REVIEW ARTICLE

Carbon nanotubes via different catalysts and the important factors that affect their production: A review on catalyst preferences

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Abstract

This review paper provides researchers with a comprehensive information about the Carbon nano tubes and the catalyst parameters that influences the production and morphology of the of Carbon nano tubes. Carbon nano tubes, referred to as CNTs, are one of the most important materials used in electrical, mechanical, thermal, chemical and textile industries. Since the discovery of CNTs in 1991, many scientists, research groups, and industries have attempted to attain large scale production of CNTs, considering the costs and yields. Catalyst plays an important role in the production of CNTs. In this review various factors that affect CNT production via using different catalysts are reviewed. Factors which are important when choosing a suitable catalyst are also discussed.

Keywords: *Carbon nano tubes; Catalysts; CNT growth; CVD Processes; Transition metals.*

INTRODUCTION

Carbon is a unique, light atom that can form one-, two-, or threefold strong chemical bond. Carbon nanotubes (CNTs) are prefect cylinders consisting of one or more layers of graphene with open or closed ends shown in Fig. 1a and 1b [1]. The planar threefold configuration forms graphene planes can, under certain growth conditions[2], adopt a tubular geometry. The properties of the carbon nanotubes, depending on whether single walled carbon nanotubes (SWNTs) or multi walled carbon nanotubes (MWNTs) change drastically [3]. Recently production of bamboo shaped carbon nanotubes was reported as well[4]. The SEM and TEM images of hallow tubes of multiwall CNT is shown in Fig. 2a and 2b respectively. The discovery of fullerenes provided

insights into carbon nanostructures and how architectures built from sp^2 carbon can result in new structures with exceptional properties [5, 6]. One decade after the discovery of fullerenes, carbon nanotubes were discovered by Iijima while he was studying the surfaces of graphite electrodes used in an electric arc discharge [7]. More and more applications of this material are still being discovered in the industry [8]. However, for commercial applications, large quantities of purified nanotubes are needed and that is one of the reasons that still a lot of research is going on in order to obtain high yield and best quantity commercial CNTs[9]. The uniqueness of the nanotube arise from its structure which consists of a helicity in the arrangement of the carbon atoms in hexagonal arrays on their surface honeycomb

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lattices. CNTs have numerous applications that have been reviewed comprehensively in the literature. These application are such as quantum wires [10; 11], super conduction transitions [12], microelectronics [13], electron field emission [14], energy storage[15], biosensors [16], photo acoustic imaging [17; 18], composite materials [19], and supercapacitators[20]. They have also been used in pharmaceutical applications [21]. In addition to the mentioned application, the Functionalized multi walled carbon nanotubes have been reported to be used as an anticancer agents [22]. Moreover, physical properties of automotive acrylic paint have been improved by incorporation of three different types of carbon nanotubes: single-wall carbon nanotubes (SWCNTs), OH-functionalized single-wall carbon nanotubes (OH-SWCNTs), and aniline-functionalized single-wall carbon nanotubes (aniline-SWCNTs). In a study

by Flores *et al.* It was found that the addition of OH-SWCNTs and aniline-SWCNTs in acrylic paints can improve their quality of their applications. Especially when CNTs were added , the resistance against degradation by electron beam increased by ~500% [23].

Common methods to produce CNTs are: arc discharge [24], laser ablation [25], electrolysis [26], synthesis from bulk polymers [27], furnace [28], chemical vapor deposition (CVD) [29], and Plasma Enhanced Chemical VaporDeposition(PECVD) [30]. There are numerous factors which should be taken into account during production of CNT, such as method of production, catalyst, carbon feed gas; however this review focuses on the catalyst-related factors.

Catalyst diversity is one of the most important factors in the production of carbon nanotubes (CNTs), especially if high yield and perfect
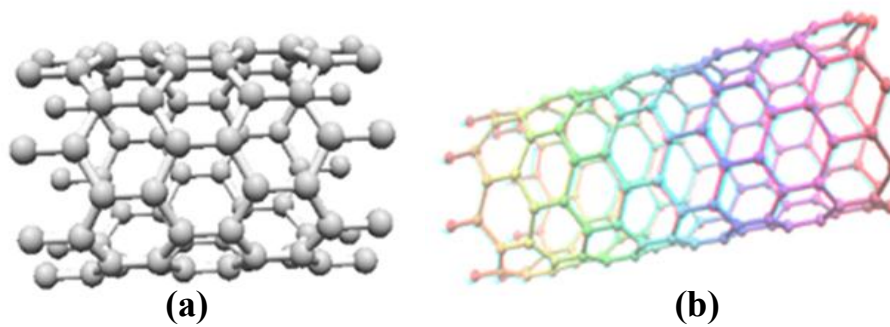

