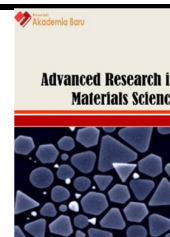




## Journal of Advanced Research in Materials Science

Journal homepage: [www.akademiabaru.com/arms.html](http://www.akademiabaru.com/arms.html)

ISSN: 2289-7992



# Investigation on the Deactivation of Cobalt and Iron Catalysts in Catalytic Growth of Carbon Nanotube Using a Growth Rate Model

Open  
Access

Muhammad Thalhah Zainal<sup>1,2</sup>, Mohd Fairus Mohd Yasin<sup>1,2,\*</sup>, Muhammad Abid Ira Irawan<sup>1,2</sup>,  
Muhammad Faizullizam Roslan<sup>1,2</sup>, Norikhwan Hamzah<sup>1,2</sup>, Mohd Zamri Mohd Yusop<sup>1,3</sup>

<sup>1</sup> School of Mechanical Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, 81310 Johor Bahru, Johor, Malaysia

<sup>2</sup> High Speed Reacting Flow Laboratory (HIREF), Universiti Teknologi Malaysia, 81310 Johor Bahru, Johor, Malaysia

<sup>3</sup> Advanced Membrane Technology and Research Center (AMTEC), Universiti Teknologi Malaysia, 81310 Johor Bahru, Johor, Malaysia

### ARTICLE INFO

### ABSTRACT

#### Article history:

Received 27 November 2018

Received in revised form 29 December 2018

Accepted 29 December 2018

Available online 30 December 2018

The deactivation of metal catalyst particles during the catalytic growth of carbon nanotube (CNT) remains a hurdle in achieving high CNT growth rate and mass CNT production. In the present study, a CNT growth rate model is employed as the main framework to investigate the catalyst de-activation and lifetime of iron and cobalt catalysts. The growth rate model is first validated against a baseline case study that employs cobalt as the catalyst, acetylene as the carbon feedstock, and operating conditions of 1100 K and 20 Torr for temperature and partial pressure respectively. In order to illustrate catalyst deactivation, two parameters are varied namely the surface diffusivity and bulk diffusivity of carbon with respect to the specified catalyst. The results show that iron is the better catalyst compared to cobalt in terms of CNT length. The physics of deactivation of Fe and Co catalysts is also shown through prediction of carbon atoms and carbonaceous layers concentrations on a catalyst particle which favours Fe catalyst.

#### Keywords:

Carbon nanotube, catalyst, deactivation,  
growth rate model, modelling

Copyright © 2018 PENERBIT AKADEMIA BARU - All rights reserved

## 1. Introduction

In catalytic growth of carbon nanotube (CNT), cobalt Co and iron Fe have been widely employed as the catalyst material to support CNT growth [1–5]. As stated by Shah and co-workers [6], these catalysts are best used to form high curvature (low-diameter) CNTs due to the stronger adhesion towards the growing CNTs compared to other transition metals. In addition, these catalysts are found to be effective for CNT growth because carbon C has high diffusion rate and solubility in these metals at high temperature [6]. Although the presence of catalyst particles provides CNT growth site and reduces the reaction temperature [7], the issue of catalyst deactivation remains a challenge that begs attention as it determines the CNT yield and growth rate. It is highly desirable

\* Corresponding author.

E-mail address: Mohd Fairus Mohd Yasin ([mohdfairus@mail.fkm.utm.my](mailto:mohdfairus@mail.fkm.utm.my))

to have a synthesis process that produces CNT at high yield and at high growth rate as the present state of the CNT market demands large volume of CNTs for various electrical, mechanical, and composites applications [8].

In previous experiments on catalytic growth of CNTs, formation of amorphous carbon layers or carbonaceous layers that encapsulates the catalyst surface is frequently observed and linked to the degrading performance of the catalyst as the synthesis process progresses [9–12]. Previous analyses on catalyst performance are focused on the out-put that each catalyst offers. One study described the efficiency and yield of Fe, Ni, and Co catalyst by the percent-age of carbon deposited on the catalyst and the weight ratio of CNTs against catalyst [5]. However, this calculation method is rather simplistic and does not clarify the deactivation process of the catalyst particles that is caused by carbonaceous materials. Furthermore, the catalyst metal employed in the study features catalyst metal mixed in mesoporous composites which may have different effects on carbon diffusivity and thus CNT growth which are not modelled in their calculations. Sivakumar et al. reported catalyst effects on CNT yield from the perspective of methane conversion into carbon atoms and hydrogen gas [13]. The study claims that Fe performs better at catalytic decomposition of methane feedstock into carbon atoms compared to nickel catalyst though the portion that is converted into single carbon atoms is not explicitly mentioned. Thus, it is not conclusive as to which catalyst provides better carbon supply for CNT growth. In relation to this, Xiang and co-workers claimed that catalyst deactivation may be influenced by carbon feedstock diffusion to the catalyst particle [14]. In another study, it is shown that the trend of CNT growth rate only partially follows the trend of the bulk diffusivity of carbon inside the catalyst. On the other hand, the size of catalyst particle could also have influence on the CNT growth rate [15].

Based on the brief review above, the aspect of catalyst deactivation on catalyst performance and CNT growth rate has not been explored systematically. Furthermore, the various postulations of catalyst deactivation suggest that the real cause of catalyst deactivation remains unclear. The modelling perspective on catalyst deactivation is not widely investigated though several studies proposed CNT growth rate models that incorporate the deactivation processes [12,16–18]. In the previous modelling studies, the proposed routes towards catalyst deactivation include the presence of carbonaceous layers that encapsulates the catalyst particle and inactive catalyst sites [17]. However, detailed investigations on the effects of both parameters on CNT growth rate are not provided. A recent modelling study attempted to explain catalyst poisoning of Fe, Co, and Ni in CNT synthesis using an atomic model where a unique concept of phonon vibration model is employed [19]. The model is actually an improvement of a previous model from the same research group [20] where a catalyst deactivation variable is introduced. The study predicts Ni to be the better catalyst compared to Co and Fe in terms of growth rate. However, the absence of any investigation on the catalyst deactivation term suggests that there is hardly a conclusive evidence that one catalyst is better than the other [19]. To the best of authors' knowledge, the investigation on the effects of catalyst deactivation on the deceleration of CNT growth rate has not yet been explored in detail.

