

A Review on Carbon Nanotubes Production via Catalytic Methane Decomposition

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S.P. Chai, S.H.S. Zein, and A.R. Mohamed*

School of Chemical Engineering, Engineering Campus
Universiti Sains Malaysia, Seri Ampangan,
14300 Nibong Tebal, P.Pinang, Malaysia.

Email: *chrahman@eng.usm.my

ABSTRACT

Methane decomposition is a promising approach to produce high purity, high yield and perfect orientation of carbon nanotubes and is viable for scaling up its production at a relatively low cost. The current research of methane decomposition is widely focusing on the aptness of catalyst system and the reaction conditions for optimizing the production of carbon nanotubes. The appropriate interaction of metal-support is vital in improving the catalyst activity, deactivation rate and selectivity of the carbon nanotubes for lower activation energy consumption. In this case, the traditional catalysts, iron group metals (Fe, Ni, Co) supported on silica, alumina, magnesia, titania, zirconia and graphite are extensively used. Methane decomposition is an attractive process in view of its potentiality in producing single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs), depending on the specific range of reaction temperature and a particular catalyst system in use. Therefore, selectivity of SWNTs and MWNTs is possible to be achieved by altering the composition of metal and support in a catalytic process. Large-scale production of carbon nanotubes remains a question due to the lack of comprehensive knowledge of the carbon nanotubes growth mechanism. The catalytic process and the morphology of the carbon nanotubes formed can be vividly revealed if the carbon nanotubes growth mechanism is well understood. Three main growth mechanisms have been reported, including base growth model, tips growth model and base-tips growth model. Conversely, the growth mechanism is an arguable issue that needs further investigation to clarify it. This paper reviews the catalysis for the production of carbon nanotubes via methane decomposition, the morphology of carbon nanotubes produced and the proposed growth mechanisms, in order to create more understanding on carbon nanotubes and their related studies.

Keywords: Carbon nanotubes, catalytic filamentous carbon, catalytic methane decomposition, catalysis

1.0 INTRODUCTION

Carbon nanotubes have been receiving fabulous research interest from scientists worldwide, since it was first discovered by Sumio Iijima in 1991 (Iijima, 1991), to explore their application and to develop the efficient carbon nanotubes synthesis system. Carbon nanotubes have structure similar to graphene sheet rolled into a cylinder form with a diameter ranging from 0.8 to 300 nm. Carbon nanotubes can be categorized into single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs) depending on the number of graphene layer. SWNTs consist of single layer graphene sheet and MWNTs consist of several layers of graphene sheets rolled into a cylinder.

Along the years, various synthesis processes such as electric-arc-discharge (Iijima, 1991; Iijima et al., 1993; Bethune et al., 1993) and laser ablation (Thess et al., 1996) have been used in the production of carbon nanotubes. However, all these processes have significant drawbacks and limitations. Electric-arc-discharge method, a technique used to synthesize fullerene, is reported to yield significantly less carbon nanotubes with large amount of undesirable carbonaceous byproducts. Laser ablation is the most recent achievement in producing high ly pure carbon nanotubes, but the high cost of operation and equipment as well as low production rate limit the plausible scaling up in the production of nanotubes.

Catalytic growth method (Yacaman et al., 1993; Ivanov et al., 1994, Amelinckx et al., 1994) appears as a promising technique for scaling up the production of carbon nanotubes at a relatively low cost. Catalytic decomposition of carbon-containing molecules by means of utilizing methane, acetylene, ethylene, propylene, benzene, toluene, hexane, alcohol and acetone (Hernadi et al., 2000; Ermakova and Ermakov, 2002) as carbon feedstock, has been studied in establishing a continuous process that drives the interest in high volume and low cost carbon nanotubes production. The use of methane gas in catalytic decomposition process is reported to be the most suitable over the aforementioned carbon-containing molecules due to the fact that methane is a cheaper carbon source (Liu et al., 2003) which produces little or practically no amorphous carbon and methane has a high stability characteristic at elevated temperatures in preventing self-pyrolysis (Liu et al. 2003; Kong and Cassell, 1998). A typical schematic diagram of methane decomposition reactor system is shown in Figure 1.

