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Hydrodynamic Studies of Fluidized Bed Chemical Vapor Deposition Reactors to Produce Carbon Nano Tubes via Catalytic Decomposition over Co/Pd MgO

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A B S T R A C T

In this study, carbon nano tubes have been successfully synthesized in a fluidized bed chemical vapor deposition (FBCVD) process over bi- metallic Co/Pd catalyst supported on MgO. The hydrodynamic studies of fluidized bed reactor has been reported in terms of pressure drop, minimum fluidization velocity and bed volume expansion to contribute to the optimization of the Carbon Nano Tubes (CNTs) production parameters in fluidized bed reactors. Minimum fluidization velocity and pressure drop, as the most important parameters, were taken into account for the investigation of the hydrodynamic behavior of the catalyst particles inside the fluidized bed and CNTs growth and deposition. The effect of carbonous gas to inert gas ratio (CH_4:N_2) was studied based on design of experiment (DOE) using Response Surface Methodology. It was found that N_2:CH_4 flow rate ratio must be 3:5 to obtain the highest bed volume expansion for maximum carbon nanotubes accumulation. The carbon nanotubes are multiwalled with diameter of 14 nm and volume bed expansion of 85% occurred when ratio of methane to nitrogen is 5:3. The optimum parameters for higher conversion of methane to CNT occurs when temperature is 1000 ◦C and the flow rate ratio of Nitrogen to methane is 3:5 in FBCVD.

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1. INTRODUCTION

The most famous properties of CNTs are their strength and elasticity value which has been reported for Young's Module up to 2 TPa [1, 2]. They are used in application toward various kinds of continuum-based simulations of nano-structures like nano-composites and nano-probes where the fracture resistance studies become important [3]. Their electronical properties have also attracted much attention .The conductivity of CNTs depends on their diameter and chirality [4]. They have been used in superior thermal conductivity within oil nano particles suspensions [5]. They act transistor –like and due to this characteristic, they are favorable in electronics [6]. Their electrical conductivity is of much interest as they have high aspect ratios (1000:1) and they impart electrical conductivity at much lower loading compared with stainless steel and carbon nano fiber [7]. Their super conductivity at temperature below 20 k has been reported [8]. They have superior field emission properties, because they emit at low voltage and are much more preferable to conventional electron sources [9]. They have also been used in hydrogen storage [10]. In addition, to the mentioned applications they have been used in biomedical, composites, lithium batteries, sensors [11], polymer composites and catalyst support [12].

Numerous methods have been employed to synthesize CNTs, including plasma based arc discharge, laser ablation, thermal methods such as chemical vapor deposition (CVD), plasma enhanced chemical vapor deposition (PECVD), alcohol catalytic CVD (ACCVD), hydrothermal or sono-chemical, and high-pressure CO conversion (HiPCo) [13]. Nevertheless, the CVD method has significant advantages over the other methods [14]. The CVD method is widely used for carbon nano tube synthesis because of its high

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production yield and scale-up capability [15]. Fluidized bed chemical vapor deposition has been also used to produce CNTs. Fluidization has many advantages in production of CNT. Fluidization gives high space velocity leading to efficient solid-gas interaction and consequently the high mass and heat transfer. In line with that high process yield, purity, homogeneity and selectivity of the final product are attained [16, 17]. Moreover, fluidized bed is a flexible process due to varying the operating conditions and parameters (gas mixture and temperature) which can be finely adjusted according to the requirement of the desired product. In addition, accessible space for CNTs growth and their resistance time can also be controlled which favors the selective mass production of CNTs with uniform properties [16]. For example Zhang et al studied the fluidized bed reactor due to many advantage of these kinds of reactors for large scale production of CNTs. They demonstrated a brand new methodology of fluidizing bed Metal-Organic Chemical Vapor Deposition (MOCVD). It also acted as one-step preparation, with supported catalysts of highly dispersed metal followed by FBCCVD to synthesize CNTs [18]. However, there are still many factors in the hydrodynamic studies of the fluidization specifically for CNTs production in these types of reactors. Here, the hydrodynamic parameters of Fluidization has been studied in FBCVD. The hydrodynamic studies of fluidized bed reactor has been reported in terms of pressure drop, minimum fluidization velocity and bed volume expansion to contribute to the optimization of the CNTs production parameters in fluidized bed reactors. Minimum fluidization velocity and pressure drop, as the most important parameters, were taken into account for the investigation of the hydrodynamic behavior of the gas-particle interaction inside the fluidized bed reactor. The volume bed expansion of carbon nanotubes has been investigated. Besides, the effect of the N_2:CH_4 flow rate ratio to obtain the highest bed volume expansion for maximum carbon nanotubes accumulation has been reported. The other objective of the present work was to study the methane conversion as well. Thus, the novelty of this work is the synthesis of carbon nano structures (CNTs) successfully on ni metallic catalyst on one hand and reporting hydrodynamic studies in order to produce higher yield of CNT in FBCVD is the other important aspect of the present study. To our knowledge, these studies have not been reported elsewhere.