Therefore, the present study aims at investigating the deactivation and lifetime of Co and Fe catalysts using an established CNT growth rate model as the main framework. In the growth rate model, the concentration of carbonaceous layer on the surface of a catalyst particle will be used as the parameter to measure catalyst deactivation and lifetime where the formulation of this parameter will be discussed in detail in the next section. The validation of the model will be shown followed by the study on the effects of surface and bulk diffusivity of carbon in Co and Fe on the catalyst deactivation.

## 2. Methodology

The present study employed improved Naha-Puretzky model for catalytic growth of CNT proposed by Zainal *et al.*, [18]. This growth rate model is developed based on diamond nucleation model and CNT growth rate model proposed by previous studies [16,17,21,22]. Further details and explanation of the evolution of this growth rate model are reported elsewhere [18,23]. The model is able to predict CNT length, CNT growth rate, and catalyst deactivation where single value of temperature and partial pressure are required as inputs for the prediction. It should be noted that the model's capability to predict CNT length is focused on aligned growth of CNTs. The present study is aimed at explaining the deactivation of catalyst particles through the surface density of C atoms on a catalyst particle,  $n_1$  and the concentration of the carbonaceous layer at catalyst particles,  $n_{p1}$  which are computed using a system of ordinary differential equations ODE.

A baseline case is first established for model validation where the CNT length is compared to that of a CVD experiment that grows CNT at 1100 K and 20 Torr temperature and partial pressure respectively using ethylene  $C_2H_4$  gas and cobalt as the carbon source and catalyst respectively [24]. The main ODE that calculates the surface density of carbon nanotubes  $n_1$  on a catalyst particle is represented in Equation (1) where  $R_a$ ,  $R_d$ ,  $R_{bd}$ ,  $R_{sc}$ ,  $R_{cc}$ , and  $R_{cd}$  represent the rate of adsorption of C atoms onto catalyst particle, the rate of desorption of C from catalyst particle, the rate of bulk diffusion of C atoms through catalyst particle, the rate of formation of stable clusters, the rate of formation of critical clusters, and the rate of catalyst deactivation respectively. In essence, the main ODE in Equation (1) describes the main stages for catalytic growth of CNT.

$$\frac{dn_1}{dt} = R_a - R_d - R_{bd} - R_{sc} - R_{cc} - R_{cd} \quad (1)$$

After the breakdown of fuel molecules into single carbon atoms, the early interaction between the solid carbon atoms and catalyst particle occurs in the form of surface adsorption. The rate at which carbon atoms adsorb on the catalyst surface is modelled by the term  $R_a$  which is expressed by Equation (2).

$$R_a = F_{b1} p_1 \exp\left(-E_{a1}/k_B T\right) \quad (2)$$

$$F_{b1} = \frac{1}{4} S_0 n \left( \frac{k_B T}{2\pi m} \right)^{1/2} \quad (3)$$

The constants  $p_1$  and  $k_B$  are the pre-exponential factor and Boltzmann's constant respectively. The process of catalytic dissociation of the carbon source is modelled by  $E_{a1}$  which is the activation energy required to decompose a hydrocarbon molecule. For the present study,  $E_{a1} = 0.6$  eV is used which is based on previous study that grew aligned CNT using ethylene [12]. A fixed value of  $E_{a1}$  is employed with the intention of studying the effects of surface and bulk diffusion in isolation from the effects of surface reactions on hydrocarbon decomposition. The variable  $F_{b1}$  represents the flux of the carbon source molecule and is expressed by Equation (3). The surface area of the catalyst particle is defined as  $S_0 = \pi d^2$  where the catalyst diameter  $d$  is 50 nm in the present study. The variables  $n$  and  $m$  are the mass and the partial density of the feedstock ( $C_2H_4$ ) molecule respectively. The partial density  $n$  is related to partial pressure  $P$  by the gas law  $n = PM/RT$  where  $P$  follows the operating condition of 20 Torr and constants  $M$  and  $R$  are the feedstock molecular weight and the universal gas constant respectively.

The second term on the right hand side of Equation (1) is the rate of desorption of carbon atoms away from the catalyst nanoparticle and is defined by Equations (4) and (5). Variable  $\nu$  denotes the vibrational frequency of the adsorbed species which is assumed to be  $1.36 \times 10^{-18} \text{ s}^{-1}$  [21] whereas  $E_a$  is the activation energy for adsorption to occur and assumes the value of 6.228 eV [17]. Note that wherever  $T$  appears from Equations (2) to (5), the value of the temperature follows the experiment operating condition of 1100 K.

$$R_d = n_1/\tau_{res} \quad (4)$$

$$\tau_{res} = \frac{1}{\nu} \exp(E_a/k_B T) \quad (5)$$

The rest of the carbon atoms that do not desorb experience diffusion through the catalyst particle as modelled by the diffusion term  $R_{bd}$  in Equation (6). Diffusion takes place at saturation time  $t_s$  after which additional carbon atoms could no longer impinge on the surface of the catalyst particle. The variable  $D_b$  denotes the carbon bulk diffusivity which varies based on catalyst type. Variable  $C_0$  denotes the volume concentration of C atoms at the substrate surface and is approximated by  $C_0 \approx n_1/a_c$  where  $a_c$  is the diameter of a C atom.

