

Theoretical Model for Prediction of Metal Catalyst in the Chemical Vapour Deposition of Carbon Nanotubes

Danlami Umar Zuru^(1,4), Zulkarnain Zainal^{(1,2)*}, MohdZobir Hussein⁽²⁾, AdilaMohamadJaafar⁽¹⁾, Hong-Ngee Lim^(1,3) and Sook-Keng Chang⁽²⁾

Abstract—One of the major challenges in the fields of heterogeneous catalysis and carbon nanotubes (CNTs) synthesis via chemical vapour decomposition (CVD) method is lack of established theoretical model for direct selection of carbon precursor/metal catalyst matrix, which constitutes the most important material parameters of the whole process. In the present report, a theoretical model is proposed via kinetic theory and applied in correlating gas stoichiometry equations and the decomposition of carbon precursors with electrons of metal atoms. Theoretical predictions of this model were found to be in conformity with recent advances in the fields of heterogeneous catalysis in general and CVD synthesis of CNTs in particular. The proposed theory may compliment the current selection of carbon precursor/catalyst matrix through experimental trial and error.

Index Terms—Chemical vapour deposition, CNTs, heterogeneous catalysis, theoretical model

1 INTRODUCTION

In a typical CVD process of CNT synthesis, a carbon source (mainly hydrocarbon) is made to collide on a metal surface where it decomposes, nucleate and grow into CNTs; this signifies that the metal catalyst and the carbon source constitute the most important material parameters [1]. However, despite advancements in the fields of heterogeneous catalysis in general and CVD synthesis of CNTs in particular, there is no established theoretical model for the direct selection of metal catalyst/carbon source matrix, which necessitated selections through tedious experimental trial and error [2]. Although various theoretical models were developed to explain the adsorption of atoms and molecules on metal surfaces [3] they failed in correlating the stoichiometric decomposition of gas molecules with any parameter of the surface metal atoms.

In this report, a theoretical model was proposed with the attempt of correlating gas stoichiometry equations directly with metal atomic electrons and used in predicting suitable carbon precursor/metal catalyst matrix for CVD processes. The collisional kinetic properties of H_2 , N_2 , O_2 , CO_2 , CO , CH_4 , NH_3 , C_4H_{10} and C_2H_4 gas molecules, in addition to their Leonard-Jones intermolecular attractive-repulsive parameters were used to develop a volume-energy constant term with which each gas molecule may interact with an atom of a metal surface, Hooke's law was employed to correlate gas stoichiometry to atomic electrons of corresponding metal atoms. The resulting theoretical expression was then applied in deriving

similar expressions for predicting the decompositions of common hydrocarbons used in the CVD synthesis of CNTs. It is hoped that the current approach may augment the trial and error approach.

2 THEORETICAL METHODOLOGY

The collisional kinetic properties of gas molecules and their Leonard-Jones attractive-repulsive potentials were considered in developing the model equations, while Hooke's law was applied to correlate some heterogeneously catalyzed gas stoichiometry to metal catalyst atomic electrons, in order to check the efficiency of the model. The model equations were then applied in predicting the decomposition of the various carbon precursors used in the CVD synthesis of CNTs.

2.1 Theoretical Basis

Effective collision was known to form the basis for breaking and remaking of chemical bonds and according to Barrow [4], the parameters that determine the collisional properties of a gas are the diameter and viscosity, and are related as in equation (1).

$$d = \sqrt{\frac{\mu m}{2\sqrt{2}\pi\eta}} \quad (1)$$

The diameter, d , is related to the mean free path, L , (i.e. the distance a gas molecule travel before it collides with another molecule), the collision frequency, Z_1 , (i.e. the average number of collisions per second) and collision rate, Z_{11} , (i.e. the average number of collisions per second per unit volume) as in equations (2), (3) and (4).

$$L = \frac{1}{\sqrt{2}\pi d^2 N} \quad (2)$$

*Corresponding author, E-mail: zulkar@upm.edu.my

⁽¹⁾Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, 43400 UPM Serdang Selangor, Malaysia

⁽²⁾Materials Synthesis and Characterization Laboratory, Institute of Advanced Technology, Universiti Putra Malaysia, 43400 UPM Serdang Selangor, Malaysia