Methane decomposition is an endothermic process. Introduction of high temperature condition in the reactor system improves the carbon accumulation and increases the methane conversion by switching the equilibrium to the right. Nevertheless, high temperature condition is subjected to faster deactivation of catalyst. To keep the stability of the catalyst, lower reaction temperature is applied or with diluted methane, but these reduce the catalytic activity.

The current practice of carbon nanotubes production is preferable at moderate temperature as it can prolong the catalyst lifetime, but in this case, low methane conversion becomes the major concern. However, low methane conversion can be tackled by separation of the methane-hydrogen mixture at the reactor effluent, followed by recycling of methane. Alternatively, membrane reactor can be used to remove continuously produced hydrogen from methane decomposition reaction. This alternative is believed to increase the methane conversion and to enhance lower temperature reaction. However, separation of methane from hydrogen product increases the operation cost and the hydrogen permeating membrane makes the reactor structure complex and difficult to be scaled up (Ermakova et al., 2000; Chen et al., 2004).

The importance of catalytic decomposition of methane in producing high purity, high yield and perfect orientation of carbon nanotubes can only be provided by the use of deliberately designed catalysts at the optimum operating conditions. For that reason, it is of importance to develop an efficient catalyst in terms of high catalytic activity, stability, selectivity and lower activation energy requirement. This catalyst system and the optimum operating conditions are expected to contribute effectively towards large-scale production of carbon nanotubes and hydrogen through methane decomposition reaction by using methane gas as carbon source.

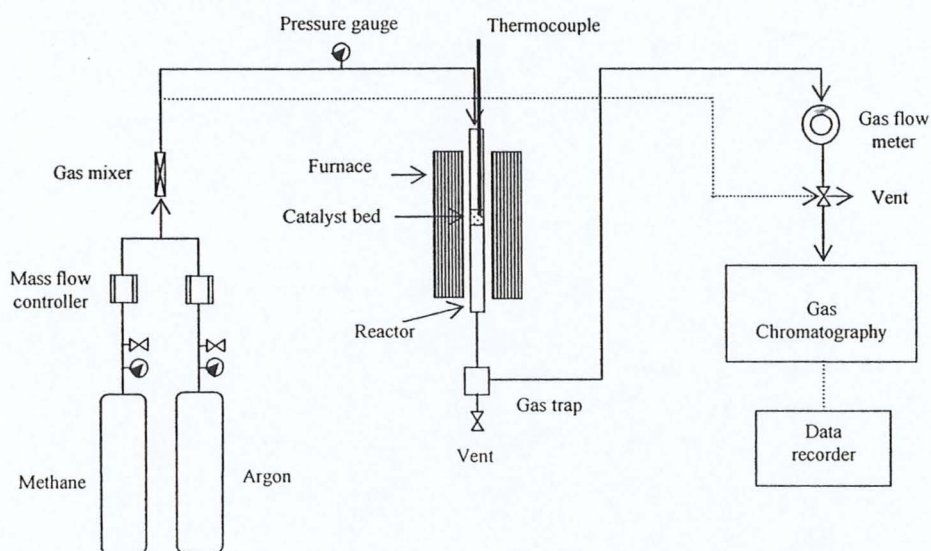


Figure 1: A typical schematic diagram of methane decomposition reactor system.

2.0 THE EFFECT OF METALS IN CATALYTIC METHANE DECOMPOSITION

Transition metals, especially metals from group VIII (Fe, Co, Ni) in the periodic table, are extensively used in catalytic decomposition of methane. With regard to the catalysts for the decomposition of methane, it is well-known that supported nickel is the most effective catalyst where it shows highly catalytic activity at lower temperature (450°C-550°C) (Ermakova et al., 1999; Otsuka et al., 2000; Choudhary et al., 2001; Zhang and Amiridis, 1998). Cobalt catalysts are hardly used due to their lower activity and lower carbon capacity against nickel (Otsuka et al., 2000; Avdeeva et al., 1999; Avdeeva et al., 1996). Reshetenko et al. (2004) reported Fe/Al₂O₃ was very efficient in carbon deposition at temperature range of 600-650°C. But, in terms of methane conversion and carbon capacity, once again, nickel is more active than iron on the similar support and at the similar reaction conditions (Otsuka et al., 2000; Reshetenko et al., 2004; Takenaka et al., 2003a). Noble metals (rhodium, ruthenium and platinum), chromium and manganese supported on silica do not provide heartening result in terms of methane conversion in catalytic methane decomposition (Otsuka et al., 2000).