2. METHODOLOGY

All the materials were bought from sigma Aldrich and received as purchased. The methodology is modification of Bethune et al. [19]. In this experiment, $Co(No_3)_3.9H_2O$, $Pd(Br)_2(MeCN)_2$ which was heated were dissolved in distilled water. They were stirred while heating at 100 ◦C, then they were sonificated for 1 hr. The metal contents was kept at 6 wt% and the molar ratio of Co-Pd was 1:2. They were dried at 100 ◦C and calcined at 500 ˚C. Then, the Co-Pd catalysts were impregnated by MgO with an aqueous solution. They were stirred followed by drying in oven at 100 ˚C and Calcination at 550 ˚C [20].

Catalytic Cracking system of methane decomposition was used as fluidized bed chemical vapor deposition (FBCVD) instrument. The fabrication was done by Shanghai (Kuantan Branch, Malaysia) Sunny Scientific collaboration Co. Ltd. The parameters which affect the design of the bed was calculated before the design of the bed and the bed was fabricated and designed according to the density and particle size of the catalyst to be used. Figure 1 shows the schematic representation of the designed and fabricated FBCVD. The FBCVD reactor used in this study is made of stainless steel and contained a cylindrical zone of 5 cm inner diameter, 80 cm height and a membrane zone, which allows particles to drop back into the bed. The gas distributor was also installed.

The bed temperature was controlled by a temperature control system comprised of furnaces, temperature controllers and thermocouples located at the central axis of the reactor. A pressure sensor was also installed in order to measure the pressure drop across the bed and the total pressure in the reactor. Particles that were generated were entrapped by filter. The parameters such as flow rate, temperature and pressure were recorded every second in online software and were used for hydrodynamic studies. The outlet gas was connected to Gas Chromatography (GC) to analyze the gas and methane conversion.

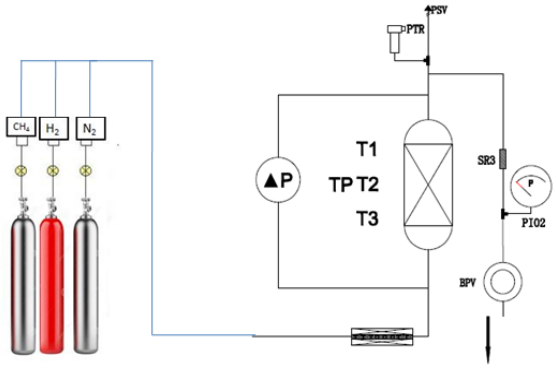

Figure 1. Schematic representation of FBCVD

In a typical experiment, 2g of the prepared catalyst was placed in the middle of the tubular decomposition reactor (Figure 1) heated by an electric muffle furnace. The catalyst was pre-heated under nitrogen atmosphere at 600°C (1 h), followed by the reduction at 600 ◦C (1h) using continuous flow of H_2 gas (500 ml/min). After that, the temperature of the reactor was increased to 1000 °C using N_2 (500 ml/min). Once the temperature was stabilized at 1000 °C, the methane gas was introduced to the reaction tube with a flow rate of 600 ml/min for 3 hours at atmospheric pressure. After the decomposition reaction, the reactor was cooled down while passing N_2 gas for 30 minutes. The obtained powder was collected and purified using 50 ml concentrated HCl for further characterization.

3. RESULT AND DISCUSSION

3. 1. Methane Decomposition Over Co/Pd The SEM Image of the Co/Pd MgO supported is shown in Figure 2. As can be seen, the morphology of the catalyst is homogenous and with a homogenous distribution. They are having spherical morphology.