⁽³⁾Functional Devices Laboratory, Institute of Advanced Technology, Universiti Putra Malaysia, 43400 UPM Serdang Selangor, Malaysia

⁽⁴⁾Department of Chemistry, School of Sciences, Adamu Augie College of Education, Argungu 234, Kebbi State, Nigeria

$$Z_I = \sqrt{2} \pi d^2 \mu N \quad (3)$$

$$Z_{II} = \frac{1}{\sqrt{2}} \pi d^2 \mu (N)^2 \quad (4)$$

Where:

μ = average molecular speed (m s⁻¹)

m = mass of 1 molecule (kg)

η = viscosity (kg m⁻¹ s⁻¹)

N = Number of molecules (m⁻³)

The Leonard-Jones attractive-repulsive potential is given by the relation as shown in equation (5).

$$\psi(r) = 4\beta \left[\left(\frac{\alpha^{12}}{r} \right) - \left(\frac{\alpha^6}{r} \right) \right] \quad (5)$$

Where,

β = Extent of attraction between pairs of molecules

α = Extent of molecular separation.

2.2 Theoretical Procedure

In spectroscopic studies, the energy term with which a quantum of light interacts with a given sample is given by the Planck's relation of equation (6).

$$E = h\nu \quad (6)$$

Hooke's law is then used to predict how these phonons are displaced from their equilibrium positions by the atoms of the sample. Based on the assumption that displacement of phonon is proportional to the number of atomic electrons of the sample atom, the finger print of the sample atom can be identified.

To develop similar relation for a gas molecule, it is assumed in the current model that, on collision with a metal atom, each of the H₂, N₂, O₂, CO₂, CO, CH₄, NH₃, C₄H₁₀ and C₂H₄ gas molecules must loss a certain minimum volume, in order to stick to a metal atom. This volume may be estimated by the quotient of collision frequency and collision rate, as represented in equation (7) and illustrated in Fig. 1.

$$V = \left(\frac{Z_I}{Z_{II}} \right) \quad (7)$$

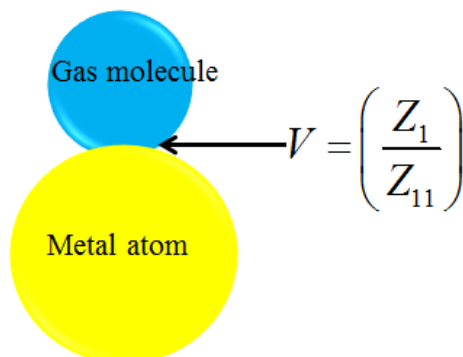


Fig. 1. Gas-metal interaction showing minimum volume lost by a gas molecule.

In order to sustain the collision of equation (7), each gas molecule should possess a unique reciprocal energy term in accordance with equation (8), in order to overcome the forces of molecular repulsion, α , and molecular attraction, β , as illustrated in Fig. 2.

$$E = \frac{1}{\beta} \left(\frac{L}{\alpha} \right)^2 \quad (8)$$

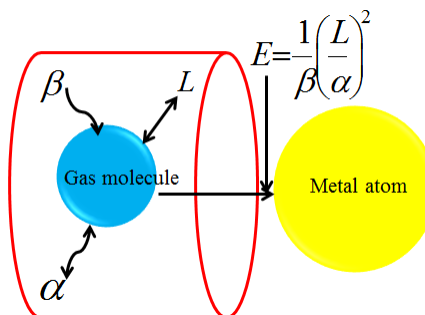


Fig.2. Gas-metal atom interaction showing the reciprocal energy term, E , with which a gas molecule overcomes the forces of molecular attraction, β , and molecular repulsion, α .

This is based on the assumption that the quotient of the mean free path, L , and the extent of molecular separation, α , may render the gas molecules dimensionless such that the probability of molecular collision is almost zero; contribution of the molecular attraction, β , may prevent collision of the molecule with walls of the container. Therefore, a gas molecule, in Fig. 2, with this reciprocal energy is assumed to collide directly with the metal atom.

