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EFFECT OF PROCESS PARAMETERS ON CNT DIAMETER THROUGH THE CATALYTIC THERMAL DECOMPOSITION OF METHANE

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Abstract: Carbon nanotubes (CNTs) bear physical and chemical properties which allow them to be used in a wide range of applications, such for structural support, adsorbents, batteries and hydrogen fuel cells. CNTs are most commonly synthesized through the catalytic thermal decomposition of methane (CTDM). Recent studies are being done on cleaner alternative sources of energy indicating a demand for both utilizing CNTs for hydrogen fuel cells and reducing the amount of greenhouse gases, such as methane. The capability of the CNTs to adsorb H_2 has been found to be mainly dependent on the diameter of the CNTs. As such, it was of interest to study the effect of the process parameters on the CNT diameters for the production of CNTs through CTDM. The process parameters investigated were the inlet CH_4 concentration, the reaction temperature and the catalyst metal loading. The determination of the significance of the process and catalyst parameters was done using ANOVA and general regression. Catalyst pre-characterization confirmed the presence of γ-Al_2O_3, NiO and NiCu catalyst components which have been found to be necessary in the production of CNTs. BET Analysis confirmed the proportional relationship of the surface area of the catalyst with the catalyst metal loading. Catalyst post-characterization measured the CNT diameters through SEM analysis. CNTs with the minimum average diameter of 48.5nm were synthesized with 5% ($^{vol}/_{vol}$) inlet CH_4 concentration, 30% Ni catalyst loading with 12:5 mol:mol Ni:Cu, and 950°C reaction temperature, while CNTs with the maximum average diameter of 135.0nm were synthesized with 20% ($^{vol}/_{vol}$) inlet CH_4 concentration, 30% Ni catalyst loading with 12:5 mol:mol Ni:Cu, and 750°C reaction temperature. Catalyst post-characterization quantified the effects of the process parameters on the diameters of the CNTs formed. Among the parameters, the reaction temperature from 750°C to 950°C had the strongest effect while the initial surface area of the catalyst with values from of 80m^2/g to 90 m^2/g had the least effect on the CNT diameter. Both the catalyst metal loading from 10% to 30% Ni (w/w) with 12:5 mol:mol Ni:Cu and the inlet CH_4 concentration from 5% to 20% (v/v) had weaker effects on the diameters of the CNTs.

Key Words: carbon nanotubes, catalysis, methane decomposition, process parameters

1. INTRODUCTION

The mechanical and physical properties of CNTs, which led to the wide range of its utility, had been bringing CNTs much attention in the field of research (Calvillo et al., 2009; Mitchell et al., 2011). One of the possible uses of CNTs is its application as a hydrogen-storing medium for fuel cells, where it has been found that the ability of CNTs to adsorb H_2 is mainly dependent on the tube diameter (Nikitin et al., 2008).

One of the most common methods of producing CNTs is the Catalytic Thermal Decomposition of Methane (CTDM) process in a fluidized bed. A study (Ziebro et al., 2010) showed that modifying the parameters of Catalytic Chemical Vapor Deposition (CCVD) processes control the physical characteristics of the resulting CNTs, such as the effect of reaction temperature on the activity of the catalyst and the conversion of the feed gas. In addition to this, another study (Gu et al., 2010) found that certain process parameters, such as the type of catalysts used, alter the structure of the CNTs produced.

The viability of Ni-Cu/Al_2O_3 catalysts for the CTDM has been identified in several studies (Pinilla et al., 2010; Ashok et al., 2008). The susceptibility of Ni-based catalysts to coking and the acidic nature of Al_2O_3 favor the production of CNTs through CTDM. Furthermore, Ni has been identified to be the most active metal for the CTDM for the production of H_2 and CNTs, while Cu performs well as a promoter in the process (Cheskonov et al., 2009).

Many studies (Ashok et al., 2008; Cheskoonv et al., 2009) had the objective of increasing H_2 yield and improving catalyst performance and stability, but only a few have focused on improving the quality of the carbon produced since it was often considered to be one of the main causes of catalyst deactivation. Only a few investigated the effects of those parameters on the production of CNTs (Jiang et al., 2006). Hence, it was necessary to determine the parameters that would contribute to the production of CNTs that could be capable of storing H_2 sufficient for industrial and commercial application.

