Theoretical Reaction Mechanism for Ammonia Synthesis

by

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Dissertation submitted for partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
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Universiti Teknologi PETRONAS
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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
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Approved by,

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(A.P. Dr. Suriati Binti Sufian)

UNIVERSITI TEKNOLOGI PETRONAS
BANDAR SERI ISKANDAR, PERAK
September 2015

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgment, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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NURUL ALIA BT MOHAMAD

ABSTRACT

In this paper, reaction mechanism of ammonia synthesis is studied using Density Functional Theory method. A model reaction mechanism is chosen from the literature and simulation is carried out for each elementary steps. For this job, Optimization and Frequency calculation were carried out. The output file from frequency calculation generated thermochemical data which is required to calculate the reaction energy and the reaction rate in order to determine the raction mechanism for ammonia synthesis and the rate-limiting step.

ACKNOWLEDGEMENT

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Special thanks to Thien Duc Nguyen for his assistance and guidance throughout the course of completing this project. I would also like to thank my parents and fellow friends who have been my pillar of strength in facing the many challenges.

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CHAPTER 1
INTRODUCTION

1.1 Background Study

Long before Haber-Bosch process was discovered, scientists has inferred the great importance of ammonia to the survival of mankind around the world. As population of human increases each year, the need for food supply increases proportionally. However, the current production of fertilizer from ammonia for agriculture was seen to be inadequate and unable to keep up with the rising demand thus creating a need for the scientists and engineers to find and develop a way in which ammonia production can be increased to meet the demand. The renowned Haber-Bosch process which was established after years of research and study has given a great impact to the development of technology for ammonia synthesis. Various studies were conducted later on to further advance the present technology for a better, cost-saving process and larger production capacity.

Catalyst is one of the main subject which scientists effortlessly studied due to its essentiality and great importance in industrial ammonia synthesis reaction. The current technology in catalyst today mainly uses iron-based catalyst to enhance production and more researches are currently undergone to discover a new technology for catalyst. A significant study will be on the catalyst support such as carbon nanofiber (CNF).

1.2 Problem Statement

Ammonia synthesis is one of the most widely-studied subject due to its simplicity. Various reaction mechanism has been proposed for ammonia synthesis after many research and studies. In this project, Density Functional Theory (DFT) method will be used to determine the reaction mechanism of ammonia reaction and the rate-limiting step will also be determined.

1.3 Objectives

The main objectives of this project are:

i. To investigate the reaction mechanisms of nitrogen hydrogenation
ii. To optimize the reaction mechanism using DFT method

1.4 Scope of Study

The scope of this project is to apply Density Functional Theory (DFT) method in determining the reaction mechanism of ammonia synthesis. Job types of optimization (Opt) and Frequecy (Freq) will be applied based on the selected density functional theory (B3LYP) and basis set of 3-21G.

CHAPTER 2
LITERATURE REVIEW

2.1 Ammonia

2.1.1 Properties of Ammonia

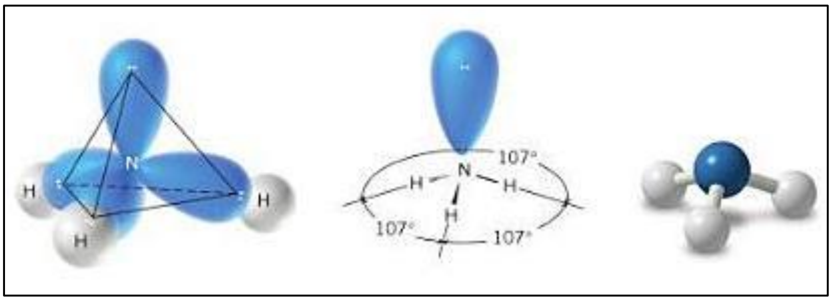


Figure 2.1 Molecular geometry of NH_3

Ammonia is a chemical compound consisting of one atom of nitrogen and three atoms of hydrogen with a chemical formula designated as NH3. It is normally found as colorless gas and has significant characteristics of pungent odor and high solubility in water which makes it different from any other gases.