Metal in catalyst system plays significant roles in determining the type of carbon nanotubes formed. Resasco et al. (2000) demonstrated that the ratio of Co and Mo was critical in synthesizing SWNTs. In 2003, Liu et al. (2003) had successfully synthesized 70% SWNTs and about 30% DWNTs over Fe-Mo/Al₂O₃ without the formation of amorphous carbon. In the same year, Hu et al. (2003) had reported Co was more active for the formation of SWNTs than iron on MgO support at the same reaction conditions and the purity of SWNTs produced reached 90% over Co/MgO catalyst at 1273°C. Similarly, Colomer et al. (2000) also obtained 70-80% of SWNTs at 1000°C by using Co/MgO.

The addition of right promoter in the catalyst system improves the carbon capacity, influences the type and morphology of carbon nanotubes forming as well as gives rise to considerable increase in the catalytic lifetime compared with those of individual metals (Avdeeva et al., 1996; Avdeeva et al., 2002; Reshetenko et al., 2003; Reshetenko et al., 2004; Takenaka et al., 2003). For example, introducing Cu into Ni-Al₂O₃ catalyst increases the carbon capacity from 22.4 g_c/g_{cat} to 525 g_c/g_{cat} and prolongs the catalyst lifetime from 2 hours to 54 hours at 625°C (Reshetenko et al., 2003). Takenaka et al. (2003) noted that the addition of Pd into silica supported nickel improved significantly the catalytic lifetime and hydrogen yield for methane decomposition with carbon capacity 1170 g_c/g_{cat} and it is the highest carbon capacity ever reported in literature. In addition, the application of bimetallic catalyst system in methane decomposition permits one to control the properties of the produced hydrogen and carbon nanotubes as well as to improve the catalyst stability.

Diameter of the metal coated on support influences the growth of carbon nanotubes. Carbon nanotubes can only be grown on the specific diameter of metallic particles in catalyst system. Nickel particle with diameters in the range of 60-100 nm have the longest catalytic life for methane decomposition (Takenaka et al., 2003b) and the maximum yield being observed at the range of 20-60nm (Ermakova and Ermakov, 2002). The diameters of the carbon nanotubes synthesized are basically similar to the diameters of the metallic particles doped on the catalyst support. Therefore, carbon nanotubes with the diameter 20-100nm are commonly produced; whereas carbon nanotubes with the diameter exceeding 100nm will become unstable and very rare to be grown.

3. THE EFFECT OF SUPPORTS IN CATALYTIC METHANE DECOMPOSITION

It is generally accepted that carbon nanotubes synthesized from catalytic decomposition process is strongly influenced by the metal-support interaction (MSI) effect. Choosing the appropriate support which is complementary to the active metal is of importance in a catalyst system. As examples, nickel supported on SiO₂, TiO₂ and graphite is effective for catalytic decomposition of methane (Takenaka et al., 2001). However, H-ZSM-5 supported nickel cannot be used to produce filamentous carbon (Choudhary et al., 2001). Additionally, Al₂O₃ supported metal catalyst except nickel, on the whole, does not provide inspiring result in methane decomposition (Reshetenko et al., 2004; Takenaka et al., 2001). ZrO₂ supported either Fe or Ni is subjected to lower methane conversion, lower carbon capacity, and higher catalyst deactivation rate (Ermakova and Ermakov, 2002; Takenaka et al., 2001).