2. METHODOLOGY

2.1 CATALYST PREPARATION AND PRE-CHARACTERIZATION

The catalyst precursor was prepared by impregnating $Ni(NO_3)_2 \cdot 6H_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$ solutions with 10%, 20%, and 30% Ni loading and a Ni-Cu ratio of 12:5 mol:mol onto the powdery Al_2O_3 support following the outline of (Cristiani et al., 1998). These precursors were then calcined at 650°C for 4.0 hours in air and then reduced in 50 $^{mL}/_{min}$ 1:9 (vol:vol) H_2:He at 500°C for 2.0 hours.

Catalyst pre-characterization involved SEM-EDX Analysis for the determination of surface characteristics and metal particle dispersion, XRD Analysis for the determination of the bulk crystal structure, and FTIR Analysis for the determination of the general chemical and molecular structure of the catalysts. BET Analysis confirmed the proportional relationship of the surface area of the catalyst with the catalyst metal loading.

2.2 OPERATING CONDITIONS FOR CNT SYNTHESIS

CNT synthesis was done in a fluidized-bed continuous-flow quartz tube reactor. The reactor was loaded with 0.100g of catalyst set inside an electric variable temperature nichrome wire furnace. The reaction was carried out under atmospheric pressure with a 30-minute data sampling interval. The total gas flow was set at the determined minimum fluidization flow rate of 90 $^{mL}/_{min}$.

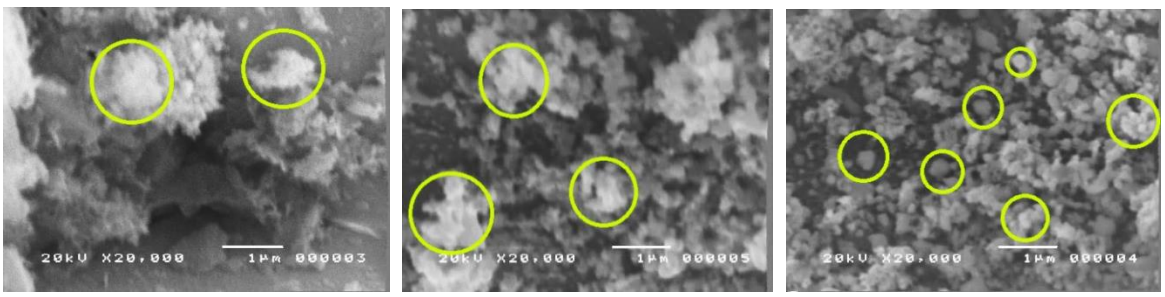
Since none of the process parameters are non-interacting in theory, the experimental design was set according to the Taguchi Design of Experiments (TDE) orthogonal matrix, with the parameters enumerated in Table 1.

Table 1. Taguchi Design of Experiment Parameter Values

Level	Inlet CH_4 composition	Catalyst Loading	Reaction Temperature
1	5%	10% w/w	750°C
2	10%	20% w/w	850°C
3	20%	30% w/w	950°C

3. RESULTS AND DISCUSSION

The dispersion of the Ni and Cu particles on Al_2O_3 is shown in Fig.1a, b, c. Increasing the loading of the catalyst increased the porosity of the catalyst as a result of the covering up of the surface of the support by the Ni and Cu particles. This is supported by the proportional increase of the catalyst surface area with catalyst metal loading. The increase in porosity and catalyst surface area resulted in more active sites for the catalysis reaction to take place.