In terms of geometry, ammonia is a four-atom molecule with a triangular pyramidal geometry due to the tetrahedral arrangement of the electron pairs. It has four groups of electrons with one group of unshared pair of electrons, and based on Valence-Shell Electron-Pair Expulsion (VSEPR) theory, the four electron groups around a central atom will be directed towards the corners of tetrahedron to give maximum separation. Its central atom has both shared and unshared electron pairs resulting in three bonding pairs of electrons and one non-bonding pair. The bond angle in a molecule of ammonia is 107° because the non-bonding pair occupies more space than the bonding pairs.

2.1.2 Development of Ammonia Synthesis

The history of ammonia discovery may not be well known by many. But its progress and development throughout the centuries were extremely remarkable that ammonia synthesis in large scale was made possible in the present days using the Haber-Bosch process. The process was named after Fritz Haber and Carl Bosch who contributed and dedicated themselves in finding ways to produce ammonia synthetically and thus, scale it up to the industrial level (Varotto, 2014). Besides that, A. Mittasch and W. Frankenburger (1929) also mentioned the contribution of Nernst in his introductory researches which was combined with the fundamental work of Haber and Badische Anilin und Soda Fabrik (BASF) led to the success of practical and large-scale methods. Kenzi Tamaru described in detailed chronology the effort made by past scientist and engineers in ammonia synthesis amongst who, were, Fritz Haber, Carl Bosch and BASF of Germany. In 1904, it is stated that “Haber began his work on the thermodynamic equilibria between ammonia, hydrogen and nitrogen.” (Tamaru, 1991). In 1909, only after years of working did Haber successfully synthesized ammonia at the rate of 80 grams per hour whose demonstration was witnessed by Bosch and Mittasch (Tamaru, 1991). The breakthrough then led to many more developments and advancement in the technology for ammonia synthesis up until today.

2.2 Ammonia Synthesis

Ammonia is produced by the reaction between nitrogen gas and hydrogen gas involving the coupling of nitrogen molecule with molecular hydrogen with a presence of a catalyst (Hwang & Mebel, 2004). The reaction is carried out at high pressures and temperatures and occurs with large yields when iron catalysts are present. The iron catalyst consists of reduced magnetite ore (Fe3O4) which is enriched (“promoted”) most frequently with Al- and K- (or Ca, Mg, Si)-oxides while its reaction temperatures for optimal performance is around 400ºC and pressures from 150-300 atmospheres (Bencic, 2001).

The overall chemical reaction is given by

$$N_2 + 3H_2 \rightleftharpoons 2NH_3, \quad \Delta H^0_{298} = -46.1 \text{ kJ mol}^{-1}$$

where ΔH^0_{298} is the standard enthalpy change at 298 K.

The reaction is an exothermic reaction as it releases a significant amount of heat. Another important point to note is that the reaction is a reversible reaction which means it can proceed both in forward direction resulting in ammonia synthesis; or backward direction resulting in ammonia decomposition (Modak, 2011). This is where Le Chatelier’s Principle comes to surface to ensure the reaction favors ammonia synthesis.

2.2.1 Reaction Mechanism of Ammonia Synthesis

A reaction mechanism is a series of steps that explains how an overall reaction proceeds on a molecular level. Each step is known as elementary process or elementary step which describe the changes in one or more molecule due to the addition or omission of another interacting molecule. However, a reaction mechanism is only a prediction at how a reaction proceeds and does not necessarily limited to only a single mechanism.

In the case of ammonia synthesis reaction, the formation of ammonia molecules involves two principle reaction pathways (Schlögl, 2008). Schlögl in his explanation states that both reaction pathways involve the activation of molecular hydrogen into reducing agent atomic hydrogen, and some form of activation of the nitrogen molecule. The difference between the two lies in nitrogen dissociation step which could occur before hydrogenation of atomic nitrogen or after the partial hydrogenation of di-nitrogen to dimine and hydrazine.

Meanwhile, Iyngaran et al. (2011) suggested that the necessary steps for ammonia synthesis may be broken down into several steps where the adsorption of nitrogen (*step ii*) is strongly believed to be the rate-determining step:

(i) dissociative adsorption of H_2, yielding H adatoms;
(ii) dissociative adsorption of N_2, yielding N adatoms;
(iii) hydrogenation of N adatoms by addition of H adatoms, sequentially forming adsorbed NH, NH_2 and NH_3; and
(iv) desorption of NH_3.