The product of equations (7) and (8) gives a volume-energy term with which each gas molecule may interact effectively with a metal atom, and is given in equation (9). The general illustration of the whole theoretical conception is shown in Fig. 3.

$$V_e = \frac{Z_I}{Z_{II} \times \beta} \left(\frac{L}{\alpha} \right)^2 \quad (9)$$

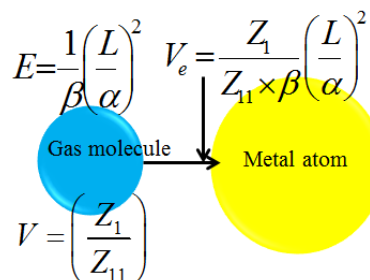


Fig. 3. General illustration of the theoretical conception illustrating the volume-energy term with which a gas molecule interact with a metal surface.

2.3 Application to Heterogeneous Catalysis

In situ spectroscopic studies of heterogeneous catalysis revealed that the catalysts undergo self-sustained dynamic oscillations [5]. And according to Einstein's model of a solid, each atom in a solid has an independent oscillation and all the atoms oscillate with the same frequency [6], as the electron shell configuration forms the fundamental basis for transition metal catalytic activity [7]. Based on these reported facts, the current model is of the assumption that the oscillation or vibration of each atom is in accordance with Hooke's law of equation (10), and is assumed to be proportional to the atomic electrons of the metal atom, which may be responsible for breaking the bonds associated with the reacting species.

$$F = kx \quad (10)$$

Since effective collision is associated with breaking and remaking of chemical bonds, let F , k , and x in the Hooke's equation represent the inter atomic force (bond enthalpy), constant term of interaction and extent of bond stretching, respectively, for each gas molecule. Therefore, the extent to which each gas molecule may be stretched to destruction due to catalyst oscillation may be estimated using equation (11).

$$x = \frac{F}{k} \quad (11)$$

If N_0 , $\sum \Delta H_g$ and $\sum V_e$ are assumed to be the number of metal atomic electrons, numerical sum of the bond enthalpies and sum of the volume-energy terms for reacting gas molecules, respectively, as indicated in each stoichiometric equation, then from equation (11), N_0 for hydrogenation and oxidation processes probed in the current model may be estimated using equations (12) and (13), respectively,

$$\therefore N_0 = \frac{\sum \Delta H_g}{\sum V_e} \quad (12)$$

$$\therefore N_0 = \frac{\sum \Delta H_g}{\sum [V_e]^2} \quad (13)$$

Equation (9) may therefore be used to estimate the constant volume-energy term with which each gas molecule interact with a metal surface and equations (12) and (13) may be used to estimate the number of atomic electrons that may catalyze the various hydrogenation and oxidation processes, respectively.

2.4 Estimation of V_e values

The L , Z_1 , Z_{11} , α and β values for the probe gas molecules were taken from Barrow [4], and were substituted in equation (9) to estimate the V_e values for each corresponding gas molecule.

Example 1: Estimating V_e for hydrogen gas

$$H_2 : V_e = \frac{14.3 \times 10^9}{17.6 \times 10^{34} \times 0.52 \times 10^{-21}} \left(\frac{12.4 \times 10^{-8}}{2.92 \times 10^{-10}} \right)^2$$

$$\therefore V_e = 28.18 m^3 J^{-1}$$

To prove that V_e is a constant volume-energy term characteristic of each gas molecule;

$$\text{Since, } V_e = \frac{m^3}{J} \text{ and } J = Pa \times m^3$$

$$\therefore V_e = \frac{m^3}{Pa \times m^3} = \frac{1}{Pa}$$

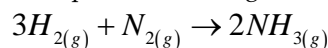
According to Boyles Law,

$$\therefore V_e = k \times \frac{1}{Pa} \Rightarrow Pa \times V_e = k$$

2.5 Estimation of N_0 Values for Hydrogenation and Oxidation Processes

Equation (12) was used in estimating the N_0 values for the various gas equations. The V_e numerical values for H_2 , O_2 , and N_2 , gas molecules estimated with equation (9) were 28.18, 2.13, and 1.997, respectively. Numerical values of bond enthalpies were considered in estimating all N_0 values based on the assumption that V_e is a constant term, which may necessitate the constancy of N_0 .

