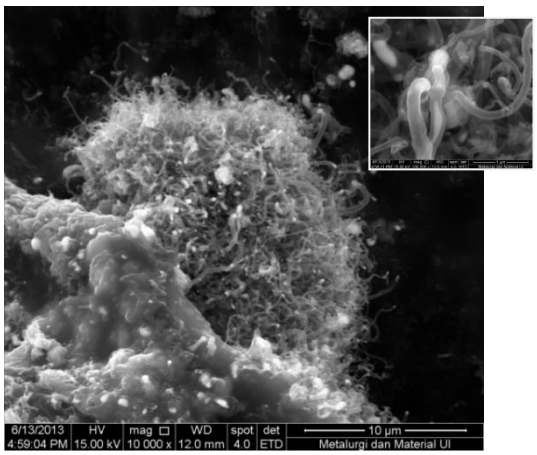


Figure 7 TEM result at 700^{o}C scale 10 μm with WA-CVD

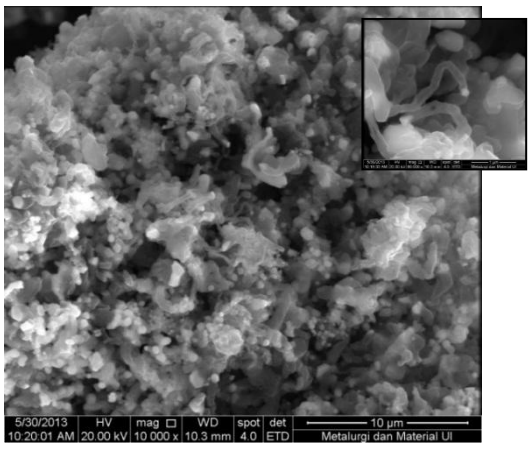


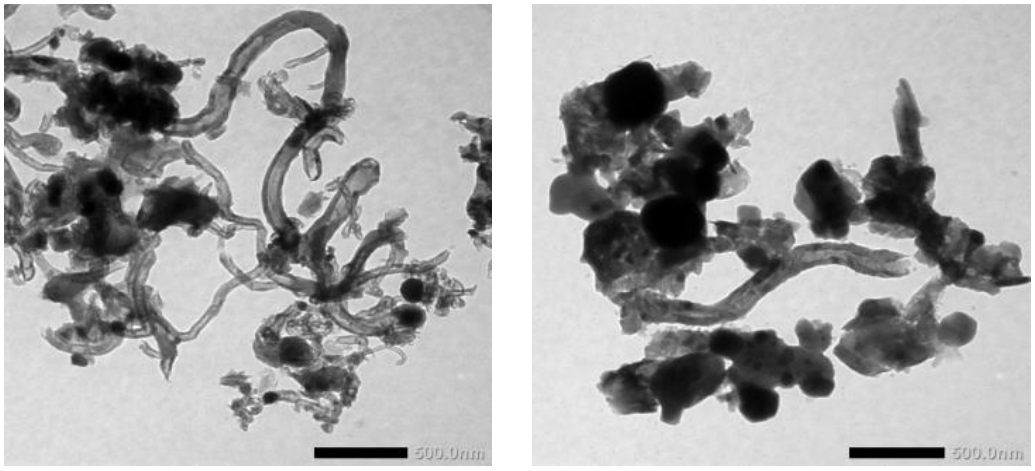
Figure 8 TEM result at 700^{o}C scale 10 μm non-WA-CVD

In contrast the results from the reaction with the WA-CVD method are shown in Figure 6(b). The characterization results indicate a higher number of CNT was formed. Nanocarbon variations were generated in fewer numbers than shown in non-WA-CVD reactions. This shows the role of water in the WA-CVD method. The water that flows during the reaction is able to assist the CNT formations. In addition, water was able to shape the tube, resulting in clearer CNT formations. The introduction of a small and controlled amount of water vapor into the growth environment under standard conditions for the CVD process will greatly improve the efficiency of the CNT synthesis (Patole et al., 2008).