$$R_{bd}|_{t=t_s} = C_0 \sqrt{\frac{D_b}{\pi t}} \quad (6)$$

As carbon atoms diffuse through the catalyst, stable and critical clusters start to form. The rate of stable and critical cluster formation is determined by the fourth  $R_{sc}$  and fifth  $R_{cc}$  term on the right hand side of Equation (1) which are expressed by Equation (7) and (8) respectively. According to a recent CNT modelling study, when the number of C atoms that aggregate is above a certain threshold  $i$ , it is said to form a stable cluster [18]. On the other hand, if the amount of C atoms that aggregate is below the said threshold, a critical cluster is formed. A critical cluster could be viewed as an aggregate of carbon atoms that could potentially be decomposed into single atoms that contribute to CNT nucleation and growth. For the present study, the threshold value of 10 is chosen to be consistent with previous studies [18,23].

$$R_{sc} = \sigma_x D_s n_1 n_x \quad (7)$$

$$R_{cc} = (i + 1) \sigma_i D_s n_1 n_i \quad (8)$$

$$\frac{dn_x}{dt} = \sigma_i D_s n_1 n_i \quad (9)$$

$$n_i = \begin{cases} \frac{1}{2} n_1 (x - i), & x > i \\ 0, & 1 < x \leq i \end{cases} \quad (10)$$

$$\frac{dx}{dt} = \sigma_i D_s n_1 \quad (11)$$

The constants  $\sigma_x$  and  $\sigma_i$  in Equation (7) and (8) represents the capture number of C atoms forming a stable nuclei and a critical nuclei respectively. The values are set to 5 and 4 respectively to be consistent with previous studies [16–18]. The solution for the surface density of stable clusters  $n_x$  is determined from Equation (9) where  $n_i$  is the surface density of critical clusters as

expressed by Zinsmeister's relation in Equation (10) where stable cluster formation that does not contribute to CNT growth is achieved only if the first condition ( $x > i$ ) is met. Finally, the variable  $D_s$  represents the carbon surface diffusivity which is the manipulated variable of the present study alongside the carbon bulk diffusivity  $D_b$ . The difference between both diffusivities is that surface diffusivity could be viewed as the degree of carbon transport over catalyst surface which includes nucleation of C atoms whereas bulk diffusivity is the rate of carbon diffusion into that particular catalyst. Just like  $D_b$ , the value of  $D_s$  also varies with different catalyst. In the present study, the effects of Fe and Co catalyst material on growth deactivation is investigated where different values of carbon diffusivity are used as described in table (1). Other than the diffusivity properties, all other variables remain fixed. It is important to note that the parameter  $E_{a1}$  from Equation (2) may also vary with catalyst but due to the limited data on the reactivity of hydrocarbon towards different catalyst and due to the reason that has been stated earlier, the value of  $E_{a1}$  is assumed constant. In Equation (10), the amount of C atoms that is present in a stable cluster  $x$  is obtained by solving the ODE in Equation (11).

**Table 1**

Carbon surface diffusivity  $D_s$  and bulk diffusivity  $D_b$  for different catalysts

<b>Metal Catalyst</b>	<b><math>D_s</math> (<math>m^2/s</math>)</b>	<b>Ref.</b>	<b><math>D_b</math> (<math>m^2/s</math>)</b>	<b>Ref.</b>
Cobalt (Co)	$5.20 \times 10^{-21}$	[18]	$1.36 \times 10^{-18}$	[18]
Iron (Fe)	$2.55 \times 10^{-16}$	[25]	$1.00 \times 10^{-9}$	[26]

Catalyst deactivation is modelled by the final term on the right hand side of the main ODE in Equation (1) as expressed by Equation (12). Catalyst surface could be poisoned either by encapsulation of carbonaceous layers or by inactive catalyst particles. Both deactivation routes are described by Equation (13) and Equation (14) respectively where the surface densities of carbonaceous layers and inactive particles are denoted by  $n_{p1}$  and  $n_{p2}$  respectively. In the present study, the dependent variable  $n_{p1}$  is of main interest where the solution of  $n_{p1}$  for different catalyst carries different influence on the rate of catalyst deactivation. Variables  $\phi_{c1}$ ,  $\alpha_m$ , and  $n_m$  in Equation (12) represent the rate constant for catalyst deactivation, the number of carbon monolayer, and the surface density of the monolayer whose values are based on previous studies ( $\phi_{c1} = 3 \times 10^5 \text{ atoms/s}$ ,  $\alpha_m = 1$ , and  $n_m = 3 \times 10^5 \text{ atoms/s}$ ) [17,23]. Variable  $\phi_c$  represents the carbon flux from the deposition of pyrolysis products of hydrocarbon species where a constant value of  $3 \times 10^5 \text{ atoms/s}$  is assumed and  $k_{cl}$  is the rate constant for carbonaceous layer formation and is assumed to be  $3 \times 10^{-5} \text{ s}^{-1}$  [12]. The variable  $R_c$  denotes the rate constant of deactivation via inactive catalyst particle with the value of  $6.54 \times 10^{-7} \text{ s}^{-1}$  [17].

$$R_{cc} = \phi_{c1} \left( \frac{n_{p1} + n_{p2}}{\alpha_m n_m A_{np}} \right) \quad (12)$$

$$\frac{dn_{p1}}{dt} = \phi_c \left( 1 - \frac{n_{p1} + n_{p2}}{\alpha_m n_m A_{np}} \right) + k_{cl} n_1 \quad (13)$$

$$\frac{dn_{p2}}{dt} = R_c \left( 1 - \frac{n_{p1} + n_{p2}}{\alpha_m n_m A_{np}} \right) \quad (14)$$