Example 2: Estimating N_0 for the hydrogenation of nitrogen

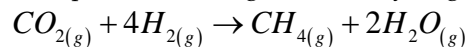


$$\sum \Delta H = 3(H-H) + (N \equiv N) = (3 \times 436) + (1 \times 946) = 2254$$

$$\sum V_e = (3 \times 28.18) + (1 \times 1.997) = 86.537$$

$$\therefore N_0 = \frac{2254}{86.537} = 26$$

Example 3: Estimating N_0 for the hydrogenation of CO_2

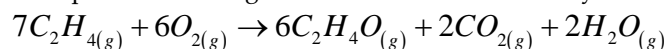


$$\sum \Delta H_{(g)} = (O=C=O) + 4(H-H) = (1 \times 724) + (4 \times 436) = 3192$$

$$\sum V_e = (4 \times 28.18) + 0.336 = 113.056$$

$$\therefore N_0 = \frac{3192}{113.056} = 28.$$

Example 4: Estimating N_0 value for oxidation of ethylene

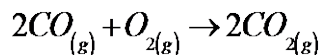


$$\sum \Delta H_g = (7 \times 344) + (6 \times 495) = 5378$$

$$\sum [V_e]^2 = [(7 \times 0.162) + (6 \times 2.13)]^2 = 193.6$$

$$\therefore N_o = \frac{5378}{193.6} = 28$$

Example 5: Estimating N_o value for oxidation of carbon monoxide



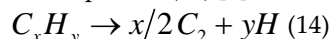
$$\sum \Delta H_{(g)} = 2(O-C) + (O=O) = (2 \times 350) + (1 \times 495) = 1195$$

$$\sum V_e = [(2 \times 1.453) + (1 \times 2.13)]^2 = 25.361$$

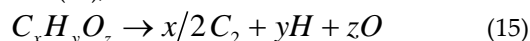
$$\therefore N_o = \frac{1995}{25.361} = 47$$

2.6 Theoretical Application in the CVD Synthesis of CNTs

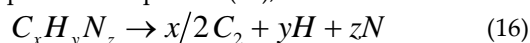
The carbon precursors used in the CVD synthesis of CNTs were reported to decompose and produce C_2 or C species bonded to coordination sites of catalyst and are considered as building blocks for the nanotubes [8]. Reports on the heat of sublimation of carbon and gas-phase equilibrium analysis revealed that both atomic carbon, C , and di-carbon, C_2 , molecules has the same value of heat of formation (718.38 kJ/mol.) estimated from atomization of graphite [4]. Based on these considerations, the current model is of the assumption that for a carbon feedstock with a single C-C bond or C=C double bond, its decomposition on metal surface is assumed to occur as in equation (14) [9]



Oxygen containing hydrocarbon may decompose as in equation (15),



and nitrogen containing hydrocarbon is assumed to decompose as in equation (16),



The N_o values for equations (14), (15), and (16) may be estimated using equations (17), (18) and (19), respectively,

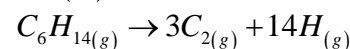
$$N_o = \frac{\sum \Delta_f (x/2 C_2 + yH)}{\sum V_e (y/2 H_2)} \quad (17)$$

$$N_o = \frac{\sum \Delta_f (x/2 C_2 + yH + zO)}{\sum V_e (y/2 H_2 + z/2 O_2)} \quad (18)$$

$$N_o = \frac{\sum \Delta_f (x/2 C_2 + yH + zN)}{\sum V_e (y/2 H_2 + z/2 N_2)} \quad (19)$$

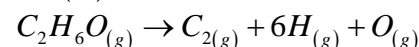
Numerical V_e values for H_2 , O_2 , and N_2 gas molecules estimated with the current model were 28.18, 2.13, and 1.997, respectively; numerical ΔH_f values for C_2 , H , O and N atoms were 718.38, 217.94, 247.52 and 473, respectively [4].