Figure 3 shows the XRD result of the obtained Co/Pd Catalysts. The peaks located at 2θ= 40, 46.5 and 68.2 are characteristics peaks of the (111), (200) and (220), respectively for FCC structures of the Co/Pd bi metallic catalysts and the peak at 2θ=78 corresponds to MgO peak with plane (222). The crystalline size was also calculated from Scherer formula and it was found to be 39 nm.

Figure 4 shows the SEM and TEM images of obtained carbon nanotubes from Co/Pd MgO catalysts. The spaghetti and tube like structure of carbon nano tubes are seen in the SEM figure which exhibits the growth of CNTs. The TEM micrograph shows the Multiwalled CNT with diameter of 14 nm.

Figure 5 illustrates the TGA spectra from Co/Pd MgO. The CNTs grown on Co/Pd started to gasify and loss weight at 540 ˚C. It shows 50% of weight loss. CNTs with less crystalline react preferentially with the oxidant and lose weight at a lower temperature compared to the more highly crystalline CNTs [21].

Raman Spectroscopy of the obtained CNTs is shown in Figure 6. The G and D bands represent the two most prominent original graphite features. The Raman spectroscopy confirmed the presence of D band and G band related to the vibration of sp^2-bonded carbon atoms in a two-dimensional hexagonal lattice. Therefore, we can conclude the formation of graphitic nanotubes. The I_D/I_G ratio was calculated to be 1.89 which is indicative of a low defect carbon crystalline structure [22].

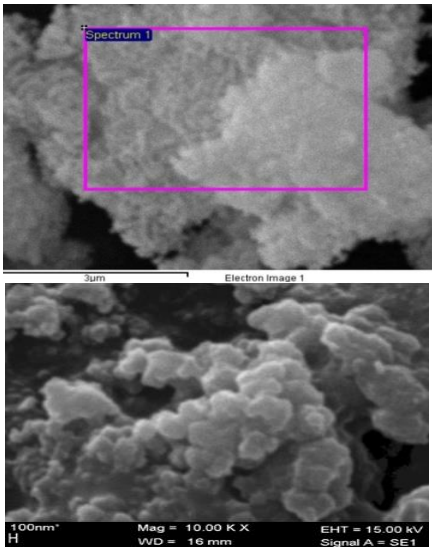

Figure 2. SEM images of the Co/Pd MgO

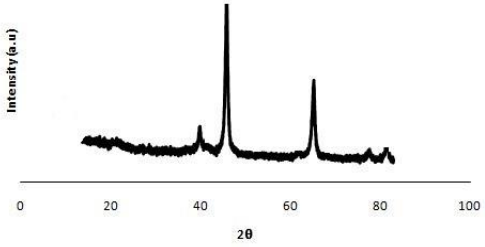

Figure 3. XRD result for Co/Pd nano catalysts

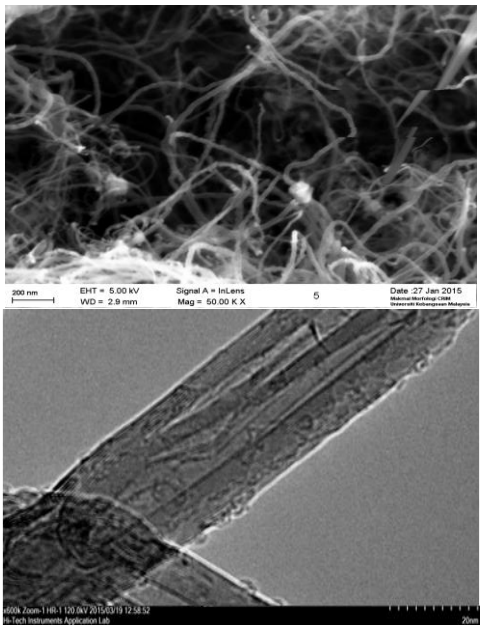

Figure 4. SEM and TEM image of the obtained CNT from Co/Pd MgO

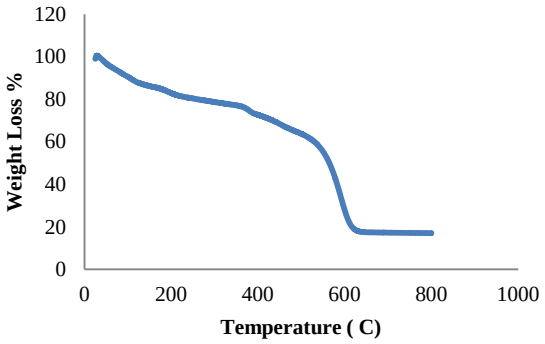

Figure 5. TGA spectra of obtained CNTs from Co/Pd MgO.