One of the proposed elementary steps of the ammonia synthesis reaction can be written as (Kolasinski, 2002):

$$\mathrm{N_{2(g)}} + * \rightleftharpoons \mathrm{N_2} - * \qquad [1.1]$$

$$\mathrm{N_2} - * + * \rightleftharpoons 2\mathrm{N} - * \qquad [1.2]$$

$$\mathrm{N} - * + \mathrm{H} - * \rightleftharpoons \mathrm{NH} - * + * \qquad [1.3]$$

$$\mathrm{NH} - * + \mathrm{H} - * \rightleftharpoons \mathrm{NH_2} - * + * \qquad [1.4]$$

$$\mathrm{NH_2} - * + \mathrm{H} - * \rightleftharpoons \mathrm{NH_3} - * + * \qquad [1.5]$$

$$\mathrm{NH_3} - * \rightleftharpoons \mathrm{NH_{3(g)}} + * \qquad [1.6]$$

$$\mathrm{H_{2(g)}} + 2 * \rightleftharpoons 2\mathrm{H} - * \qquad [1.7]$$

where $(\mathrm{N} - *)$ is the adsorbed nitrogen, $(\mathrm{H} - *)$ is the adsorbed hydrogen and $(*)$ is the free sites.

From the above elementary reaction, it is expected that N_2 dissociation is the rate-determining step in ammonia synthesis due to a low dissociative sticking coefficient of N_2. Therefore, an effective ammonia synthesis catalyst is needed to efficiently dissociate N_2 (Kolasinski, 2002).

2.3 Catalytic Ammonia Synthesis

Upon discussing ammonia synthesis reaction, the involvement of catalyst must be mentioned as well.

“For the catalyst is the heart of every catalytic reaction, without whose heartbeat the reaction must stop.” (Mittasch. & Frankenburger, 1929).

Catalyst is seen as extremely essential in the production of ammonia in the industry as it functions to increase the reaction rate. Varotto (2014) stated that without a catalyst, the reaction proceeds very slowly that it almost does not happen at all. Thus, the presence of catalyst will ensure the reaction proceeds in a reasonable speed. Hwang and Mebel (2004) explained that without a catalyst, the ammonia reaction will take place in three consequent steps where the addition of the first H_2 molecule is the rate determining stage of nitrogen hydrogenation.

$$N_2 + H_2 \rightarrow N_2H_2 \qquad (1)$$

$$N_2H_2 + H_2 \rightarrow N_2H_4 \qquad (2)$$

$$N_2H_4 + H_2 \rightarrow 2NH_3 \qquad (3)$$

Meanwhile, Varotto (2014) stated that the presence of an iron-based catalyst will lower the energy required to dissociate molecular nitrogen into nitrogen atoms which are then absorbed (ads) onto the catalyst and proceed to further reaction as shown below:

$$N_2(ads) \rightarrow 2N(ads)$$

$$H_2(ads) \rightarrow 2H(ads)$$

$$N(ads) + 3H \rightarrow NH_3(ads)$$

$$NH_3(ads) \rightarrow NH_3(g)$$

In Haber-Bosch process, iron is used as catalyst. The reason for effectiveness of iron as a catalyst is because it lowers the barrier to N_2 dissociation by coaxing the N≡N bond to break while forming Fe-N chemisorption bond simultaneously. Because of this, the activation barrier for N_2 dissociation is much lower than the N≡N bond strength. Another significant property of iron is the ability to break N≡N bonds. But in doing so, they produce an Fe-N bond that has just the right strength. (Kolasinski, 2002)

2.4 Catalyst Support

Ammonia synthesis is one of the reactions that is heterogeneously catalyzed in which nitrogen and hydrogen in gas phase react over iron catalyst. Heterogeneous catalysts consist of three components i.e. support, active phase and promoter (Van Santen R.A., Mouljin, & Averill, 1999). The main function of the support is to keep the active phase, where the reaction takes place in the catalyst, highly dispersed (Bitter, 2006).

The role of catalyst support was explained by de Jong, K.P. (1999) which include; (i) increase the effective surface area and provide suitable pore structure to improve reactivity and selectivity, (ii) increases the mechanical strength to withstand stresses caused by pressure, temperature, phase transformation, etc. (iii) increase the thermal stability to prevent aggregation and sintering so that the active components will stay dispersed (iv) provides acidic or basic sites needed for catalytic reactions and it will form new compound with active component (such as solid solution) and change the activity of the catalyst (v) enhances the ability to withstand poisoning by either decomposing or adsorbing poisoning species (vi) reduce the amount of active component and lower the cost.