Example 4: Estimating decomposition of hexane using equation (17),



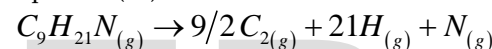
$$\therefore N_o = \frac{[3(718.38) + 14(217.94)]}{7 \times 28.18} = 26$$

Example 5: Estimating decomposition of ethanol using equation (18),



$$\therefore N_o = \frac{[(718.38) + 6(217.94) + (247.52)]}{(3 \times 28.18) + (0.5 \times 2.13)} = 26$$

Example 6: Estimating decomposition of tripropylamine using equation (19),



$$\therefore N_o = \frac{[9/2(718.38) + 21(217.94) + (473)]}{(10.5 \times 28.18) + (0.5 \times 1.997)} = 28$$

3 RESULTS AND DISCUSSION

3.1 Correlation of V_e Values with Number Molecular Bonds

Table 1 shows the V_e numerical values the probed gas molecules with their corresponding total number of bonds, estimated using equation (9). From Table 1, it was suggested that the volume-energy term with which the gas molecules interact with the metal surface is inversely proportional to the total number of bonds present in each gas molecule, and it decreases in the order $H_2 > O_2 > N_2$, CO , $NH_3 > CO_2$, $CH_4 > C_2H_4 > C_4H_{10}$.

Implication of this outcome may be that in hydrogenation and oxidation processes, hydrogen and oxygen gas molecules, respectively, may be assumed to have a greater interaction with the metal surface. The constant volume of interaction (V) for all the gas molecules was estimated at an average of $0.812 \times 10^{-25} \text{ m}^3$, in accordance with equation (7). However, more chemical considerations are required to fully explain the physical meaning of this term.

TABLE 1

VALUES OF L , Z_1 , Z_{11} , α AND β FOR THE PROBE GAS MOLECULES

Gas	L (10^{-8} m)	Z_1 (10^9 s $^{-1}$)	Z_{11} (10^{34} m 3 s $^{-1}$)	α (10^{-10} m)	β (10^{-21} J)
H ₂	12.4	14.3	17.6	2.92	0.52
N ₂	6.56	7.2	8.9	3.69	1.28
O ₂	7.16	6.2	7.6	3.51	1.59
CO ₂	4.41	8.6	10.6	4.24	2.61
CO	6.50	7.23	8.97	3.94	1.51
CH ₄	5.44	11.52	14.17	3.85	1.96
NH ₃	4.64	13.11	16.12	3.38	2.52
C ₂ H ₄	3.79	12.49	15.27	5.22	2.68

3.2 Correlation of N_o Values to Hydrogenation and Oxidation Processes

Table 2 contains the N_o values and suspected metal catalysts for some hydrogenation and oxidation processes, predicted using the current model.

TABLE 2
 N_o VALUES AND SUSPECTED METAL CATALYSTS FOR HYDROGENATION AND OXIDATION PROCESSES

Stoichiometry	N_o	Predicted metal catalyst
$3H_{2(g)} + N_{2(g)} \rightarrow 2NH_{3(g)}$	26	<i>Fe</i>
$CO_{2(g)} + 4H_{2(g)} \rightarrow CH_{4(g)} + 2H_2O_{(g)}$	28	<i>Ni</i>
$H_2C = CH_{2(g)} + H_{2(g)} \rightarrow C_2H_{6(g)}$	28	<i>Ni</i>
$CO_{(g)} + 3H_{2(g)} \rightarrow CH_{4(g)} + H_2O_{(g)}$	28	<i>Ni</i>
$2CO_{(g)} + O_{2(g)} \rightarrow 2CO_{2(g)}$	47	<i>Ag</i>
$7C_2H_{4(g)} + 6O_{2(g)} \rightarrow C_2H_4O_{(g)}$	28	<i>Ni</i>
$4NH_{3(g)} + 5O_{2(g)} \rightarrow 4NO_{(g)} + 6H_2O_{(g)}$	42	<i>Mo</i>
$C_4H_{10(g)} + 3.5O_{2(g)} \rightarrow C_2H_2C_2O_{3(g)} + 4H_2O_{(g)}$	90	<i>Th</i>