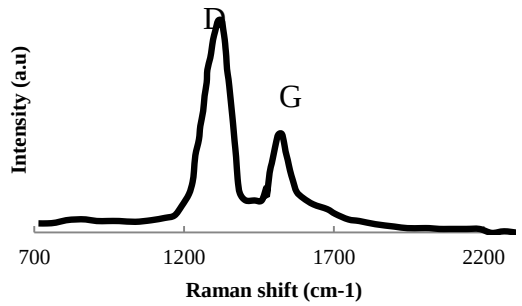

Figure 6. Raman spectra of the obtained CNTs from Co/PdMgO

To explain the growth mechanism in this process a general Langmuir-type mechanism, similar to that suggested for CH_4 exchange over metal films may be applied to metal-catalyzed methane decomposition reaction:

$CH_4 + 2^* \rightarrow CH_3^* + H^*$

$CH_3 + * \rightarrow CH_2^* + H^*$

$CH_2 + * \rightarrow CH^* + H^*$

$CH + * \rightarrow C + H^*$ where, * is an active site [23].

Hydrocarbons adsorb on the metal particles and are catalytically decomposed. This results in carbon dissolving into the particle forming a liquid eutectic. Upon super-saturation, carbon precipitates in a tubular, crystalline form.

3. 2. Effect of Flow Ratio at Different Temperature on the Bed Expansion 20 runs of experiments were run as shown in the Table 1. Gas flow parameters (N_2/CH_4 gas) at different temperature was used as factors. The parameters selection was based on design of experiment (DOE) using Response Surface Methodology (RSM). The central Composite Design (CCD) model was used for optimization.

TABLE 1. RSM (Response Surface Methodology) experiments to investigate the effect of flow at different temperature.

FLOW N_2 (ml/min)	FLOW CH_4 (ml/min)	Tem (°C)	Bed expansion (%)	U/Umf	Methane conversion (%)
4	4	800	76	9.09	72
4	4	800	76	9.09	72
3	3	1000	54	6.82	60
5	5	600	61	11.37	64
4	4	800	76	9.09	72
4	4	800	76	9.09	72
5	3	600	29	9.09	38
3	3	600	34	6.82	52
3	5	600	82	9.09	92
3	5	1000	85	9.09	93
5	3	1000	30	9.09	40
5	5	1000	81	11.37	88
4	5.633	800	83	10.95	91
4	4	473.4	26	9.09	32
2.367	4	800	80	7.23	80
4	4	800	76	9.09	72
4	4	800	76	9.09	72
4	4	1126	30	9.09	41
5.633	4	800	40	10.95	62
4	2.367	800	31	7.23	60

As can be seen the highest bed expansion occurred when higher flow of methane to nitrogen (5:3) is used at higher temperature of 1000 ◦C. It can also be concluded that methane conversion has happened mostly at the experiments in which the temperature is higher and also the highest amount of methane conversion to carbon has happened when the ratio of methane is higher. When this fact happens, more of carbonous gas methane is converted to CNTs. When the temperature is 1000 ◦C (considered as quite high) and the ratio of methane to Nitrogen is 5:3, the highest amount of methane conversion and bed expansion has occurred. When the flow of methane is lower than that of nitrogen flow, the bed expansion has been decreased, resulted in lower deposition of carbon. It can be concluded that when the flow of methane is lower than nitrogen, the bed expansion has been decreased. Therefore, we can conclude that if we want to obtain more expansion, the methane flow should be higher than that of nitrogen and not equal and lower. The residual plot from RSM (Figure 7) also shows a normal probability of the factors flow, and temperature affecting the bed expansion.