(a) **(b)**

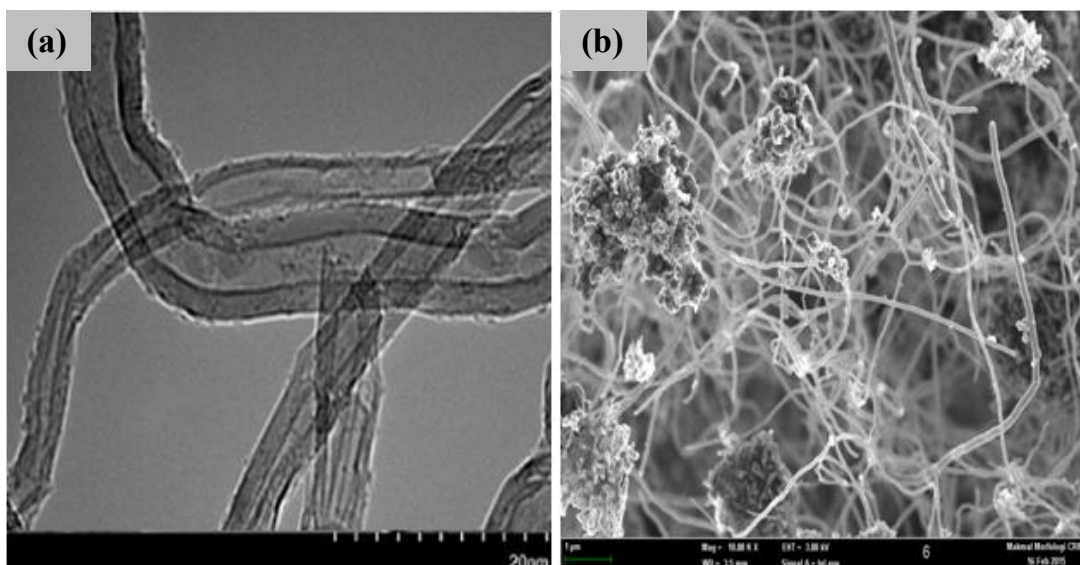Fig. 1: Images of CNT showing its chirality (a-b)

Fig. 2: a) TEM image of the Multiwall CNTs; b) SEM image of the CNTs

orientation and structure are desired. However, there have been many reports in the literature on the production of CNTs in the absence of a catalyst. For example, porous Al_2O_3 has been shown to facilitate CNT growth without the use of catalyst [31]. Catalyst-free CNT growth was also demonstrated by Merchan-Merchan *et al.* in oxy-fuel flames [32]. The process of production without the presence of a catalyst resulted in multi-walled carbon nanotubes (MWCNTs), whereas the production of CNT in the presence of a catalyst resulted in the formation of single-walled carbon nanotubes (SWCNTs) [33].

The design of an efficient catalyst is essential for a catalyst synthesis which has high catalytic activity, stability, selectivity, and lower activation energy. Numerous studies have been conducted on the synthesis of catalysts to produce CNTs; along with the development of methods for efficient catalysts synthesis[34-36] .The efficiency of the catalyst determines the diameter of the CNTs produced,as the growth is highly dependent on the support and catalyst. An example of growth mechanism is shown in Fig. 3 exhibiting the stages of CNT growth on catalyst. Efficiency of the catalyst is defined as the mass of purified CNTs over the mass of the supported catalyst introduced. Methods to avoid agglomeration of supported catalyst particles have also been the subject of interest in CNT production industry [37].

Important parameters in catalyst selection
Numerous studies have concentrated on showing the importance of catalyst preparation and its effects on the CNT production [38]. A study by Flahaut *et al.* focused on the influence of catalyst preparation conditions on the number of walls in the obtained CNTs [39]. They emphasized that a catalyst of a given chemical composition can lead to different products, depending on the preparation method used. Having single wall or multiple walls structure in CNTs depends on the selection of the catalyst, which is based on the alteration of the metal's composition and support [40]. A comprehensive investigation by Kitiyanan *et al.* identifies the effects of metal composition [41]. Fonseca *et al.* highlighted several parameters in selection of a suitable catalyst to produce CNTs[42]. These parameters include: the nature of the catalyst, the method of catalyst preparation, the pore size of the support, the concentration of the catalyst, the nanoparticles size and diameter, the quantity of catalyst-active particles, metals-support interaction, the shape of the nanoparticles, the initial amount of catalyst, melting point, the addition of promoter, and metal support interaction. These parameters are summarized in Table 1.

Concentration and composition of catalyst
Aside from the types of the catalyst, the concentration and composition of the catalyst are important; lower concentration leads to SWCNTs, while higher concentration leads to MWNTs. In a study by Kumar and Ando (2010), the catalyst concentration in zeolite catalyst was found to be varied in a wide range of 1–50 wt %. No CNTs formed for a catalyst concentration of less than 2.4 wt% in zeolite showing the effect of lower concentration catalyst. Lower catalyst concentrations such as 2.4–5% exhibited SWCNT growth at 850ºC and above, whereas higher
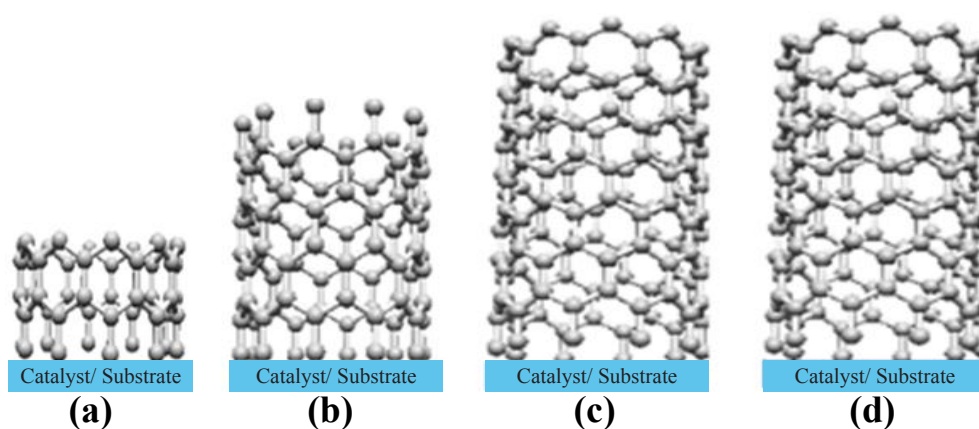

Fig. 3: Growth of CNT on a catalyst substrate (a-d)