From the theoretical outcome in Table 2, and applying Einstein's view of a solid, it is suggested that the phonons emitted by the vibration of 26 electrons of atomic Fe may be suitable for the decomposition of the reacting specie involved in the hydrogenation of nitrogen to ammonia. This is in agreement with the experimental report that metallic Fe possesses an adsorption binding energy in the range -1.1 ± 0.3 eV, which is suitable for ammonia synthesis [10], [11]. Vibrations produced by 28 electrons of Ni were predicted to catalyze methane formation from the hydrogenation of CO₂ on Ni catalyst, as supported by the density functional theoretical study [12]. Hydrogenation of CO by 28 electrons, is also in agreement

with experimental report of 87% methane yield from the flow of H₂/CO in the 3/1 ratio using Ni/Al₂O₃ catalyst [13]. Mousavipour [14] reported a 97% conversion of ethylene to methane using NiO/SiO catalyst, all in conformity with the model prediction of Table 2. In the oxidation processes, Ag catalyst was predicted to catalyze the oxidation of CO, which is correlated with the experimental finding that nanocluster of Ag catalyst showed strong catalytic activity towards CO oxidation [15]. Thorium dioxide (ThO₂) was reported as an efficient catalyst for the synthesis of large ring products [16], which may be also efficient in the synthesis of maleic anhydride via oxidation of butane, as predicted by the current model. Epoxidation of ethylene on Ni catalyst and the oxidation of ammonia on Mo catalyst were also supported by the report of Bartholomew [17].

3.3 Correlation of N_o Values with Decomposition of Carbon Precursors

Table 3 shows the estimated N_o values of the common carbon precursors used in the synthesis of CNTs via CVD method and their corresponding predicted metal catalyst, estimated using equations (15), (16) and (17). On the decomposition of carbon precursors for CNT synthesis via CVD method, the current model suggested theoretically, that vibration of 26 electrons from Fe metal seems to show high catalytic effect on the decomposition of hydrocarbons, such as butane, pentane, and hexane, which is in conformity with reports of Kumar [1]. It is also indicated in Table 3 that Fe catalyst may be effective in the decomposition of alkane alcohols which include methanol and ethanol, and is in agreement with experimental report on the synthesis of highly purified SWCNTs by the pyrolysis of ethanol on Fe catalyst [18]. Nickel with 28 atomic electrons may be a suitable catalyst for the decomposition of ethylene, and tripropylamine, as predicted by the current model. The catalytic decomposition of ethylene on nickel catalyst was reported by Sawa and co-workers [19], while Minchev and group members [20] reported the decomposition of tripropylamine on Ni catalyst, all confirming the prediction of the current model as indicated in Table 3. Ti appears to be good for methane decomposition, which is in conformity with methane decomposition on TiO₂ catalyst reported by Awadallah and his group [21]; Cr was predicted for ethane molecule decomposition and was supported by the reports of Garcia [22] and Fu and co-workers [23]. Mn was predicted to suitably decompose propane and agrees with the report of Puertolas and group members [2].

TABLE 3

N_o VALUES FOR DECOMPOSITION OF COMMON CARBON PRECURSORS AND PREDICTED METAL CATALYSTS

Stoichiometry	N_o	Predicted metal catalyst
$CH_{4(g)} \rightarrow 1/2 C_{2(g)} + 4H_{(g)}$	22	Ti
$C_2H_{6(g)} \rightarrow C_{2(g)} + 6H_{(g)}$	24	Cr
$C_3H_{8(g)} \rightarrow 3/2 C_{2(g)} + 8H_{(g)}$	25	Mn
$C_4H_{10(g)} \rightarrow 2C_{2(g)} + 10H_{(g)}$	26	Fe
$C_5H_{12(g)} \rightarrow 5/2 C_{2(g)} + 12H_{(g)}$	26	Fe
$C_6H_{14(g)} \rightarrow 3C_{2(g)} + 14H_{(g)}$	26	Fe
$C_2H_{4(g)} \rightarrow C_{2(g)} + 4H_{(g)}$	28	Ni
$C_6H_{6(g)} \rightarrow 3C_{2(g)} + 6H_{(g)}$	41	Nb
$C_{12}H_{26(g)} \rightarrow 6C_{2(g)} + 26H_{(g)}$	27	Co
$CH_4O_{(g)} \rightarrow 1/2 C_{2(g)} + 4H_{(g)} + O_{(g)}$	26	Fe
$C_2H_6O_{(g)} \rightarrow C_{2(g)} + 6H_{(g)} + O_{(g)}$	26	Fe
$C_{12}H_{22}O_{11(g)} \rightarrow 6C_{2(g)} + 22H_{(g)} + 11O_{(g)}$	37	Rb
$C_9H_{21}N_{(g)} \rightarrow 9/2 C_{2(g)} + 21H_{(g)} + N_{(g)}$	28	Ni