The mean data and mean of bed expansion has been shown in Figure 8. CH_4 flow has a high effect on bed expansion. As the methane gas flow increases, the bed expansion increases too and more CNTs is produced. This fact shows methane conversion is increased as

well. The main effects plots for bed expansion in terms of CNTs formation has been drawn and shown in Figure 8. Bed expansion occurred at flow rates of methane above 4 and 5. It should be noted that flow of nitrogen should be lower than that of methane for production of CNTs in this process.

The interaction effect has been also shown in Figure 8. It can be said that flow of methane has a high impact on bed expansion. The inert gas flow affects the CNT production only when the mean of CH_4 flow is higher than the inert gas itself at high temperature of above 1000 ˚C. Thus, in this section it was concluded that the flow of nitrogen and methane influenced bed expansion. This fact is shown in the contour plot of the interaction between bed expansion, nitrogen flow and methane flow (Figure 9).

3. 3. Effect of N_2: CH_4 Flow Dilution on Bed Expansion In order to study the effect of flow rate ratio per se and without considering temperature in the reactions, other sets of experiments were run to investigate the effect of flow on bed expansion. So, the temperature was fixed at 1000 ˚C .This is because in the last section the highest bed expansion and methane conversion was achieved when the temperature was 1000 ˚C. So, in this section of work, the flow ratio was varied in the experiments and the temperature was kept constant at 1000 ˚C. The reaction running parameters and the obtained responses are shown in Table 2. The parameters were first obtained by design of experiment (DOE) and the responses for each run of experiment is reported practically.

It can be concluded that the ratio of the methane plays a key role in the production of CNTs. When higher flow of methane is used than that of the nitrogen, more of its carbonous gases have been converted to CNTs and the achieved yield is 79%. Also, the highest bed expansion (~92%) is occurred when the methane to nitrogen flow is 5:3. When the ratio of the gas flow rate is equal such as 5:5, 4:4 or 3:3, the bed expansion is 76, 74 and 74%, respectively. However, when the methane to nitrogen ratio decreased, the bed expansion decreased tremendously too. As an example when the flow of methane to Nitrogen (CH_4:N_2) is less than nitrogen flow such as 258:400, the bed expansion is the least (~ 47%). This fact and the effect of bed expansion versus the velocity is shown in Figure 10. This graph shows that there is a positive correlation between the formation of carbon soot and bed expansion with the Flow rate of methane to nitrogen. More CNT is formed when flow of methane is more than the flow of nitrogen.

Figure 11 shows the contour plot of the flow rate ratio versus the bed expansion. When methane flow increased and reached even slightly higher than that of nitrogen, then the bed expansion increased too.

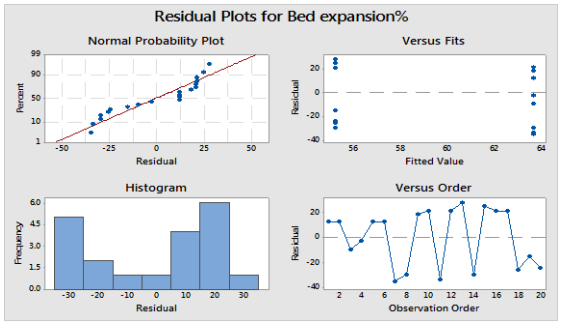

Figure 7. The residual plots for bed expansion at different flow and different temperature