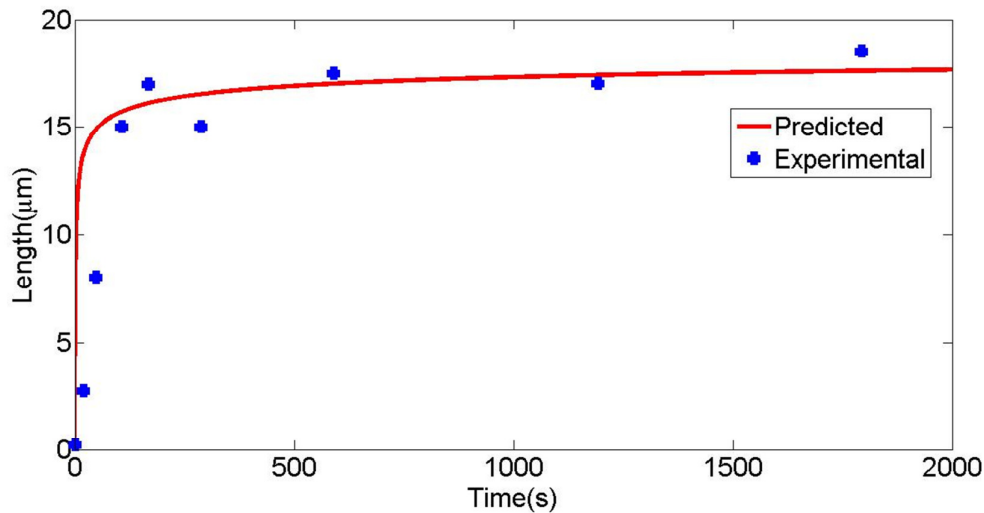
Equations (1)-(14) are solved using the MATLAB ODE15s stiff solver due to the stiff nature of the ODE system that features constants with large difference in order of magnitude. Once the solution of  $n_1$  is obtained, calculation at the post-processing stage involves utilisation of  $n_1$  as input for Equation (15) to predict CNT length where  $C^* = 4.83 \times 10^{26}$  atoms/m<sup>3</sup> is assumed for the amount of C atoms necessary to form a carbon monolayer [22].

$$L = \left[ \frac{1}{a_c C^*} \sqrt{\frac{D_b}{\pi}} \right] \times \int_0^t \frac{n_1}{\sqrt{t}} dt \quad (15)$$

### 3. Results

#### 3.1 Baseline case study

The baseline case is based on previous CVD experiment that synthesizes CNTs at operating conditions mentioned in the previous section [24]. Figure 1 shows the validation of CNT length over time for a growth period of approximately 30 minutes where the trend and magnitude of the predicted CNT length show an excellent comparison with that of the experiment. Moreover, the maximum CNT length as the length reaches plateau closely predicts that of the experiment which is approximately 17  $\mu$ m.

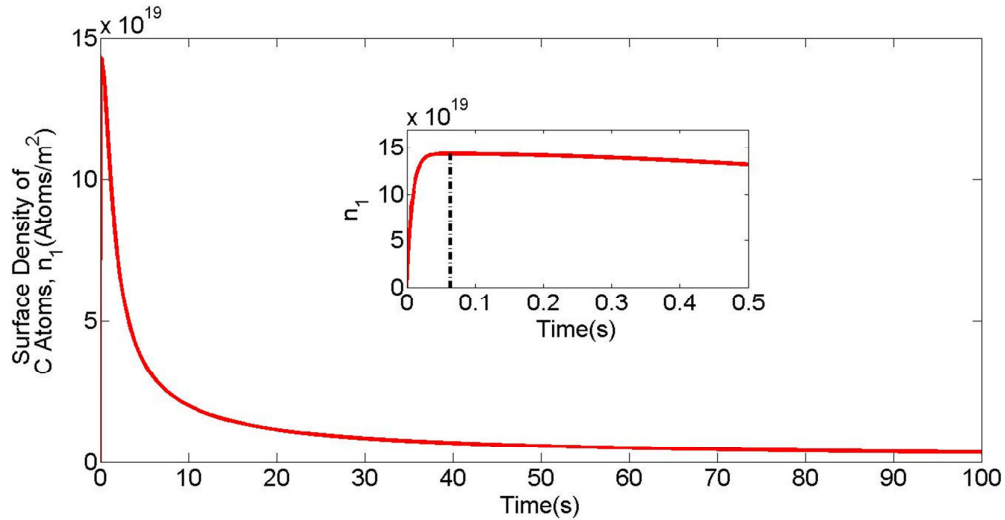


**Fig. 1.** Validation of CNT length against experimental data [24] for catalytic growth of CNT using cobalt catalyst

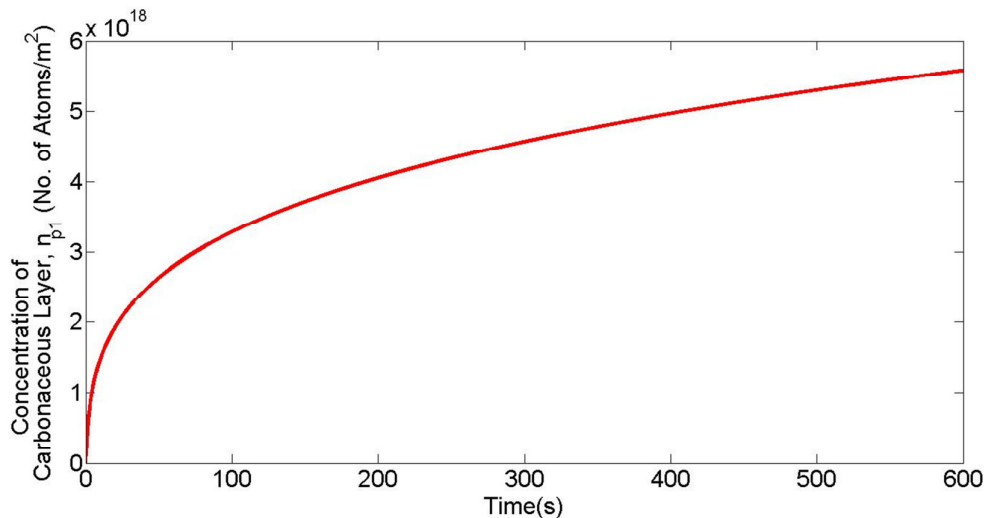
The behaviour of the CNT length plot in figure 1 could be described by the line plot in figure 2 which illustrates the surface density of carbon atoms  $n_1$  with respect to growth time. The region started from  $t=0$  s where the deposited carbon atom accumulates on the surface of catalyst particle up to the saturation point which is indicated by the peak. At the saturation point of 50 ms (dashed lines), catalyst surface is packed with C atoms with the amount of  $15 \times 10^{19}$  atoms/m<sup>2</sup>. Bulk diffusion of C atoms into the catalyst particle occurs afterwards and is indicated by the significant drop from 50 ms to approximately 10 s. Essentially, the number of carbon atoms that remain dispersed on the catalyst surface reduces over time as bulk diffusion takes place. Additionally, C atoms that have undergone bulk diffusion roam within the vicinity of the catalyst surface and combines with one another, signaling the nucleation of nanotubes. As the growth time progresses