The current theory also suggested that Co, with 27 atomic electrons may be suitable for the decomposition of dodecane, which is in correlation with the reported catalytic decomposition of hydrocarbons on cobalt catalyst [24]. Decompositions of benzene and sucrose on Nb and Rb respectively may be supported with the fact that, depending on the experimental conditions, any metal can catalyze CNT growth process, just as any carbon-containing material is a potential candidate for CNT yield; however, chemical considerations suggest that the active catalyst should be in the oxide form [25].

4 CONCLUSION

A theoretical model was proposed and applied to correlate gas stoichiometry with electrons of metal atoms which was also used in predicting the decomposition of thirteen carbon feedstock used in the CVD synthesis of CNTs. The predictions of this theory were found to be in agreement with experimental advances in the field of heterogeneous catalysis in general, and CVD synthesis of CNTs, in particular. The model may serve to compliment the modern selection of carbon precursors through tedious experimental trial and error and may also be viewed as a possible corner stone towards better understanding of heterogeneous surface catalysis.

ACKNOWLEDGEMENTS

Research grant from the Ministry of Higher Education Malaysia and the financial support from AdamuAugie College of Education, Argungu (A. A. C. O. E Argungu), Kebbi-State, Nigeria for Danlami Umar Zuru are acknowledged. However, all contents in this report do not necessarily represent the views the sponsors, but is the sole responsibility of the authors.

REFERENCES

- [1] M. Kumar and Y. Ando, "Chemical Vapour Deposition of Carbon Nanotubes: A Review of Growth Mechanism and Mass Production," *J. Nanosci. Nanotech.*, vol. 10, pp. 3739–3758, 2010.
- [2] B. Puertolas, A. Smith, I. Vazquez, A. Dejoz, A. Moragues, and T. Garcia, "The Different Catalytic Behavior in the Propane Total Oxidation of Co and Mn Oxides Prepared by Wet Procedure," *Chem. Eng. J.*, vol. 2291, pp. 547–558, 2013.
- [3] A. Dabrowski, "Adsorption from Theory to Practice," *Adv. Colloid and Interface Sci.*, vol. 93, pp. 135–224, 2001.
- [4] G.M. Barrow, *Physical Chemistry*. McGraw-Hill International Book Company, pp. 1–183, 1979.
- [5] S.B. Vendelbo, C.F. Elkjaer, H. Falsig, I. Pulpitasari, P. Dona, L. Mele, B. Morona, B.J. Nelissen, R. Van Rijn, J.F. Creemer, P.J. Kooyman, and S. Helveg, "Visualization of Oscillatory Behavior of Pt Nanoparticles Catalyzing CO Oxidation," *Nat. Mater.*, vol. 13, pp. 884–890, 2014.
- [6] N. Aquino, V. Granados, and H. Yee-Madeira, "The Einstein Model and the Heat Capacity of Solids under High Pressure," *Revista Mexicana De Fisica*, vol. 55, pp. 125–129, 2009.
- [7] V.V. Kaichev, A.Y.U. Gladky, I.P. Prosirin, A.A. Saraer, M. Havecker, R. Schlogl, and V.I. Bukhtiyarov, "In situ XPS Study of Self-sustained Oscillations in Catalytic Oxidation of Propane over Nickel," *Surf. Sci.*, vol. 609, pp. 113–118, 2013.
- [8] A. Fonseca, K. Hermadi, P. Piedigrosso, J.F. Colermer, K. Mukhopadhyay, R. Domme, S. Lazarescu, L.P. Biro, Ph. Lambin, P.A. Thury, D. Bernarets, and J.B. Nagy, "Synthesis of Single- and Multi- wall Carbon Nanotubes over Supported Catalysts," *App. Phys. A*, vol. 67, pp. 11–22, 1998.
- [9] J.P. Tessonier and D.S. Su, "Recent Progress on Growth Mechanism of Carbon Nanotubes: A Review," *ChemSuschem*, vol. 4, pp. 6–11, 2011.
- [10] M.D. Argyle and C.H. Bartholomew, "Heterogeneous Catalyst Deactivation and Regeneration: A Review," *Catalysts*, vol. 5, pp. 145–269, 2015.
- [11] J.K. Nørskov, M. Scheffler, and H. Toulhoat, "Density Functional Theory in Surface Heterogeneous Catalysis," *MRS Bulletin*, vol. 31, pp. 345–352, 2006.
- [12] P. Bothra, G. Periyasamy, and S.K. Pati, "Methane Formation from the Hydrogenation of Carbon Dioxide on Ni (110) Surface – A Density Functional Theoretical Study," *Phys. Chem. Chem. Phys.*, vol. 15, pp. 5701–5706, 2013.
- [13] D.W. Goodman, C.H.F. Peden, and M.S. Chen, "Co Oxidation on Ruthenium: The Nature of the Active Catalytic Surface," *Surface Science*, vol. 601, pp. L124–L126, 2007.
- [14] S.H. Mousavipour, M.M. Doroodman, S. Amini, and M. Shahamat, "Catalytic Decomposition of Methane/Ethylene into Carbon and Hydrogen," *Phys. Chem. Res.*, vol. 3, pp. 46–57, 2015.
- [15] K.-I. Shimizu, K. Sawabe, and A. Satsuma, "Self-regenerative Silver Nanocluster Catalyst for CO Oxidation," *ChemCatChem*, vol. 3, pp. 1290–1293, 2011.