Table 1: Common catalysts used for CNT production

Catalyst/s	Comments	Properties
Fe, Co, Ni	More common; Fe has higher catalytic activity, but the CNT deposits will be poorly graphitized. Comparing Fe and Ni: Ni is more efficient and it shows higher activity at lower temperatures, 500- 600 ∘ C. Among these common catalysts, Co is the least common due to its lower activity. Their activities follow this order: Fe> Ni> Co, but their performance in growth is Ni>Co> Fe	Depending on all other factors, such as the substrate or temperature, and method of preparation, the results can be MWNT or SWNT, ie: Fe on SiO_2 or Alumina substrate results in MWNT [78].
Bimetallic from the Fe/Co)(Ni/Co) (Fe/Mo)	CNT could be grown at lower temperatures; Fe/Mo successful in growing SWNTs [79]	Fe/Mo and Ni/Co produce MWNTS , Co/Mo on quartz produces SWNTs
The elements in the group of the common transition metals and also not the most common catalysts in transition group such as: Zr,Rh,Ru,Cd,W	Acts the same as the common transition metals, however, does not act as efficiently. Produces SWNTs. Cu and Pb have shown to be superior for growing CNTs on silicon and quartz substrates, without metallic contaminations [80]	Acts the same as the transition metals. Resulting in SWNTs and MWNTs
Au,Ag,Pt,Pd,Rh,Os	Noble metals such as Au, Ag; do not provide satisfactory results in terms of methane conversion in catalytic methane decomposition method	At temperatures where the VLS model (Vapor Liquid Solid) is expected to be valid, they exhibit very low carbon solubility and negligible carbide formation. Zhou, et al. argue that low carbon solubility results in an elevated precipitation rate [80]
Semiconductors such as Si or Ge	Nanoparticles should be heated in the presence of air before the CVD; CNT growth takes place only when oxygen is present [56]	Among the non-metallic catalysts for the CNT production, SiC is the most widely used and is one of the first to be exploited. The early investigations involved the high annealing temperature (>1500 °C) of SiC and was first demonstrated by Kusunoki et al. for SWNT production [81]
Introducing promoter in bi -metallic catalysts, example : Cu act as promoter in Ni-Al_2O_3 or addition of Pd when synthesizing metallic catalyst also acts as promoter	Increases the carbon capacity, prolong the catalyst lifetime	With trace halide as a promoter in an iron sulfide catalyst, comparable results in perfect structural integrity double-walled carbon nanotubes; DWNTs have been synthesized in large quantity [82]; Mo and W can work as promoters to improve the DWNT yield [83]
Molecular cluster based on transition metals i.e: H_X-$PMO_{12}O_{40}$c$H_4Mo_{72}Fe_{30}(CH_3COO)_{15}O_{254}$(H_2O) Fe, Mo	Reasonable molecular structure because controlling the nano particle size is possible; SWNTs with narrow diameter obtained. The preparation of the cluster is through aqueous solution, easier than thermal decomposition [55]	Continuous growth of a single-walled carbon nanotube (SWNT) on an Fe cluster at 1500 K has been done in a study by Yasuhitoet al. [84]

concentrations favored MWCNT growth. A combined Fe + Co concentration of 40% resulted in the highest yield of MWCNTs with negligible metal contamination. Their findings confirmed that SWCNTs or MWCNTs can be selectively grown by the proper selection of catalyst materials and their concentration [43, 44].

Catalyst composition is one of the factors need to be investigated in catalyst preparation. There are numerous studies investigated the effect of catalyst composition, such as the work by Magrez *et al.* and Resasco *et al.* [45; 46]. They demonstrated that the ratio of Co and Mo was critical in synthesizing SWNTs. In a study by Bai *et al.*, the influence of the concentration of Fe

nanoparticles was examined. As the ferrocence Fe $(C_5H_5)_2$ concentrations increased, the growth rate of the aligned CNTs also increased, until the maximum growth rate of 16.7μm/min at 0.01 g/mL was reached. Afterwards, the growth rate decreased with subsequent increases in the ferrocence concentrations [47].

Resasco *et al.* explained that at lower ferrocence concentrations, the lower CNT growth rate is due to the lack of sufficient Fe clusters to catalyze the growth of the aligned CNTs. At high ferrocence concentrations, the reduced CNT growth rate is caused by the low catalytic activity of the larger Fe clusters, since high ferrocence concentrations decompose more Fe clusters,

which then aggregate and grow into larger clusters with weaker catalytic effects than the smaller clusters. Since the Fe clusters produced at lower concentrations are smaller than those produced in higher concentrations, the aligned CNTs catalyzed by lower ferrocence concentrations will have better crystal structures and smaller diameters than those catalyzed by higher ferrocence concentrations. Therefore, lower ferrocence concentrations provide better conditions for the growth of SWCNTs and aligned CNTs with smaller diameters [46].

Catalyst shape

The shape of the metal particles also plays an important role in determining the properties of the CNTs produced. A study by Heyning *et al.* showed that hexagonal and trigonal particles favor the formation of branched CNTs [48]. The particular shapes of CNTs have been reported over transition metal supported catalyst [49; 50]. A good example is a study by Seung *et al.* in which Au nano particles were used. They have concluded that if Au particles are strongly contacted with the carrier and have an elliptical shape, the base growth model can be adapted to the formation of CNTs with well-arranged layers [51]. On the other hand, if the Au particles are spherical, then the CNT may easily form over the particles lifted from the surface of the carriers.