towards 100 s and beyond, the number of C atoms on the catalyst surface reaches a steady state which indicates that bulk diffusion no longer takes place and thus CNT growth ends.

The evidence of growth truncation is further supported by the surface density plot of carbonaceous layer on the catalyst particle as shown in figure 3. The number of carbonaceous layers grows rapidly at the early stage of CNT growth that explains the early onset of the plateau region in figure 1. The amount of carbonaceous layer keeps on increasing throughout the growth time. It could be inferred that the increasing trend of  $n_{p1}$  leads to the end of the catalyst lifetime and thus CNT growth is put to stop.



**Fig. 2.** Plot of surface density of carbon atoms on a cobalt catalyst particle for growth time of 100 seconds. Inset shows a close up of the saturation region



**Fig. 3.** Plot of surface density of carbonaceous layer encapsulating cobalt particle that determines the truncation of CNT growth.



### 3.2 Effects of catalyst material on catalyst lifetime

CNT length is predicted for Co and Fe catalyst based on the carbon surface diffusivity  $D_s$  and bulk diffusivity  $D_b$  values in table 1 and is presented in figure 4. The terminal length is higher for Fe compared to Co with predicted values of  $38 \mu\text{m}$  and  $17 \mu\text{m}$  respectively. The higher CNT length for Fe implies better CNT growth rate. A study suggested that Fe being an excellent catalyst for CNT growth could be attributed to its high catalyst diffusivity and carbon solubility [27] which is evident from the  $D_s$  and  $D_b$  values in table 1. Another study that synthesised CNTs from Fe, Co, and Ni via CVD showed that Fe catalyst produces the longest CNT among the three catalysts [28]. In fact, the authors' estimate of  $50 \mu\text{m}$  [28] for Fe-catalysed CNTs from SEM images is reasonably close to the CNT length for Fe predicted by the present model.

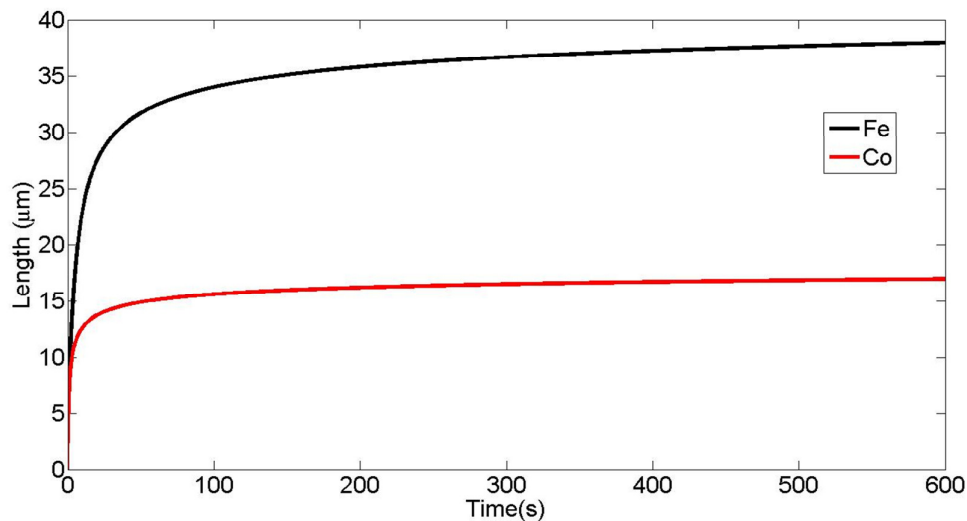


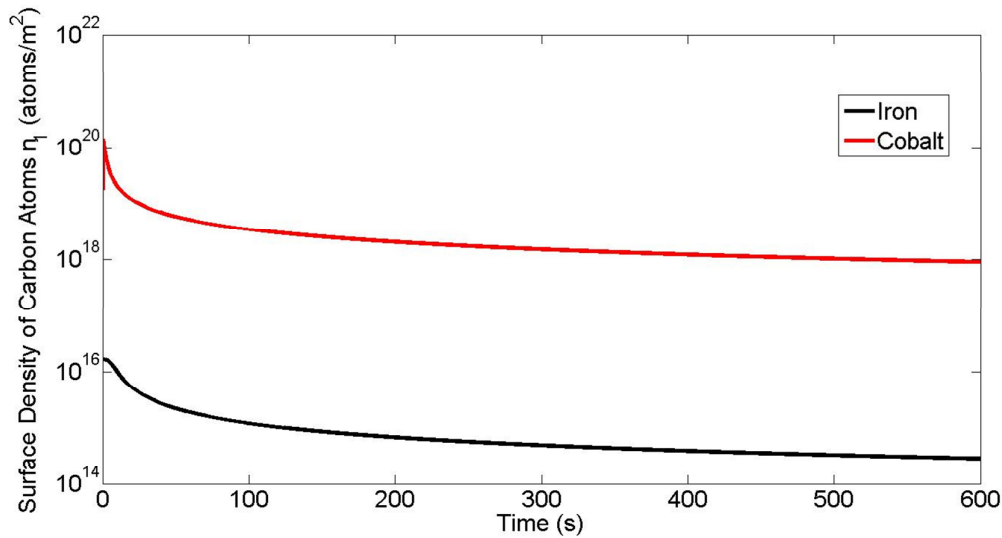
Fig. 4. CNT length plot for Co and Fe.