MgO as a catalytic support has widely been studied due to the advantages over Al₂O₃ and SiO₂: MgO can be easily dissolved in acid and that simplifies the carbon nanotubes

purification steps. Besides that, MgO supported Co is capable in producing SWNTs (Hu et al., 2003; Colomer et al., 2000). Nevertheless, metals supported on MgO showing low catalytic activity towards decomposition of methane and this reason impels the researchers to search the suitable transition metals supported on MgO for effective SWNTs production.

Ni/TiO₂ has an advantage over Ni/SiO₂ by reason of the catalytic activity of Ni/TiO₂ is kept higher during catalyst regeneration cycles (Takenaka et al., 2003a; Takenaka et al., 2004; Zein et al., 2004; Zein and Mohamed, 2004). Conversely, catalytic activity of Ni/SiO₂ for methane decomposition is higher at early cycles and decreases gradually with the regeneration cycles (Takenaka et al., 2003a; Takenaka et al., 2004). This phenomenon is mainly due to the changes of these metallic particles size after several regeneration cycles, i.e. nickel particles in Ni/TiO₂ approach the optimum size for methane decomposition (60-100nm) with the regeneration cycles while nickel particles in Ni/SiO₂ aggregated into size larger than 150nm, which are inactive for methane decomposition, after several regeneration cycles. Zein et al. (2004) also reported that TiO₂ helps to reduce the activation energy in methane decomposition, and 60 kJ/mol was achieved over 13wt% Ni/TiO₂ in methane decomposition reaction. This activation energy is the lowest activation energy reported in literature for this reaction. In addition, Ni/TiO₂ catalyst achieves 92% methane conversion at temperature of 900°C without rapid deactivation of the catalyst (Zein et al., 2004).

Among the aforesaid catalyst supports, silica is the most appropriate catalyst support for the process of methane decomposition especially used with nickel. Silica supported nickel is the most active catalyst towards methane decomposition at moderate temperature (500°C-600°C) and it has the greatest resistance towards deactivation (Choudhary et al., 2001; Takenaka et al., 2001; Takenaka et al., 2003). For example, 70 hours catalyst lifetime has been achieved over 40wt%Ni/SiO₂ catalyst at temperature 500°C and this figure is one of the longest catalyst lifetimes being reported in literature at temperature 500°C or higher for a single metal catalyst system (Takenaka et al., 2003b).

Catalytic activity and catalyst lifetime depend strongly on the types of catalyst supports. The growth of carbon nanotubes is preferable on the support without pore structure. Takenaka et al. (2001) had proved that Cab-O-Sil, silica without pore structure, used as nickel support be evidence for the highest catalytic activity and the longest catalyst lifetime in methane decomposition. The scientists explained that if the metallic particles at the tips of carbon nanotubes, which are active in methane decomposition, come in contact with the wall of other carbon nanotubes or with inside walls of supports, the growth of carbon nanotubes can be terminated (Takenaka et al., 2001). This reveals the unsuitability of using supports with larger surface area or with highly porous in methane decomposition reaction.

4. THE EFFECT OF REACTION TEMPERATURE IN CATALYTIC METHANE DECOMPOSITION

Reaction temperature has a great influence on catalyst activity, catalyst lifetime and morphology of carbon nanotubes produced. Temperature elevation results in a disproportionately rapid catalyst deactivation. At high temperature, it is believed that catalyst will appear in quasi-liquid state where the catalyst particles are easily cut into small particles and the small particles are found easily encapsulated by the carbon layer formed during methane decomposition, contributing to faster catalyst deactivation. On the other hand, at low temperature, the catalyst remains in solid state rather than in quasi-liquid state (Chen et al., 2004) and it sustains the activity of catalysis process.

Lower temperature is inappropriate for methane decomposition process because of a noticeably longer reaction time due to the decrease in the methane conversion. Basically, decision on the desired reaction temperature is determined based on the optimized profitability between the cost of recycling un-reacted methane resulting from lower methane conversion at lower temperature and the cost of the catalyst replacement, due to faster catalyst deactivation, at high temperature operation conditions.