Promoter addition

The addition of a promoter to the catalyst enhances the carbon capacity and affects the morphology of CNTs. It also increases the catalytic lifetime [52]. In a study by Becker, correlation was observed between the added Mn promoter and the catalytic performance, which was of high importance for the production of CNT on an industrial scale. It has been reported that different oxides can be used as a support or as a promoter to enhance the dispersion of nanoparticles' active phase and to improve the yield of CNT [28]. In another report by Kiang *et al.*, large SWCNTs were synthesized by adding promoters [53]. They found that the SWCNTs produced by transition metal catalysts alone have diameter distributions between 1 and 2 nm. However, when a promoter was added, the diameter distribution was altered with a variety of hellicities and the nanotubes' yield was dramatically increased. They also found that S-Bi and Pb enhance the single layer CNT

yield in the presence of Co, although they did not catalyze the tube growth without a catalyst. The factor of promoter addition is shown in Table 1.

Catalyst size

In production of CNTs, nano-sized metal particles are commonly used for the hydrocarbon decomposition at lower temperatures than the spontaneous decomposition temperature of the hydrocarbon. One of the factors that should be considered when preparing the catalyst is the diameter of the catalysts. The particle size of the catalyst affects the growth mechanism and the diameter of the obtained CNTs. There are many studies reporting on the relationship between the catalyst diameter and the size of nanotubes [54].

In the synthesis of CNTs via chemical vapor deposition (CVD) method, the size of nanoparticles tends to change during the CVD process because of metal atoms' evaporation at high temperatures and the dissolution of carbon species in the nanoparticles [55]. Usually a carbonous gas such as methane, ethylene is used as carbon sources, however there are reports that have used carbon dioxide and carbon monoxide as well[56]. One factor to be considered in catalyst selection for the synthesis of CNTs is that the particle size of the catalysts dictates the tube diameter. Controlling the catalyst particle size will control the diameter of the CNTs produced.

Moreover, obtaining single or multiple walls depends on the size of the catalyst, as reported by Sinnot *et al.* In their study, they correlated the nanotube diameters to the size of the catalyst particles; when catalysts with a few nm diameter was used, SWNTs was formed, and when catalysts with a few tens of nm diameter was used, MWCNTs was formed [57].

There are various studies conducted to control the particle size by further increasing the decomposition rate, or even by attaining rapid decomposition [58; 59]. The particle size of the catalyst is crucial in the synthesis of SWCNTs; only the particles with the right size can nucleate the SWCNTs. The small particles are overactive and dissolve extra carbon at the beginning. The excess carbon will form a thin layer of continuous graphite covering the surface of the nanoparticles. As a result, no SWCNTs can be grown using smaller particles. On the contrary, the larger nanoparticles cannot efficiently catalyze the decomposition of carbon stocks. Consequently, the carbon supplied

to nucleate SWCNTs will not be enough [60].

Metal nanoparticles of controlled size, can be used to grow CNTs of controlled diameters. For example, Kumar and Ando reported that noble metals (Au, Ag, Pt, Pd, etc.) have extremely low solubility for carbon, but they can dissolve carbon effectively for CNT growth when their particle size is very small, i.e. less than 5 nm [44]. Well-defined nanocluster catalysts can be used for diameter-controlled CVD synthesis of nanotubes. Cheung *et al.* synthesized iron nanoclusters with distinct and nearly mono disperse diameters by thermal decomposition of iron pentacarbonyl (Fe (CO) $_5$). The Fe(CO)$_5$ was decomposed in the presence of an excess of oleic acid, lauric acid or octanoic acid, which was functionalized as capping ligands for the nanoclusters. TEM images of the iron nanoclusters produced showed the ability to control the magnitude and uniformity of the nanocluster diameters. They found that the growth of smaller diameter nanoclusters is favored in the presence of longer chain-length capping ligands [61]. A study by Moisala *et al.* reported that using catalysts of mono disperse nanoparticles with desired sizes resulted in the formation of SWCNTs

with uniform diameters. Individual SWCNTs and tightly packed SWCNTs consisting of concentric sets of SWCNTs obtained were depended on the nanoparticles' diameters. Their study highlighted the correlation between the catalyst size and the nanotube diameter. Nanotube diameter defines the formation of SWNTs or MWNTs, which is affected by the size of the catalyst particle. If the particle is just few nanometers in diameter, the nanotubes formed are SWNTs, and if the particle is a few tens of nano meters in diameter, it will most likely form MWNTs [38]. Table 2 shows the particle size dependency of CNTs on the catalyst size. As can be seen in Table 2, the catalyst particle size influences the properties of the CNTs produced regarding their size and the number of walls (single wall or multiple walls).

A close correlation between the SWCNT diameter and the catalyst particle size was reported by Zhao *et al.* and Nasibudin *et al.* In addition to the mentioned studies, Cheung *et al.* reported that iron nanoparticles with average number mean diameters of 3, 9 and 13 nm yielded CNTs with wall diameters of 3, 7 and 12 nm respectively [62; 63]. The CNTs produced with the

Table 2: Particle size dependency of CNTs on catalysts [38]

Particle size (nm)	Catalyst compound precursor	Properties of CNTs
1-3	$(NH_4)Fe(SO_4)_2$	Individual (14) D $\sim$ DP $\sim$ 1–3 nm, L = 2 –420 nm [62]
1–2, 3–5	$(NH_4)Fe(SO_4)_2$	Individual and bundles, D = 3.0 ±0.9(nm), 1.5±0.4 nm
1–2	$FeCl_3$	D = 1–3(nm), L = 1–600(μm)
Dave = 3.2, 9.0	$Fe(CO)_5$	DCNT, ave $\sim$ 2.6, 7.3, 11.7 (nm) DWCNTs, MWCNT
<10, 20–30	Cobalt, molybdenum	SWCNTs, DWCNTs
2-3	$FeCl_3 + (NH_4)_2 + MoO_4$	D = 0.9–2(nm) (AFM)
2-3	Fe_2Cl_3, NH_4, MoO_4	D = 2–3(nm) (MWCNTs)
< 10	Fe_2O_3, iron , Nickel	D= 2-3(nm) MWCNTs