The reason for Fe having the higher CNT length could be attributed to the higher bulk diffusivity and surface diffusivity. The combination of the said characteristics is seen to yield better results in CNT length compared to the Co catalyst. Theoretically, during CNT growth, a finite number of carbon atoms will remain on the surface of the catalyst particle. As bulk diffusion takes place, the carbon adatoms will diffuse into the catalyst particle. While some C atoms could be trapped within the catalyst matrix and combine with metal catalyst to form metal carbide, the rest of the diffused atoms will be forced out of the catalyst due to the cooling of the metal catalyst prior to CNT growth. Outside of the catalyst, the surface diffusion of C atoms will lead to nucleation of the nanotubes. Therefore, for a catalyst metal with higher bulk diffusion rate, more C atoms is likely to diffuse through the catalyst and contribute to the nucleation and growth of CNT. On the other hand, a catalyst with low bulk diffusion rate will cause less carbon to penetrate back to the catalyst surface for CNT nucleation. From another perspective, the catalyst lifetime is lengthened since the accumulation of carbon atoms on the catalyst surface is not immensely saturated and the possibility of carbonaceous layer being formed is reduced. Therefore, with the superior bulk diffusivity of Fe ( $10^{-9}$ ) over cobalt ( $10^{-18}$ ), the prediction of higher CNT length in figure 4 is expected. Additionally, the larger magnitude of surface diffusivity of Fe ( $10^{-16}$ ) compared to Co ( $10^{-21}$ ) indicates that CNT nucleation in Fe happens at a faster rate than that in Co.



It is also important to note that bulk diffusion could potentially be a rate-limiting step of the CNT growth process [29]. The formation of metal carbide could cause the catalyst metal to become inactive. It might be compelling to infer that catalyst with lower  $D_b$  would be more effective in growing CNT. However, it comes with a poorer transport of C atoms through the catalyst to support surface diffusion of carbon atoms into CNT nuclei.

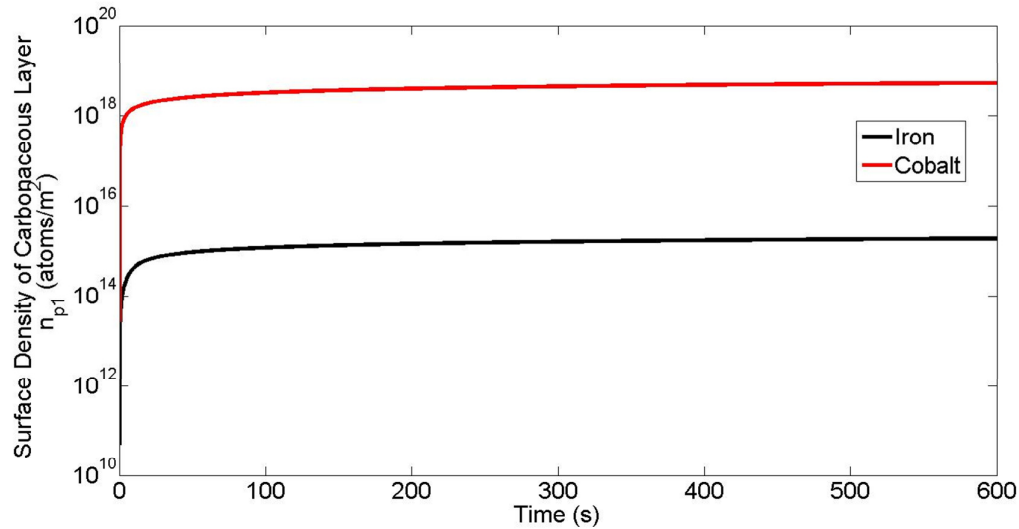
Figure 5 shows the semi-logscale plot of carbon surface density against time for Co and Fe. It appears that Co has the higher carbon surface density compared to Fe and is supposed to promote better CNT length according to the direct relation of  $n_1$  with CNT length  $L$  in Equation (15). However, as Equation (15) also depends on  $D_b$ , taking  $D_b$  into consideration changes the magnitude of the overall length. The combination of a high  $D_b$  value and moderately high  $n_1$  of Fe outweighs the large  $n_1$  value but small  $D_b$  for Co. In other words, although there is potentially lower carbon atoms at the iron catalyst surface compared to that of a cobalt, the higher carbon diffusion rate into iron leads to higher CNT growth rate compared to cobalt. Furthermore, the low  $D_b$  value of Co signals that there are a significantly large amount of C atoms that are left undiffused on the catalyst surface. As the bulk-diffusion process is inhibited, so does the nucleation of C atoms into CNTs. In a nutshell, it could be inferred that there exists a competition between the availability of C atoms for growth and the ones effective for growth which is dictated prominently by the bulk diffusivity  $D_b$ .



**Fig. 5.** Plot of surface density  $n_1$  of carbon atoms on Co and Fe particles. Insets show the saturation region of CNT growth for each catalyst particle.