It is well known that different types of catalysts active at different reaction temperature. Nickel based catalysts are highly active in methane decomposition. Decomposition of methane over silica supported nickel catalyst occurs at the minimum temperature of 450°C (Zhang and Amiridis, 1998) and its optimum temperature falls in between 500 to 600°C (Ermakova et al., 2000; Takenaka et al., 2003b). At temperature higher than 650°C, silica supported nickel catalyst cannot decompose methane efficiently

because of a very rapid deactivation. Methane decomposition over iron-containing catalysts usually takes place at 680-1200°C (Avdeeva et al., 2002; Ermakova et al., 2001; Reshetenko et al., 2003). MgO supported Co works best at high temperature range of 900-1000°C (Colomer et al., 2000; Hu et al., 2003; Wang and Ruckenstein, 2002). However, using Al₂O₃ as Co support reduces the optimum reaction temperature to the range of 475-500°C (Avdeeva et al., 1999).

The major concern in reaction temperatures selection is to produce desirable morphology of carbon nanotubes. Decomposition of methane over Ni/SiO₂ catalyst at 700°C is favorable for the forming of MWNTs while carbon nanofibers, solid structures, are formed at a lower temperature of 500°C (Takenaka et al., 2003b). Furthermore, diameters of carbon nanofibers become smaller with a rise of reaction temperature (Takenaka et al., 2003b). 15Ni 3Cu-2Al catalyst produces carbon nanofiber at 500-600°C while producing carbon nanotubes at a temperature of 740°C (Chen et al., 2004). Constant reaction temperature at 1000°C can produce SWNTs in abundance over Co/MgO, and reaction temperature over or below 1000°C would lead to the formation of other materials such as MWNTs and amorphous carbon (Hu et al., 2003). The structure morphology of carbon nanofiber, SWNTs and MWNTs are shown in Figure 2.

In general, carbon nanofibers are produced at lower temperature; conversely, carbon nanotubes are produced at higher temperature. This finding can be explained by using carbon nanotubes' tips growth model. At low temperature, the rate of carbon nucleation is low compared to the rate of carbon diffusion through the metal. This nucleation results in a uniformly carbon layer formed over the whole metal-support interface. When the carbon layers are excreted by continuous carbon nucleation, the metallic particle is nicely lifted from the support forming carbon nanofibers with solid core.

At high temperature, carbon layer nucleation is instantaneous, inherently much faster than the rate of carbon diffusion. Owing to the carbon diffusional path at metal-gas interface is shorter than that at metal-support interface, intrinsically, the nucleation will occur at the area near to metal-gas interface. As soon as carbon excretion starts near to metal-gas interface, the concentration of carbon in nickel drops sharply to the saturation concentration of carbon. Therefore, no driving force is present any longer for nucleation at places with high diffusional path lengths (centre of metal-support). No carbon excretion will take place at this part, therefore, carbon nanotubes, hollow structure, are obtained. Figure 3 shows the mechanism of the formation of carbon nanofibers and carbon nanotubes.

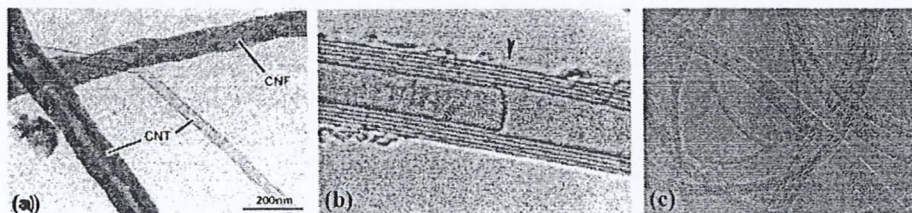


Figure 2: TEM images showing: (a) carbon nanotube (CNT) and carbon nanofiber (CNF) (Pan et al., 2004); (b) MWNTs (Harris, P.J.F.); (c) SWNTs in bundles (Zhu et al., 2002).