Dave = average diameter, ID = inside diameter, OD = outside diameter, L = length, D = diameter,
DB = bundle diameter, L B = bundle length [58]

smallest catalyst particles were primarily SWCNTs with a few double-walled carbon nanotubes (DWCNTs). With larger catalyst particles, the numbers of DWCNTs and thin MWCNTs increased with the product. Their findings have been the motivation for decreasing the catalyst particle size close to 1–2 nm range in order to produce the most desirable CNT product, i.e. SWCNTs [57].

In a molecular dynamics study of catalyst particle size dependence on the CNT growth, conducted by Ding et al, it was concluded that large catalyst particles that contain at least 20 iron atoms, nucleate SWNTs and have far better tabular structure than SWNTs nucleated from smaller clusters. In addition, the SWNTs grown from the larger clusters have diameters that are close to the cluster diameters, whereas the smaller clusters with diameters less than 0.5 nm nucleate nanotubes that are approximately 0.6-0.7 nm in diameter [64].

Phase of catalyst

A study by Ning *et al.* reported that unlike SWCNTs, multi-walled carbon nanotubes synthesized using vapor deposition of a hydrocarbon reactant on a solid catalyst (powder) in a chemical vapor deposition (CVD) method, would not assemble into bundles structure [65]. However, in their work they demonstrated a method to grow multi-walled carbon nanotube bundles with a solid catalyst, showing that a solid phase can also form bundles. Their work was different from the work carried out by Mukhopadhyay *et al.* since the assembly of nanotubes into bundles was more apparent in their experiment [66]. The doping of molybdenum into sol–gel prepared catalyst, which results in carbon nanotube bundles with high yield, is an example of a successful synthesis of novel nano-structured materials through a chemical route. Tri metallic method was used in their work. The Co–Mo–Mg–O catalyst used in their experiments was prepared by sol–gel technique; molybdenum was doped into the catalyst through oxidation and diffusion at 750 °C. This work has shown that small changes to the catalyst preparation led to the growth of single walled carbon nanotubes (SWCNTs).

It is important to note that the melting point of nanoparticles below 10 nm falls abruptly. For instance, an 8 nm Fe and Au particle (or 4 nm Ni particles) can melt at about 800 °C. Typical CNT growth temperature range is 700–900 °C, implying that in some cases the catalyst metal may be in liquid state, while in other cases (less than 800°C) it may be in a solid state [58]. Also, in any experiment, all particles are not strictly the same size. It is unclear whether the catalyst remains in a solid or liquid state. Since hydrocarbon decomposition on a metal surface is an exothermic reaction; it is likely that the extra heat generated during hydrocarbon decomposition helps the metal liquefaction to some extent. Hence the dominant opinion is that the active catalyst for SWCNT growth is in a liquid phase, as reported in [67]. The case of MWCNTs, which usually grow on bigger (>20 nm) metal particles, also should be considered. Bigger particles must be in a solid state; in turn, MWCNTs would involve a different growth mechanism than that of SWCNTs.

Common catalysts used for synthesis of CNTs

In many numbers of CNTs synthesis methods, metal nanoparticles are employed [68]. For the synthesis of CNTs, common metal catalysts used are Fe, Co or Ni. Traditionally, in CNT production, the transition metals are used as a catalyst since they offer nucleation and growth sites for CNTs [69]. This is because carbon has a high solubility in these metals at high temperatures. The other reason is that carbon has a higher diffusion rate in these metals. The high melting point and low equilibrium-vapor pressure of these metals also offer wide temperature options for the CVD method for different ranges of carbon precursors. Previous studies have found that Fe, Co and Ni have stronger adhesion with CNTs when compared to the other transition metals. The adhesion characteristics of these metals made them more efficient in the formation of low diameter CNTs and SWCNTs [56].

In addition to the metals which were mentioned, the organometalleocene forms of the metals, such as ferrocence, cobaltocene, and nickelocene, are also common in CNT production, acting as a catalyst. A metallocene is a compound typically consisting of two cyclopentadienyl anions bound to a metal center (M) in the oxidation state II, with the resulting general formula $(C_5H_5)_2M$. Closely related to the metallocene are the metallocene derivatives, e.g. titanocene dichloride and vanadocene dichloride. Certain metallocene and their derivatives exhibit catalytic properties; a metallocene contains a transition metal and two cyclopentadienyl ligands coordinated in a sandwich

structure. The reason for this selection is that they liberate in-situ metal nanoparticles and catalyze the hydrocarbon decomposition more efficiently [56]. As an example, in a study by Mohlala *et al.* organometallic precursors were used as catalysts in the CNT synthesis and MWCNTs was observed as the result [70].

In general, multi component materials such as bimetallic nanoparticles (bi-MNPs) are more reliable catalysts than single element catalysts because both metals in the bi-MNPs can enhance certain functions by playing complementary catalytic roles. Furthermore, some functions can only be offered by bi-MNPs because both metals are structurally arranged in such a specific manner that the combined properties would otherwise be impossible to access by monometallic nanoparticles (mono-MNPs).

Bi-MNPs (e.g., Ni/Co) have been used to produce SWCNTs. It has been shown that the yield increases by many folds in comparison to using their monometallic counterparts. In addition, bi-MNPs have been used to produce SWCNTs of different diameters, cleanness and lengths. Previous studies on bi-MNPs have revealed that their superior catalytic abilities can generally be attributed to the unique geometric and electronic structures they possess [59].