Figure 7 shows the CNTs growth patterns are long tubes with an excellent purity at a temperature of 700°C in the WA-CVD method. Figure 7 shows the CNTs growth has not formed ACNT. CNT growth tends to lead to bundles of CNTs due to the collection at one point, forming like coral growth. The reaction results showed a non-WA-CVD condition with.CNT growth of short tubes, (Figure 8).

This condition can be caused by the presence of the water's role on the catalytic decomposition reaction of the methane. Water can be used as an amorphous carbon purifier produced during the reaction process (Tohji et al., 1996). In addition, amorphous carbon can be removed effectively from the MW-CNT produced in the CVD reactor with the addition of water (Cao et al., 2001). Therefore, it shows that the addition of water occurs, as a protective agent against the amorphous carbon coating (Hata et al., 2004). As a result of the addition of water to the reaction, the purification occurs naturally, which causes a loss of amorphous carbon in the resulting CNT. The CNT was formed with a smaller diameter, when compared with the results of the synthesis of the non-WA-CVD method.

TEM characterization results are shown in Figure 9. The purity of the CNT formed on the WA-CVD results can clearly be seen. Figure 10(a) shows the pure CNT formation with the addition of water. Figure 10(b) indicates that the CNT formation has not yet happened perfectly. These results may be due to the lack of reaction temperature or reaction time. Longer reaction time allows for the optimum purity obtained by adding water, as well as with higher numbers of CNT formations.



(a) (b)

Figure 9 TEM result of ball catalyst Ni-Cu-Al at 700^{o}C scale 500 nm: (a) WA-CVD; (b) non-WA-CVD

CNT growth mechanisms included in the tips growth model looks as shown by the results of TEM in Figure 10. The catalyst has not reacted with the gas completely to form a CNT (indicative of tip growth). This happens because the carbon has not yet reached the optimum

growth stage, so the full reaction time is still needed in order that the catalyst will reach the end of the carbon process. The CNT formation process consists of three stages, namely the induction gas process, nucleation and growth, (Grujicic, 2002). The nucleation stage is where the formation of thin carbon occurs on the catalyst. Furthermore, carbon continues to grow until the entry stage, forming CNT growth along with the increasing time period.

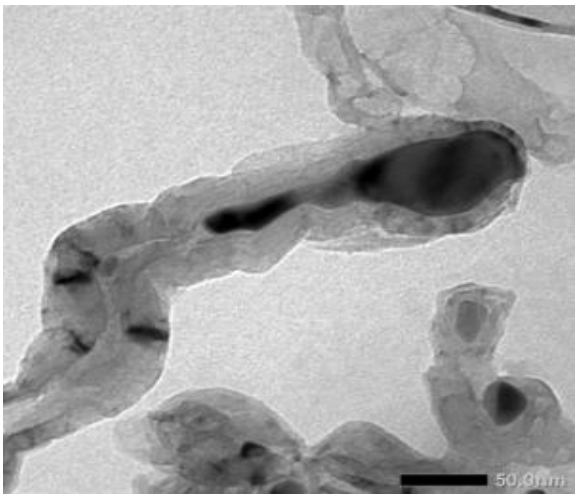


Figure 10 TEM result at 700^{o}C WA-CVD

4. CONCLUSION

The Aligned CNT synthesis (ACNT) with WA-CVD method through the catalytic decomposition reaction of methane has not shown any perfectly formed ACNT. In addition, the number of CNTs produced was higher than those produced with the absence of water. The quality of the resulting CNT also has a high purity level and the resulting growth tends to straighten out, although not yet produce neatly and uniformly formed CNTs. The presence of water on the reaction of methane decomposition is to facilitate the formation that leads to a level of high purity and therefore, prevents sintering of the catalyst that leads to increased catalyst lifetime. Without the addition of water, the conversion of methane in the reaction (non-WA-CVD) is higher than the WA-CVD method, leading to low-quality carbon (amorphous carbon), in the CNT formations.

5. ACKNOWLEDGEMENT

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