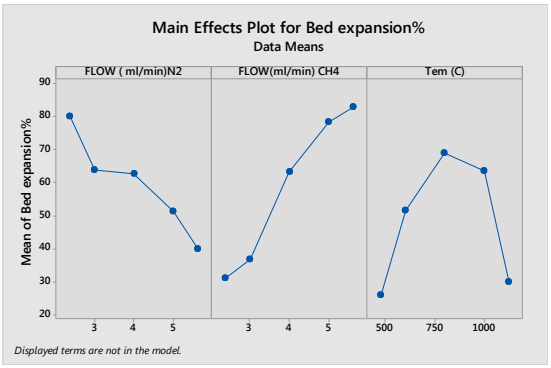

Figure 8. Data means and mean of bed expansion at different flow and temperature

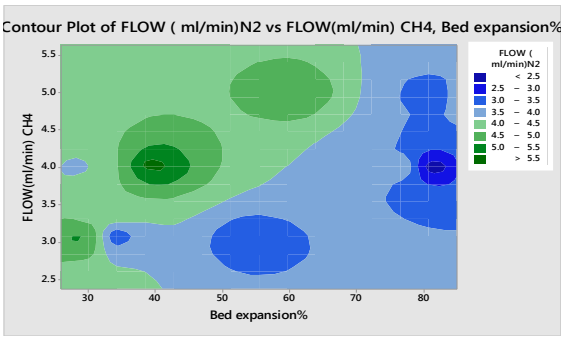

Figure 9. The contour plot of bed expansion and flow rate interaction

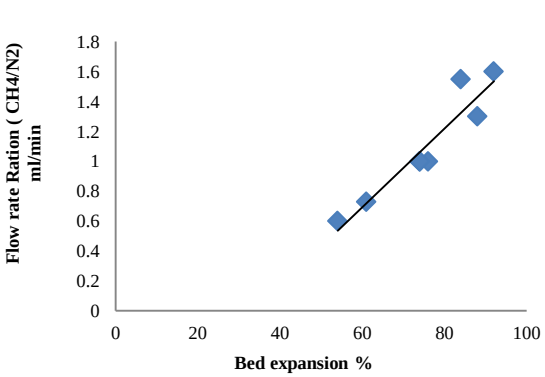

Figure 10. Bed expansions vs. flow rate dilution ratio

TABLE 2. Responses for different gas dilution ratios.

Flow N_2 (ml/min)	Flow CH_4 (ml/min)	Bed expansion (%)	CNT yield (%)
300	500	92	79
500	300	54	34
500	500	76	60
400	400	74	51
300	300	74	51
400	400	74	51
400	400	74	51
400	400	74	51
400	400	74	51
400	258.579	47	30
400	400	74	51
400	541.421	88	72
258.579	400	84	68
541.421	400	61	38

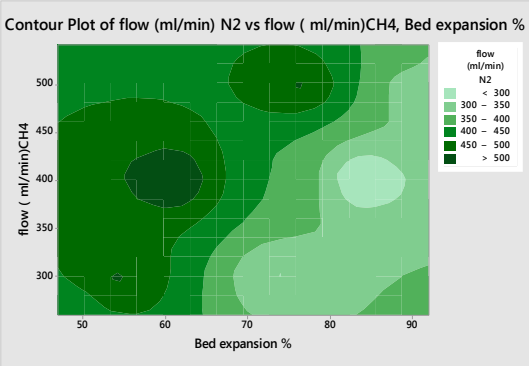

Figure 11. The contour plot of bed expansion vs. the gas flow rate

TABLE 3. Catalyst particles density and mean particle size

Catalyst	articles Density (kg/m^3)	Mean Particle size (µm)	U_{mf} (m/s)
Co/Pd	7300	91	88

This fact indicates that the carbonous gas is more influential in production of CNT and when higher flow of methane than nitrogen is used the bed expansion has increased.

3. 3. 1. Region for Fluidization One method of measuring the fluidization region is by theoretical calculation. Later, the calculated result can be compared with experimental results. The catalyst particle density and mean particle size are listed in Table 3.

In this section, the minimum fluidization is calculated so that the fluidization inception and the starting point for the fluidization is recognized. The minimum fluidization velocity is calculated from empirical equation or experiments. Since in this work methane is deposited on catalyst to form a carbon and this in turn affects the dynamic properties of the catalyst, thus the experimental determination of U_{mf} is also carried out. In order to calculate the U_{mf} , the pressure in bed is graphed versus the velocity. As the gas velocity increases, the pressure drop increases and and it reaches a point in which it will be remained as constant. This point is minimum fluidization velocity in which the pressure drop reaches its maximum in relation to minimum gas velocity. The Ergun equation is commonly expressed as follows in different references:

$$\frac{\Delta P}{\rho_f u_\infty^2}\frac{D_p}{L}\frac{\varepsilon^3}{(1-\varepsilon)} = \frac{150}{Re_p} + 1.75$$