Apart from the popular transition metals, other metals of this group were found to catalyze hydrocarbons to synthesize CNTs. Some other metals such as Cu, Pt, Pd, Mn, Mo, Cr, Sn, Au, Mg, and Al have been shown to be successful in producing horizontally-aligned SWCNTs. In contrast to the transition metals, the noble metals have a very low solubility for CNTs. However, when their particle size is very small (less than 5 nm), they can dissolve carbon effectively for CNT growth [56]. In the literature, there are many studies related to catalyzing CNT with noble metals [51; 71-74]. Although the use of ceramics and semiconductors have been reported [75; 76], these materials were unable to catalyze the dissociation of hydrocarbons in the CNT production. In addition, these materials do not have the catalytic functionality to produce graphite [77]. Table 1 shows the common catalyst reported for the synthesis of CNTs.

As can be seen in table 2, the most common catalysts such as Fe, Co, Ni produce both SWCNTs and MWCNTs. However, other factors such as substrate, the addition of the promoter or the nature of the catalyst play important role in obtaining different types of nanotubes. This also holds true for other transition metals. Bimetallic catalysts mostly result in obtaining SWNTs, however there are reports on obtaining MWNTs as well [85]. Semiconductors and molecular catalysts mostly produce SWNTs. Addition of a promoter to catalysts has proven to influence the efficiency of the catalysts and resulted in few walled carbon nanotubes (FWNTs) and DWNTs. More research is still needed to identify the important parameters affecting the final CNT morphology, size, and diameter. As mentioned earlier, there are also different reports on the synthesis of carbon nanotubes without catalyst [86].

Catalyst support

The catalyst support plays several important roles in CNT production: it allows the formation of metal nanoparticles with a narrow size distribution, it avoids excessive sintering of metal particles during Chemical Vapor Deposition(CVD) by immobilizing the catalyst particles, it permits easy handling of the catalyst, the size of the support can be tuned and optimized to allow the fluidization of the catalyst when using fluidized bed reactors for continuous CNT production, and the support defines the macroscopic shape of the CNT product [87].

The metal-support interaction (MSI) influences the CNT synthesis [88; 89]. Some of the common substrates used in CVD are: graphite, quartz, silicon, silicon carbide, silica, alumina, alumina silicate, and magnesium oxide [90]. Al_2O_3 and SiO_2 are very common as reported by Moisala *et al.* and Dupuis *et al.* [38; 91]. MgO is commonly used as well and has some advantages over the other supports, such as easy dissolvability in acid and easy purification of CNT [92]. Dikio *et al.* proved that the morphology of the carbon nanotubes synthesized with magnesium oxide as support material leads to a higher yield of carbon nanotubes and the obtained CNTs were consistent and had well-defined structure. However, when they used calcium carbonate the result wasn't as consistent as using magnesium oxide. The ratio of synthesized carbon nanotubes (CNTs) was 0.8544 for magnesium oxide supported compared to 0.8501 for calcium carbonate supported carbon nanotube in their studies [93]. Thus it can be concluded that in terms of decomposition factors, $Al(OH)_3$, $CaCo_3$ and other alkaline earth carbonates have been proven to influence the CNT growth [94].

Catalytic activity and catalyst lifetime depend on the type of the catalyst support. However, some other methods have been mentioned in the literature that can increase catalyst activity as well, such as using film catalyst then by bombardment break the film into particles. For instance, in PE CVD plasma ion bombardment has been shown to help the formation of catalyst particles which in turn have produced CNTs [95; 96]. Same catalyst can work in a different way on different supports [97]. For example, nickel supported on Zeolite Socony Mobil–5 zsm-5 which is alumino-silicate zeolite could not be effective in producing filamentous carbon, as stated in a report by Choudhary *et al.* [98]. The support may also alter the precipitation of crystallographic faces of the catalyst particles, which in turn influence the structural characteristics of the obtained Carbon. For example, carbon grown on iron powder using CO/H_2 as the carbon source at 600 °C possess a platelet structure, whereas carbon grown on silica-supported iron possess a tubular structure regarded as CNTs[99] .

The first and most important thing taken into consideration for the support preference is the catalyst-substrate interaction. This interaction is essential for the metal catalyst since the catalytic behavior of the metal may stop because of the metal-substrate reaction [100]. The growth of CNT depends on catalyst support interaction, in which two growth models can occur: in the tip growth model, the catalyst is lifted off of the support and CNT grows when the interaction is weak. In the root growth model, metal-support interaction is strong and catalyst particles remain on the support while CNT is growing. In the presence of a strong metal-substrate interaction (MSI), the metal particle cannot be lifted off of the support surface, prohibiting the growth of CNTs. The support properties to be considered for the selection of a catalyst support are: the substrate's material, surface morphology, textural properties, pore size, and the deposition and dispersion of nanoparticles on the substrates [101; 102]. Several studies have shown that the growth of CNTs was preferable on the supports without pore structures. They reported that CaB-o-silica without pore structure, was used as a nickel support, and has the highest catalytic activity [103].

The method of depositing catalyst over a substrate is critical for a successful CNT synthesis. Wei *et al.* emphasized that the catalysts on the substrate must be in a particle form or in a smooth or continuous film from. Regarding the deposition of nanoparticles on substrates, there are three factors that need to be considered. Firstly, there is a need to find a solvent in which the nanoparticles can be well dispersed. Secondly, the surface property of the nanoparticles should be compatible with the solvent to ensure a uniform wetting of the whole substrate. Lastly, it is desirable that there is surface affinity between the substrate and the nanoparticles [104]. For nanoparticles dispersed in non-polar organic solution, a hydrophobic substrate surface is preferred, and for nanoparticles dispersed in an aqueous solution, a hydrophilic substrate surface is favorable [55].