(a) (b) (c)

Fig. 1. SEM Micrographs for (a) 10%, (b) 20% and (c) 30% Ni-Cu/Al_2O_3 at 20,000X magnification

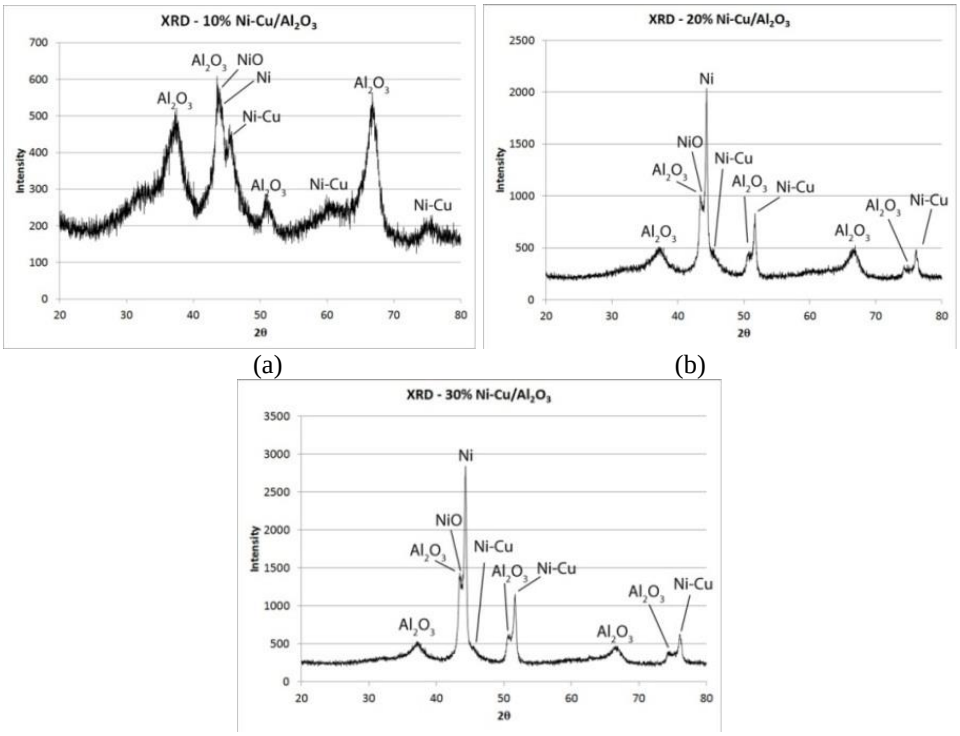


Fig. 2. XRD Diffractograms for (a) 10%, (b) 20% and (c) 30% Ni-Cu/Al_2O_3

As shown in Fig.2a, b and c, XRD Analysis confirmed the presence of γ-Al_2O_3 and Ni-Cu catalyst composites which are favorable to the synthesis of CNTs. The presence of Ni and unreduced NiO were also detected, while no unreduced CuO was detected. FTIR Analysis confirmed the presence of acidic γ-Al_2O_3, Ni-Cu composites, and NiO.

The average CNT diameters corresponding to the TDE orthogonal matrix are shown in Table 2.

Table 2. Summary of CNT Diameters through CTDM

Run	%CH_4	%Ni	T (°C)	CNT Diameter (nm)
1	5	10	750	100.0
2	10	30	850	88.0
3	20	20	950	82.0
4	5	20	850	78.0
5	10	10	950	75.0
6	20	30	750	135.0
7	5	30	950	48.5
8	10	20	750	119.0
9	20	10	850	60.0

The range of values for the CNT diameters satisfies the range for multi-walled carbon nanotubes (MWCNTs) which is between 5 and 150nm (Ziebro et al., 2010). The minimum

average diameter of 48.5nm occurred at Run 7 with 5% ($^{vol}/_{vol}$) inlet CH_4 concentration, 30% Ni catalyst loading with 12:5 mol:mol Ni:Cu, and 950°C reaction temperature, while the maximum average diameter of 135.0nm occurred at Run 6 with 20% ($^{vol}/_{vol}$) inlet CH_4 concentration, 30% Ni catalyst loading with 12:5 mol:mol Ni:Cu, and 750°C reaction temperature.

Data obtained from ANOVA as shown in Table 3 yielded the general effect of each process parameter on the diameter of the synthesized CNTs as shown in Table 3 and Fig. 3.