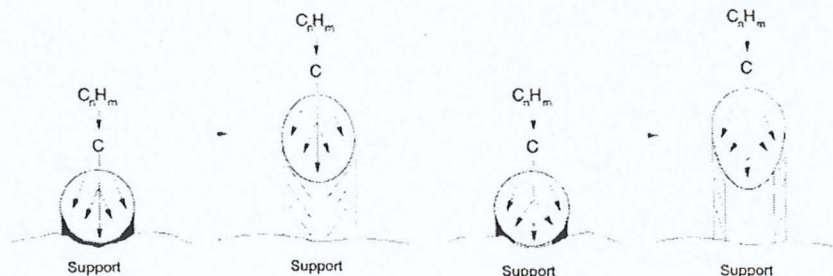


Figure 3: Schematic representation of the mechanism of CNF and CNTs formation, adapted from ref. (Snoeck et al., 1997).

5. CARBON NANOTUBES GROWTH MECHANISM

There are several growth mechanisms proposed by scientists in the recent researches based on their observation on the locations of metallic particles at carbon nanotubes. Base growth model was proposed as a result of the findings that metallic particles were solidified at the base of carbon nanotubes (Choi and Cho, 2002; Lee and Lyu, 2001). Tips growth model was proposed when metallic particles were found at the tips of carbon nanotubes (Pan et al., 2004; Snoeck et al., 1997; Toebes et al., 2002). Some scientists observed that metallic particles situated in both ends of the carbon nanotubes, so a base-tips growth model was proposed (Chen et al., 2004; Jourdain et al., 2002).

5.1 TIPS GROWTH MODEL AND BASE GROWTH MODEL

Tips growth is the most popular mechanism being proposed. Basically, methane decomposition reaction occurs on the catalyst metal surface according to the chemistry equation; $\text{CH}_4 \rightleftharpoons \text{C} + 2\text{H}_2$, forming carbon atoms and hydrogen molecules. The carbon atoms deposited on the metal surface will dissolve in the metal and diffuse through the metallic particle. Since the concentration of carbon dissolved in metal at the gas side of the metallic particle can exceed the solubility at the support side of the metallic particle, a concentration gradient over the metallic particle becomes possible, and thus, a driving force for the carbon diffusion through the metal particle is established.

The diffused carbon precipitates as a graphitic layer at the interface between the metallic particle and the support. The forming of graphitic layers detaches the metallic particle from the support. Continuous formation of carbon atoms at the support side shows the growth of carbon nanotubes with the metal lifted at the tip of the carbon nanotubes. If the carbon deposited is not removed from the surface of metallic particles, the carbon will encapsulate the metal surface and deactivate the catalyst. Figure 4(a) shows the SEM image of carbon nanotubes where the metallic particles are found at the tips. The tips growth model can be represented by the schematic diagram shown in Figure 3.

Base growth model is similar to tips growth model except that the metallic particle is located on the support side, as shown in Figure 4(b), and the growth of carbon nanotubes is contributed by the metallic particle attached on the support. This model believes that the metallic particle has strong interaction with catalyst support that cannot be easily separated by the graphitic layer formed at the interface of metal-support in a catalyst system. Therefore, if the MSI effect is strong such that the metallic particle cannot be easily detached from the catalyst support, carbon nanotubes may follow the base growth mechanism. In contrast, the presence of weak MSI during carbon nanotubes formation on supported metal catalysts will be subjected to tips-growth mechanism.

5.2 BASE-TIPS GROWTH MODEL

Base-tips growth model combined the concepts of the tips growth and base growth model. Similarly, methane decomposes on the free surface of metallic particle into hydrogen and carbon. The carbon formed on the surface will diffuse into the metallic particle. At this temperature, the metallic particle will be in liquid state rather than in solid state. The concentration of carbon in metallic particle increases until the supersaturation is reached. This situation forces carbon atoms to accumulate on the surface of the metallic particle and then initiate the growth by forming a first graphitic layer. The stretching force elongates the liquid particles and breaks the liquid metallic particle into two parts (Jourdain et al., 2002; Li et al., 2004). The bottom parts of metal have strong adhesion to the support, so they stay at the support and contribute to the growth of carbon nanotubes. The metallic particles situated at the tips of carbon nanotubes are inactive during the reaction because of the metallic particles at the tips are fully encapsulated by graphitic layer.