Although there are numerous studies that determine the CNT diameter and catalyst size, there are some problems associated with these results. Evolution of size distribution of metal particles during the CNT synthesis is inevitable due to the increased temperature required to accelerate the decomposition of carbon precursor molecules on the catalyst surface. When metal particles are heated, catalyst particles may collide due to surface diffusion. Subsequent sintering of particles has been observed to increase the average particle size[105]. As a result of sintering, reduced concentration and increased mean size of catalyst particles were obtained. The simultaneous evaporation of particles reduces the concentration and modifies the size distribution even further.

Catalyst preparation

SWCNTs are usually produced with the assistance of metal catalysts that first break down various carbon species such as graphite, carbon clusters, amorphous carbon or hydrocarbons, and then release them in the form of SWCNTs. Therefore catalysts must perform several functions such as nature of the catalyst, pore size of the support, concentration of catalyst, Nano particle size and diameter, Quantity of catalyst active particle, Metals-support interaction, Shape of nano particles, addition of promoter and Method of catalyst preparation in order to produce high quality, high yield, long SWNTs, and the finesse of these catalysts is controlled by the balance between those functions [105]. There are numerous methods of producing catalyst nanoparticles such as: thermal evaporation in a vacuum [106], laser deposition [107], cluster beam

[108], sol gel, precipitation and impregnation [109], and molecular cluster precursor[110]. However, in the synthesis of the CNT, the catalyst preparation method needs to be studied and preparation methods with less impact on the properties of CNTs should be used. As an example, in a study by Iruzrun *et al.* the sol-gel preparation method have been shown to widely vary the morphology of Co-Mo catalysts used in the synthesis of SWNT [111]. In turn, these changes in morphology result in reproducible changes in the nanotube quality and yield. In another study by Hosseini, different preparation methods and conditions were studied. In a work by Hosseini *et al.* they found that the preparation of the catalyst Fe (nm)/ Al_2O_3 involves direct mixing of commercial iron nanoparticles with alumina substrate in an easier and shorter time, but at a constant temperature of synthesis, the diameter of CNTs is close to the diameter of the catalyst particle. Therefore, controlling the CNT size is easier because it is possible to choose the catalyst size[112]. However, in another method changing the concentration of salt as a weight percentage of the catalyst resulted in a change in the yield of the nanotube; since the synthesis methods and their conditions can affect the final size of the nanoparticles. In turn, the size of these particles affects the size of CNT produced. Li *et al.* were able to prepare uniform Fe/Mo nanoparticles with controllable sizes by varying the experimental conditions in their synthesis methods [113]. These results show that the size of catalysts nano particles is one of the most important factors in controlling the size of the CNT. Precipitation methods have led to wide particle size distributions. Attempts have been made to control the size distribution and dispersion of catalyst particles. Organic carriers, such as apoferritin or polyamidoamine dendrimers have been successfully used to decrease the nanoparticle size distribution to a 1–3 nm range.

Wei *et al.* reviewed two approaches for catalyst preparation: solution-based and physical-based approaches [54]. Solution-based preparation techniques are more common in thermal CVD processes. In this preparation, several steps are usually performed, including: dissolution, stirring, precipitation, refluxing, separation, cooling, gel formation, reduction, drying, calcinations, and annealing. However, for this technique, overnight annealing is often required, and therefore this method is considered to be a time consuming method. In contrast to solution-based approaches,

physical techniques are faster. The common methods of physical-based approaches are thermal evaporation, gun evaporation, ion beam sputtering and magnetron sputtering. A thin catalyst film is typically used in this approach. Thinner films lead to smaller particles and nanotubes, especially in Plasma Enhanced CVD (PECVD) [114]. In another report by Moshkalyov, it was shown that tubes tend to grow from irregularities of Ni films; for thinner catalyst films, better results were achieved with high density nanotubes [115].

Suitable methods of catalyst preparation determine the efficiency of the catalyst for CNT production. Several studies have concentrated on showing the importance of catalyst preparation and its effects on the CNT production. There are many preparation methods in the literature, but the most important factors have often been the catalyst size, catalyst composition and concentration, catalyst calcinations, and the usage of right ligands if using the transition metals as catalysts.

Catalyst activity

Catalytic activity is mainly influenced by the amount of metal loading, catalyst preparation method, reaction temperature and the type of support material. A study by Saraswat and Pantt reported that catalyst activity and the yield of hydrogen and CNT depend strongly on Ni loading and the preparation method. 50% Ni/SiO_2 catalyst prepared by the wet impregnation method was the most suitable in terms of higher methane conversion and CNT yield, when compared to other catalysts [116]. They investigated the effects of two different catalyst preparation methods: wet impregnation and co- precipitation on the catalyst activity. They found that the precipitated catalysts showed higher deactivation than the wet impregnated catalyst in production of CNTs. Deactivation was observed because the catalyst became deactivated due to carbon decomposition. Moreover, the catalyst preparation methods also influenced the structure of the CNTs formed. Wet impregnated catalyst led to the formation of carbon nano-fibers, and the deposited carbon was filamentous in structure. In the case of the co-precipitation catalyst, the nano-fibers were not clearly distinguished.