Apart from showing the physics of active CNT growth using  $n_1$ , another way to illustrate the trend of CNT growth is by showing the cause that slows down CNT growth. Here, the presence of carbonaceous layer is the determining factor for growth termination which is modelled by the term  $n_{p1}$ . The catalyst is considered poisoned when the amorphous carbon layers encapsulate the catalyst particle and disable catalytic hydrocarbon breakup to form carbon atom at the surface. To illustrate the effects of  $n_{p1}$  on the catalyst lifetime, semi-logscale plots of  $n_{p1}$  are generated for Co and Fe as shown in figure 6. Both catalysts differ significantly in terms of magnitude of concentration of carbonaceous layer with respect to time where Co shows the higher  $n_{p1}$  value in the period of 600 s. This directly explains the shorter CNT length synthesized by Co that is predicted in figure 4. Due to the semi-logscale of figure 6 the  $n_{p1}$  appears to exhibit a plateau trend after long

exposure time. However, the actual behavior of  $n_{p1}$  for all catalysts remains the same as found in figure 3 where  $n_{p1}$  continue to grow as long as the carbon feedstock flows. There is a clear consistency in trend between figure 5 and figure 6 where both  $n_1$  and  $n_{p1}$  is higher for Co compared to Fe. This is expected from Equation (13) where the increase in  $n_1$  also results in higher  $n_{p1}$ . In more physical terms, more abundant carbon atoms on the catalyst surface could also lead to a higher rate of formation of carbonaceous layers. Additionally, the higher  $n_{p1}$  for Co results from the low amount of carbon adatoms undergoing bulk diffusion due to the low  $D_b$  value. This condition, in addition to the slow nucleation rate due to lower  $D_s$  value of Co, decelerates the CNT growth even more.



**Fig. 6.** Plot of surface density of carbonaceous layer  $n_{p1}$  encapsulating Co and Fe particles

Based on Equation (7) and Equation (8) for the formation of critical clusters and stable clusters respectively, it is obvious that  $D_s$  has a direct influence on both types of clusters. While critical clusters contribute to growth, stable clusters do not. In stable carbon clusters, carbon atoms aggregate into structures that are not useful for CNT growth. Therefore, it could be inferred that there is another competition between the formation of critical and stable clusters during CNT nucleation. In other words, catalyst with higher  $D_s$  would experience high growth of carbon clusters that contribute and do not contribute to CNT nucleation simultaneously. However, it must be noted that the stable cluster should not be interchanged with amorphous or carbonaceous layers as Equation (7) and Equation (8) do not have direct correlation with the  $n_{p1}$  term in Equation (13). Thus, the more direct relation favours  $D_b$  where higher bulk diffusion rate reduces chances of  $n_{p1}$  formation and thus provides a better catalyst lifetime.

#### 4. Conclusions

A model for catalytic growth of CNT is presented to investigate the physics of CNT growth and catalyst lifetime. The model comprises of an ODE system that describes the various stages of catalytic growth of CNT including adsorption, desorption, diffusion, formation of stable and critical clusters, and catalyst deactivation. A baseline case is established to validate the developed model where the predicted CNT length compares well with that of a CVD experiment that employed ethylene and cobalt as the feedstock and catalyst respectively. Two types of catalyst material namely Fe and Co

are investigated where the present model predicts Fe to be the better catalyst compared to Co based on the CNT length plot. The surface density of C atoms on the catalyst surface  $n_1$  as well as the surface density of carbonaceous layers  $n_{p1}$  are compared for Fe and Co catalysts. Both variables are explained in light of the carbon surface diffusivity  $D_s$  and the carbon bulk diffusivity  $D_b$  to illustrate the physics of catalyst deactivation on CNT growth rate. A few insights are gained from the present study. First, a catalyst with low bulk diffusivity may experience a large amount of carbon source on the surface but it does not guarantee high growth rate. The competition with bulk diffusion must be considered. Secondly, a catalyst with high bulk diffusion would likely slow down catalyst deactivation by reducing the chance of formation of amorphous carbonaceous layers. Finally, a catalyst with high surface diffusion promotes better nucleation rate though there is also competition with formation of carbon clusters that do not promote CNT growth.

### Acknowledgement

This research was funded by the Research University Grant (RUG) with cost centre number Q.J130000.2724.01K31 awarded by Universiti Teknologi Malaysia (UTM) and the Fundamental Research Grant Scheme (FRGS) with cost centre number R.J130000.7824.4F829 awarded by the Malaysian Ministry of Higher Education.

### References

- [1] Zhao, Jiang, Yaozhong Zhang, Yanjie Su, Xiaolu Huang, Liangming Wei, Eric Siu-Wai Kong, and Yafei Zhang. "Structural improvement of CVD multi-walled carbon nanotubes by a rapid annealing process." *Diamond and Related Materials* 25 (2012): 24-28.
- [2] Zhang, Shoumo, Deli Peng, Huanhuan Xie, Quanshui Zheng, and Yingying Zhang. "Investigation on the Formation Mechanism of Double-Layer Vertically Aligned Carbon Nanotube Arrays via Single-Step Chemical Vapour Deposition." *Nano-Micro Letters* 9, no. 1 (2017): 12.
- [3] Hoyos-Palacio, L. M., A. G. García, J. F. Pérez-Robles, J. González, and H. V. Martínez-Tejada. "Catalytic effect of Fe, Ni, Co and Mo on the CNTs production." In *IOP conference series: materials science and engineering*, vol. 59, no. 1, p. 012005. IOP Publishing, 2014.
- [4] Keteklahijani, Yalda Zamani, Mohammad Arjmand, and Uttandaraman Sundararaj. "Cobalt catalyst grown carbon nanotube/poly (vinylidene fluoride) nanocomposites: effect of synthesis temperature on morphology, electrical conductivity and electromagnetic interference shielding." *ChemistrySelect* 2, no. 31 (2017): 10271-10284.
- [5] Ahmad, Amirah, Mohd Hasmizam Razali, Karimah Kassim, and Khairul Anuar Mat Amin. "Synthesis of multiwalled carbon nanotubes supported on M/MCM-41 (M= Ni, Co and Fe) mesoporous catalyst by chemical vapour deposition method." *Journal of Porous Materials* 25, no. 2 (2018): 433-441.
- [6] Shah, Khurshed A., and Bilal A. Tali. "Synthesis of carbon nanotubes by catalytic chemical vapour deposition: A review on carbon sources, catalysts and substrates." *Materials Science in Semiconductor Processing* 41 (2016): 67-82.
- [7] Suriani, A. B., N. A. Asli, M. Salina, M. H. Mamat, A. A. Aziz, A. N. Falina, M. Maryam et al. "Effect of iron and cobalt catalysts on the growth of carbon nanotubes from palm oil precursor." In *IOP Conference Series: Materials Science and Engineering*, vol. 46, no. 1, p. 012014. IOP Publishing, 2013.
- [8] Hamzah, N., MF Mohd Yasin, MZ Mohd Yusop, A. Saat, and NA Mohd Subha. "Rapid production of carbon nanotubes: a review on advancement in growth control and morphology manipulations of flame synthesis." *Journal of Materials Chemistry A* 5, no. 48 (2017): 25144-25170.
- [9] Zhang, Yueling, Qing Yu, Xidong Wang, and Yajun Tian. "A new understanding of carbon nanotube growth: Activation and deactivation of a catalyst." *Applied Surface Science* 298 (2014): 221-224.
- [10] Unrau, C. J., V. R. Katta, and R. L. Axelbaum. "Characterization of diffusion flames for synthesis of single-walled carbon nanotubes." *Combustion and Flame* 157, no. 9 (2010): 1643-1648.
- [11] Unrau, Chad J., Richard L. Axelbaum, and Phil Fraundorf. "Single-walled carbon nanotube formation on iron oxide catalysts in diffusion flames." *Journal of Nanoparticle Research* 12, no. 6 (2010): 2125-2133.
- [12] Puretzky, Alexander A., David B. Geohegan, Stephen Jesse, Ilia N. Ivanov, and Gyula Eres. "In situ measurements and modeling of carbon nanotube array growth kinetics during chemical vapor deposition." *Applied Physics A* 81, no. 2 (2005): 223-240.