The termination of the growth of carbon nanotubes occurs when the active surface is completely consumed or when the carbon supply is stopped. The sequence of the base-tips growth model is shown in Figure 5 and the morphology of the carbon nanotubes, where the metallic particles are found at the tips and at the base of carbon nanotubes, is depicted in Figure 4(c). Base-tips growth model is good to explain a catalyst system with the presence of strong MSI effect and the metallic particles will be liquefied at high temperature. As a result, the metallic particles attach firmly on the support and the top part of the metallic particle (in liquid state) will be split during the growth of carbon nanotubes.

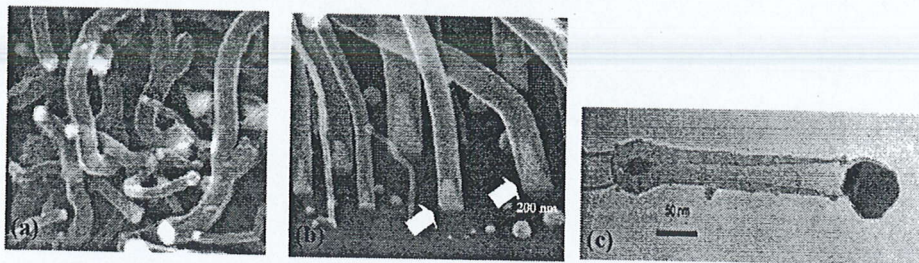


Figure 4: SEM images showing: (a) metallic particles situated at the tips of carbon nanotubes (Otsuka et al., 2000); (b) metallic particles are encapsulated at the base ends of the carbon nanotubes (Chen et al., 2004); (c) TEM image showing metallic particles located at tip and base of carbon nanotube (Jourdain et al., 2002).

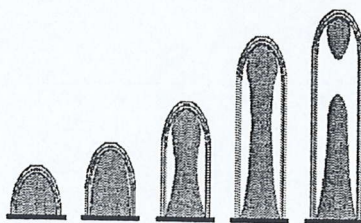


Figure 5: Schematic depiction of growth process of the carbon nanotubes, adapted from ref.. (Chen et al., 2004).

6. CONCLUSIONS

The following conclusion can be made based on the review carried out:

1. In general, Ni/SiO₂ is the most appropriate catalyst used in decomposition of methane at moderate temperature. This catalyst shows higher catalytic activity at moderate temperature (500-600°C) and longer catalyst lifetime (up to 70 hours) which hardly to be achieved by other single metal catalysts system.
2. Co/MgO and Co-Mo/MgO catalysts are critical to produce large amount of SWNTs. Nevertheless, these types of catalysts are subjected to lower carbon yield and required higher reaction temperature (>1000°C).
3. Utilizing bimetallic catalyst system improves the yield of carbon nanotubes at lower reaction temperature. Adding Pd into Ni/SiO₂ catalyst is recommended as the carbon capacity produced over this catalyst can reach up to 1170g_C/g_{cat}.
4. To date, Ni/TiO₂ is the most stable catalyst being found. This type of catalyst remains active after several catalyst regenerations. However, the regeneration process is not practical to be applied in carbon nanotubes synthesizing process because of catalyst regeneration will destroy the carbon nanotubes synthesized.
5. Metal-support interaction (MSI) has a great influence towards carbon nanotubes growth (Snoeck et al., 1997) and catalyst deactivation (Jourdain et al., 2002). In the presence of strong MSI, the metal particle cannot be lifted off the support surface and it prohibits the growth of carbon nanotubes. Hence the catalyst with weak MSI is preferable used in carbon nanotubes synthesizing process.
6. The most common mechanisms proposed, i.e. tips growth model, base growth model and tips-base growth model, are reasonable to explain the growth of carbon nanotubes. The discrepancy of these three mechanisms may be due to the difference in reaction temperatures, carbon sources, catalyst preparation methods, and different types of catalysts used. The mechanisms of carbon nanotubes growth are proposed from the observation on the locations of the metallic particles in carbon nanotubes which is lack of scientific evidence. Thus, further investigations are needed in order to create more reliable explanations which are accepted in the scientific point of view.

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