Catalyst poisoning

One of the issues that manufacturers of CNTs have to deal with is the termination of the CNT

growth. This is called poisoning. Poisoning is the inactivation or the poisoning process of catalyst particles that has been attributed to an overcoat of amorphous carbon. Although termination of CNT growth is often attributed to amorphous carbon poisoning, how this actually happens has yet to be identified [117]. In an investigation by Schunemann *et al.* it was revealed that the presence of amorphous carbon does not prevent the catalytic hydrocarbon decomposition and graphitization processes. In addition, catalytic hydrogenation, a process in which carbon in contact with the catalyst surface reacts with H_2 to form CH_4, is taking place simultaneously. There are two key findings in this work: amorphous carbon does not poison metal catalyst particles during the thermal CVD growth of carbon nanotubes, and also the study shows continued carbon nanotube growth even when the particles were exposed to large amounts of amorphous carbon and carbon tar. Catalyst particles intentionally covered with amorphous carbon prior to a CVD reaction show graphitization; the feedstock is still able to decompose and the catalyst particles are still able to form sp^2 carbon [11].

Past studies showed that controlled amounts of water vapor or hydrogen/oxygen radicals improved CNT growth. The argument is whether they reduce or remove the amorphous carbon. In some studies, the amorphous carbons upon contact with the catalyst metals are ignited for graphene formation. This contradicts the theory of catalyst poisoning by amorphous carbon when CNT is growing in the CVD method. For example, in a study by Sirkamon *et al.* a small amount of water vapor was introduced into the reactor by controlling diffusion with heated water in a flask. The vapor-assisted conditions provided increased quantity and quality of CNTs. Furthermore, the D-band/G-band ratio signifies that the defect of atomic carbon structure was decreased. These results demonstrate that water vapor is essential for a long Vertically Aligned Carbon Nano Tubes(VA-CNTs) synthesis [118].

In another study by Chen *et al.*, the role of radical atomic O, hydroxyl and perhydroxyl in multiwall CNT growth was explored. By addition of a small amount of O_2 ($\sim$0.67%) or H_2O ($\sim$0.1%), it was found that a high quantity of pure nanotubes can be grown in the downstream [119]. However, no nanotubes could be formed when the concentration of O_2 or H_2O radicals was at a

certain level, as explored in a paper by Qiang *et al.* [120]. The most severe catalyst deactivation process in SWCNT synthesis is the catalyst poisoning due to the accumulation of amorphous carbon. Accumulation of amorphous carbon may arise as a result of hydrocarbon self-pyrolysis or due to excessive carbon precursor concentration. Limiting the carbon precursor feed rate to the catalyst particle has been achieved by controlling the carbon precursor partial pressure (the case of hydrocarbons) and by selecting the carbon precursor according to the decomposition rate. This will result in preventing the excessive carbon precursor concentration which in turns result in controlling fine growth of CNTs [121; 122].

Heat Treatment

In the literature, the effects of heating, preheating and calcination have been studied as important factors. For example, Siang *et al.* studied the effects of catalyst calcination on the diameter of the carbon nanotubes. The results showed that the catalyst calcination temperature greatly affected the uniformity of the CNT diameters. The CNTs obtained from CoO–MoO/Al_2O_3 catalysts, calcined at 300°C, 450°C, 600°C, and 700°C had diameters of 13.4 ± 8.4, 12.6 ± 5.1, 10.7 ± 3.2, and 9.0 ± 1.4 nm, respectively, showing that an increase in catalyst calcination temperature produces a smaller diameter and narrower diameter distribution [104]. In addition to this, calcination of the catalyst increases the yield of carbon nanotubes [39; 123]. However, in another study by Wei *et al.*, the catalysts calcined at 500, 600 and 700 °C produced CNTs with diameters of 1.53, 1.95 and 2.97 nm, respectively. Generally, an increase in the calcination temperature increases the average diameter and decreases the quality of the CNTs produced [54]. In a study by Chai *et al.*, they found that the reduction in the temperature and calcination of the catalyst resulted in broader diameters, and the non-graphitized filamentous nanostructures in the catalyst were reduced at higher temperatures [124].

The preheating effects of catalysts have been studied in a report by Sengupta *et al.* [125]. It was revealed that preheating not only affects the degree of graphitization but also that the nanotube growth, density depends on the catalyst heat treatment before the synthesis. In their study, the CNT grown on the Fe catalyst preheated at 900 °C possessed the optimized result in terms of growth density [125].

Thus, the formation of CNTs, along with their size and structure, depends on catalyst film thickness and the heat treatment time of the catalyst used in the process. Inami *et al.* reported the dependence of growth yields of SWCNT on the heat treatment time and catalyst film thickness in the alcohol catalytic CVD process [126]. Three types of heat treatments were used: synthesis of 30 min, synthesis of 30 min after annealing of 30 min, and synthesis of 60 min. The Co catalyst thickness varied from 1 to 10 nm. They concluded that the conversion from the thicker film of Co to the nanoparticle, which acts as a catalyst, took place during the first 30 min [126].

CONCLUSION

Catalyst plays an important role in synthesis of CNTs, thus in this review paper, important parameters that affect CNT production in terms of catalyst preferencewere discussed. It is clear that catalysts play an important role in the CNTs synthesis. Parameters which influence the catalyst include: size, structure, composition, type of catalyst, and its state. It can be expected that researchers should consider these factors when dealing with CNT synthesis, and improve parameters which were mentioned in this review paper. Despite numerous reports in the literature, discrepancies exist with regards to the parameters affecting the CNT production. Consequently the lack of a comprehensive study which determines the exact parameters affecting the catalyst synthesis is felt. This review helps the researchers to select a suitable catalyst to obtain desirable carbon nanotubes in terms of yield, efficiency, type (single wall or multiple walls), size, and diameter.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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