- [16] P. Patnaik, *Handbook of Inorganic Chemical Compounds*. McGraw-Hill: New York, pp. 931, 2003.
- [17] C.H. Bartholomew, "Mechanism of Catalyst Deactivation," *Appl. Catal. A. Gen.*, vol. 212, pp. 17–60, 2001.
- [18] T. Maruyama, K. Sato, Y. Mizutani, K. Tanioku, T. Shiraiwa, and S. Naritsuka, "Low-temperature Synthesis of Single-walled Carbon Nanotubes by Alcohol Gas Source Growth in High Vacuum," *J. Nanosci. Nanotechnol.*, vol. 10, pp. 4095–4101, 2010.
- [19] P.G. Sawa, K. Polychronopoulou, V.A. Ryzkov, and A.M. Efstathiou, "Low-temperature Catalytic Decomposition of Ethylene into Hydrogen and Secondary Carbon Nanotubes over Ni/CNTs," *Appl. Catal. B*, vol. 93, pp. 314–324, 2010.
- [20] C. Minchev, V. Minkov, V. Penchev, H. Weyda, and H. Lechest, "Thermal Decomposition of Tripropylamine as a Template in MeA-PO – 5 Molecular Sieves," *J. Therm. Anal.*, vol. 37, pp. 171–181, 1991.
- [21] A.E. Awadallah, M.S. Mostafa, A.A. Abdul-Enein, and S.A. Hanaifi, "Hydrogen Production via Methane Decomposition over Al₂O₃ – TiO₂ Binary Oxides Supported Ni Catalyst: Effect of Ti Content on the Catalytic Efficiency," *Fuel*, vol. 129, pp. 68–77, 2014.
- [22] H. Garcia, "Allotropic Carbon Nano Forms as Advanced Metal Free Catalysts or as Supports," *Advances in Chemistry*, Article ID 906781, 20 pages, 2014.
- [23] X.-Y. Fu, X.-X. Luo, J.-L. Luo, K.T. Chuang, A.R. Sanger, and A. Krzywicki, "Ethane Dehydrogenation over Nano – Cr₂O₃ Anode Catalyst in Proton Ceramic Fuel Cell Reactors to Co-produce Ethylene and Electricity," *J. Power Sources*, vol. 196, pp. 1036–1041, 2011.
- [24] V.N. Nemykin, A.E. Polshyna, and S.A. Berisenkova, "Preparation, Characterization, and Catalytic Activity of Synthetic Carbon – supported Cobalt Complexes in Dodecane -1-thiol Oxidation Reaction," *J. Mol. Catal.*, vol. 264, pp. 103–109, 2007.
- [25] T. Bligaard and J.K. Nørskov, In chemical bonding at surfaces and interfaces; Nilson, A, Ed., Elsevier: Amsterdam, 2008; pp 255–321.