Table 3. ANOVA for CNT Diameters from CTDM

Source	DF	Seq SS	Adj SS	Adj MS	F-value	P-value
CH_4 Conc.	2	628.4	628.4	314.2	0.98	0.506
Loading	2	369.4	369.4	184.7	0.57	0.635
Temperature	2	4317.4	4317.4	2158.7	6.71	0.130
Error	2	643.4	643.4	321.7		
Total	8	5958.6				

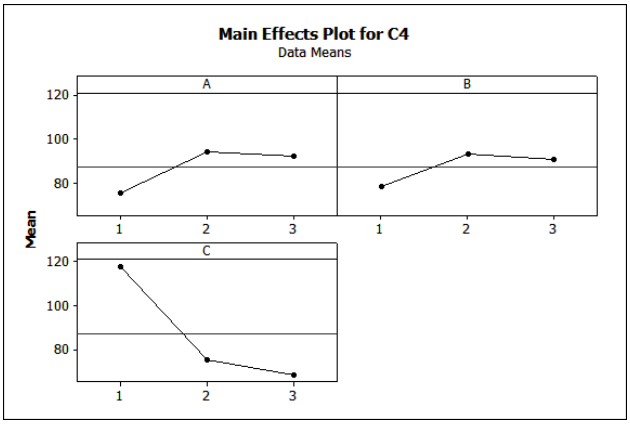


Fig. 3. ANOVA Main Effects Plot for average CNT Diameters from CTDM for CH_4 Concentration (A), Catalyst Metal Loading (B) and Reaction Temperature (C)

It can be seen from Table 2 that the diameters of CNTs were mostly affected by the reaction temperature with 87% significance, while they were only slightly affected by CH_4 concentration and catalyst metal loading with 49.4% and 36.5% significance respectively.

Similarly, the data in Fig. 3 show that the CNT diameters follow a strong negative trend with reaction temperature as reflected in Fig. 3C and a weaker positive trend with both inlet CH_4 concentration and catalyst metal loading as reflected in Fig. 3A and 3B respectively. These results supported the experimental data obtained as reported in Table 2.

Analysis of the effect of the surface area of the catalyst showed that the range of values of 80m^2/g to 90 m^2/g had a significant effect on the activity of the catalysts with 91.3% confidence. Additional ANOVA showed that the intial surface area of the catalyst did not have any significant effect on the diameters of the CNTs with a significance of 17.5%.

A general non-linear regression equation for the data in Table 2 shown in Eq. 1 showed that the CNT diameters, *y*, were mostly affected by the reaction temperature, *T*, with

a numerical coefficient higher than the sum of the coefficients of the other parameters combined. These would support the data reported in Table 2 and Fig. 3.

$$y = 27.14F^{-1} - 36.46F^{-3} + 13.33L^{2} - 3.64L^{3} + 95.14T^{-1} + 1.74T^{2} \qquad \textbf{(Eq. 1)}$$

where:

F	=	inlet CH_4 concentration
L	=	catalyst metal loading
T	=	reaction temperature
y	=	CNT diameter

4. CONCLUDING REMARKS

A study on the effect of the process parameters for the production of CNTs over Ni-Cu/Al_2O_3 in a fluidized bed reactor was done. The process parameters investigated were the inlet CH_4 concentration, the reaction temperature and the catalyst metal loading.

Catalyst pre-characterization confirmed the presence of γ-Al_2O_3, NiO and NiCu catalyst components which are necessary in the production of CNTs. Catalyst post-characterization was carried out with the measurement of the diameter of the synthesized CNTs. The range of diameters formed suggest that the CNTs formed are MWCNTs.

ANOVA and regression of the CNT diameter data showed a high dependence of the diameters on the reaction temperature, a weak dependence on catalyst metal loading and inlet CH_4 concentration, and a negligible dependence on the initial surface area of the catalyst.

Further studies investigating on the effect of an interaction among the parameters to develop a model with higher regression reliability values by considering the nature of the growth mechanism of the CNT and the thermodynamic implications accompanying the mechanism are recommended.

5. ACKNOWLEDGEMENTS

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