- [13] Sivakumar, V. M., A. Z. Abdullah, A. R. Mohamed, and S. P. Chai. "Optimized parameters for carbon nanotubes synthesis over Fe and Ni catalysts VIA methane CVD." *Rev. Adv. Mater. Sci* 27 (2011): 25-30.
- [14] Xiang, Rong, Zhou Yang, Qiang Zhang, Guohua Luo, Weizhong Qian, Fei Wei, Masayuki Kadowaki, Erik Einarsson, and Shigeo Maruyama. "Growth deceleration of vertically aligned carbon nanotube arrays: Catalyst deactivation or feedstock diffusion controlled?." *The Journal of Physical Chemistry C* 112, no. 13 (2008): 4892-4896.
- [15] Lee, Cheol Jin, Jeunghye Park, and A. Yu Jeong. "Catalyst effect on carbon nanotubes synthesized by thermal chemical vapor deposition." *Chemical Physics Letters* 360, no. 3-4 (2002): 250-255.
- [16] Zhang, Yi, and Kevin J. Smith. "A kinetic model of CH<sub>4</sub> decomposition and filamentous carbon formation on supported Co catalysts." *Journal of Catalysis* 231, no. 2 (2005): 354-364.
- [17] Naha, Sayangdev, and Ishwar K. Puri. "A model for catalytic growth of carbon nanotubes." *Journal of Physics D: Applied Physics* 41, no. 6 (2008): 065304.
- [18] Zainal, M. T., MF Mohd Yasin, and M. A. Wahid. "Investigation of the coupled effects of temperature and partial pressure on catalytic growth of carbon nanotubes using a modified growth rate model." *Materials Research Express* 3, no. 10 (2016): 105040.
- [19] Shahivandi, Hamid, Majid Vaezzadeh, and Mohammadreza Saeidi. "Theoretical study of effective parameters in catalytic growth of carbon nanotubes." *physica status solidi (a)* 214, no. 11 (2017): 1700101.
- [20] Saeidi, M., and M. Vaezzadeh. "Theoretical investigation of the growth rate of carbon nanotubes in chemical vapor deposition." *Iranian Journal of Science and Technology (Sciences)* 35, no. 1 (2011): 29-32.
- [21] Liu, Huimin, and David S. Dandy. "Nucleation Kinetics of Diamond on Carbide-Forming Substrates during Chemical Vapor Deposition I. Transient Nucleation Stage." *Journal of the Electrochemical Society* 143, no. 3 (1996): 1104-1109.
- [22] Yun, Jungheum, and David S. Dandy. "A kinetic model of diamond nucleation and silicon carbide interlayer formation during chemical vapor deposition." *Diamond and related materials* 14, no. 8 (2005): 1377-1388.
- [23] Muhammad Thalhah Zainal. Modelling the flame synthesis of carbon nanotube (CNT) in inverse diffusion flame. *Master's thesis*, Universiti Teknologi Malaysia, 2017.
- [24] Bower, Chris, Otto Zhou, Wei Zhu, D. J. Werder, and Sungho Jin. "Nucleation and growth of carbon nanotubes by microwave plasma chemical vapor deposition." *Applied Physics Letters* 77, no. 17 (2000): 2767-2769.
- [25] Shackelford, James F., Young-Hwan Han, Sukyoung Kim, and Se-Hun Kwon. *CRC materials science and engineering handbook*. CRC press, 2016.
- [26] Naha, Sayangdev, Swarnendu Sen, Anindya K. De, and Ishwar K. Puri. "A detailed model for the flame synthesis of carbon nanotubes and nanofibers." *Proceedings of the combustion institute* 31, no. 2 (2007): 1821-1829.
- [27] Shin, K. Y., H. C. Su, and C. H. Tsai. "In situ growth of single-walled carbon nanotubes by bimetallic technique with/without dielectric support for nanodevice applications." *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures Processing, Measurement, and Phenomena* 24, no. 1 (2006): 358-361.
- [28] Sharma, R., A. Kumar Sharma, G. Sharma, and V. Sharma. "Effect of different metal catalysts on the growth of carbon nanotubes by chemical vapor deposition using five step process." *J. Opto. Adv. Mat* 17 (2015): 1728-1733.
- [29] Wirth, Christoph Tobias, Can Zhang, Guofang Zhong, Stephan Hofmann, and John Robertson. "Diffusion-and reaction-limited growth of carbon nanotube forests." *ACS nano* 3, no. 11 (2009): 3560-3566.