The above equation can be used with gases using average gas density between inlet and outlet. For the designed reactor, the region for fluidization can be calculated by:

$$U_f = \frac{(\rho_p - \rho_g) g d^2 \epsilon^3}{150\ \mu(1-\epsilon)}$$

In order to calculate the pressure drop the method by Pinilla et al. was used [24]. In their approach, the minimum fluidizing velocity is determined under reaction conditions of methane cracking via the catalyst on which the carbon is deposited. The authors used inert nitrogen, and plotting the pressure drop across a bed of methane, made by using the fresh catalyst in methane cracking, against the fluidizing gas velocity, as shown in Figure 12. In this Figure, the offset in the pressure transducer reading led to measure a pressure drop at zero velocity. Then, the velocity calculated experimentally for nitrogen is multiplied by a factor to account for the effect of using methane and they determined the factor to be 1.4 as a conversion factor for methane gas. In this work, it has also taken into account the calculation of pressure drop. Calculation of pressure drop based on bed height is obtained by equation:

$$\Delta P = H(1-\epsilon)(\rho_p - \rho_f)g$$

The minimum fluidization versus the pressure drop for the Co/Pd Catalyst is shown in Figures 13 and 14 when using nitrogen and methane gas, respectively. When only nitrogen gas is used to calculate the minimum fluidization velocity, there is no fluctuation after minimum fluidization. However, when methane gas is used; a fluctuation is observed which might be due to the formation of carbon deposits on the catalyst. When fluidization occurs, the minimum fluidization velocity is 55 m/s and the pressure drop is 105 KPa. These practical obtained results are different from the calculated theoretical pressure drop and minimum fluidization. This can be attributed to the fact that in

experimental results, some factors such as carbon deposition over the catalyst or actual bed height will affect the result.

3. 4. The Effect of Bed Height In order to study hydrodynamic behavior, effect of bed height was also investigated. It was observed when the bed height increases the methane conversion increases as well. When bed height reaches from 0.5 to 2 cm, the methane conversion also increases from 60% to almost 90%. This fact is shown in Figure 15. Since the FBCVD is in fluidized mode, the bed height has a positive effect on methane conversion. In a fluidized mode, the particle and gas interaction is higher and the conversion increases too. However, above the maximum bed of 2 cm , the bed shows a different behavior [26].

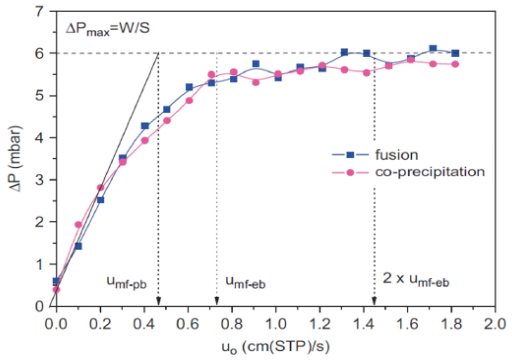

Figure12. U_{mf} and pressure drop, using nitrogen at 700°C [25]

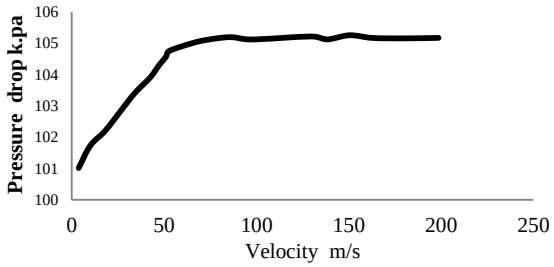

Figure 13. The velocity vs. pressure drop using nitrogen

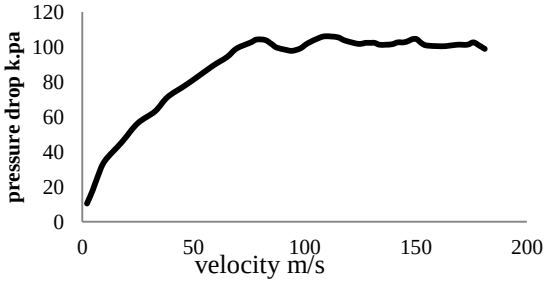

Figure 14. The velocity vs. pressure drop using methane

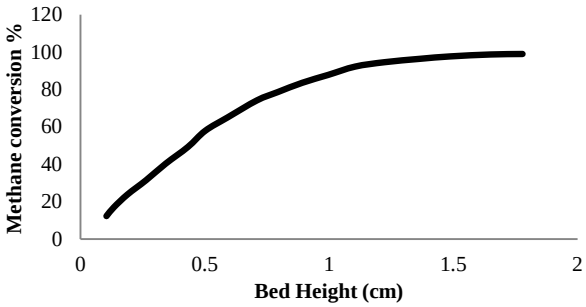

Figure 15. Bed height vs. methane conversion

Increasing bed height, particularly at the higher gas flow rates, enhanced bubble coalescence creating slugs that flow thorough the center of the bed, producing regions of low gas holdup near the walls of the fluidized bed and methane conversion will not occur efficiently above this region. Yang concluded that the slugging regime appears in beds where the bed height (H) over the bed diameter (D) is larger than 2cm. This requirement ensures that bubbles have enough time to coalesce in bigger bubbles called slugs, when the bubbles grow to 2/3 of the bed diameter the system enters to a slugging regime [27]. It should be noted that the formation of the cake on the deposited carbon does not allow efficient growth of the CNTs. This fact is due to the growth mechanism reason that during the reaction processes, carbon source diffuses into the layers and absorbed and collected in the form of carbon cake deposition result in hard interaction of solid-gas particles in the FBCVD.

4. CONCLUSION

In the present work, CNTs were successfully synthesized over catalytic decomposition of the methane gas over bi metallic Co/Pd MgO supported. The CNTs which were obtained were of multiwalled morphology. Since the FBCVD reactor is used in this work, some factors affecting the production of CNTs such as pressure drop, minimum fluidization velocity and bed volume expansion were investigate. The volume bed expansion of carbon nanotubes was also studied and the effect of the N_2:CH_4 flow rate ratio to obtain the highest bed volume expansion for maximum carbon nanotubes accumulation was reported. It was found that carbon gas feed (in this case methane) plays an important role in production of CNTs in FBCVD processes. When the ratio of the gases (CH_4:N_2) is equal, the formation of CNT is low too. However when the methane flow is higher than nitrogen flow, the methane conversion is increased and resulted in formation of more CNTs. The effect of bed height was also studied and it was found

that the process reach to a point (while still at the fluidization mode) where the CNT formation is not as efficient as the inception of the fluidization and that is where the formation of CNTs make a cake and agglomeration, making it hard for gas and solid distribution .

It can be concluded that higher conversion of methane to CNT occurs at optimum parameters which are considered as 2 g of the catalyst with N_2:CH_4 Ratio of 3:5 and temperature 1000 ◦C.

5. ACKNOWLEDGEMENT

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6. CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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Hydrodynamic Studies of Fluidized Bed Chemical Vapor Deposition Reactors to Produce Carbon Nano Tubes via Catalytic Decomposition over Co/Pd MgO

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چکیده

در این مطالعه، نانو لوله های کربنی به طور موفقیت آمیز در یک فرایند بستر سیال رسوب شیمیایی بخار (CVD) روی کاتالیست دو فلزی Co/Pd بر پایه MgO سنتز شده است. مطالعات هیدرودینامیک راکتور بستر سیال در شرایط افت فشار، حداقل سرعت سیال شدن و گسترش حجم بستر برای بهینه سازی پارامترهای تولید نانولوله های کربنی در راکتورهای بستر سیال گزارش شده است. حداقل سرعت سیال شدن و افت فشار به عنوان مهم ترین پارامترها، برای بررسی رفتار هیدرودینامیکی ذرات کاتالیست در داخل بستر سیال و رشد نانولوله های کربنی و رسوب به حساب آمده است. اثر نسبت دی اکسید کربن به گاز بی اثر (CH_4:N_2) با استفاده از طراحی آزمایش (DOE) و روش سطح پاسخ مطالعه گردید. مشخص شد که نسبت سرعت جریان N_2: CH_4 به منظور به دست آوردن بالاترین انبساط حجم بستر برای حداکثر انباشت نانولوله های کربنی باید ۳:۵ باشد. نانولوله های کربنی، نانو لوله هایی چند جداره با قطر ١٤ نانومتر و حجم انبساط بستر ۸۵ درصد هستند که هنگامی رخ می دهند که نسبت متان به نیتروژن ۵:۳ باشد. پارامترهای بهینه برای تبدیل بالاتر متان به نانو لوله های کربنی زمانی رخ می دهد که درجه حرارت ۱۰۰۰ درجه سانتی گراد و نسبت سرعت جریان نیتروژن به متان در فرایند بستر سیال رسوب شیمیایی بخار ۳:۵ است.

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