Industrially utilized catalyst support includes refractory oxides, like silica (SiO_2) and alumina (Al_2O_3) and most recently, carbon materials, which is now gaining more attention due to the potential as catalyst support. Various carbon materials have been used in the catalytic chemical industry as catalyst support such as activated carbons (AC), carbon blacks (CB), graphite, glass-like carbons and carbon nanomaterial i.e. carbon nanotubes (CNT). The most recent discovery for potential catalyst support from carbon nanomaterial is the carbon nanofiber (CNF).

Generally, there are significant advantages of using carbon material as catalyst support over traditional catalyst support (Reinoso & Sepulveda-Escribano, 2009): (i) the carbon surface is resistant to both acidic and basic media, (ii) the structure is stable at high temperature (even above 1023 K under inert atmosphere) (Serp & Machado, 2015), (iii) the pore structure can be tailored to obtain the pore size distribution needed for a given application, (iv) porous carbons can be prepared with a variety of macroscopic shapes (e.g. granules, powders, fibers, cloth, pellets, monoliths, disks), (iv) the chemical properties of the surface can be modified to control polarity and hydrophobicity, (v) the active phase can be recovered easily from spent catalyst by burning away the carbon support and (vi) carbon support are usually cheaper than other conventional catalyst supports such as alumina and silica.

2.4.1 Carbon Nanofiber (CNF) as Potential Catalyst Support

Carbon nanofibers (CNF) is defined as sp^2-based linear filaments with diameter of ca. 100 nm that are characterized by flexibility and their aspect ratio which is reported to be above 100) (Kim, Hayashi, & Dresselhaus, 2013; Bitter, 2006). Different methods to prepare CNF were described in many research papers which include impregnation, ion exchange/equilibrium adsorption, grafting, anchoring/heterogenization of homogeneous catalyst, deposition-precipitation, spreading and wetting, immobilization of metal particles and clusters and chemical vapor deposition (CVD). However, the method most widely used and recognized is the CVD method which is especially preferred for large-scale production. (Hammel, et al., 2004; Wang, Wei, Luo, Yu, & Gu, 2002)

The growth mechanism of CNF has also been observed and studied by Serp, de Jong and Geus. Figure 2.2 describes the growth mechanism of CNF using a gaseous carbon-containing gas while Figure 2.3 illustrates the typical chemical vapor deposition growth mechanism of the platelet CNFs. It was proposed that the first step is the decomposition of carbon-containing gases on the metal surface followed by carbon atoms dissolving in and diffusing through the bulk of the metal and lastly, the precipitation of carbon in the form of a CNF consisting of graphite (de Jong & Geus, 2000).

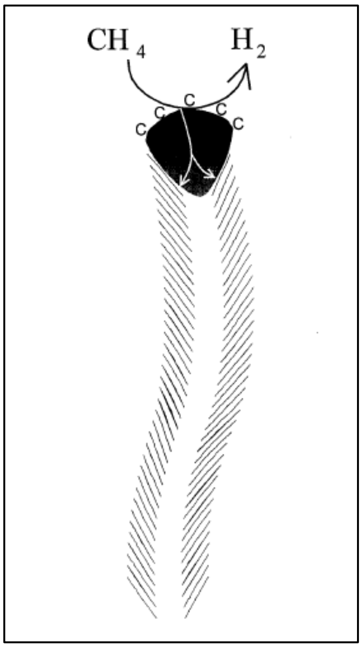


Figure 2.2 Schematic representation of the catalytic growth of a CNF using a gaseous carbon-containing gas (de Jong & Geus, 2000)

Figure 2.3 Schematic illustration of the typical chemical vapor deposition growth mechanism of the platelet CNFs

Generally, there are three types of CNFs (Figure 2.4): the herringbone (h-CNFs) or fishbone, in which the graphene layers are stacked obliquely with respect to the fiber axis; the platelet (p-CNFs), in which the graphene layers are perpendicular to the fiber axis; and the ribbon (r-CNFs), in which the graphene layers are parallel to the growth axis (Kim, Hayashi, & Dresselhaus, 2013; Serp & Machado, 2015)

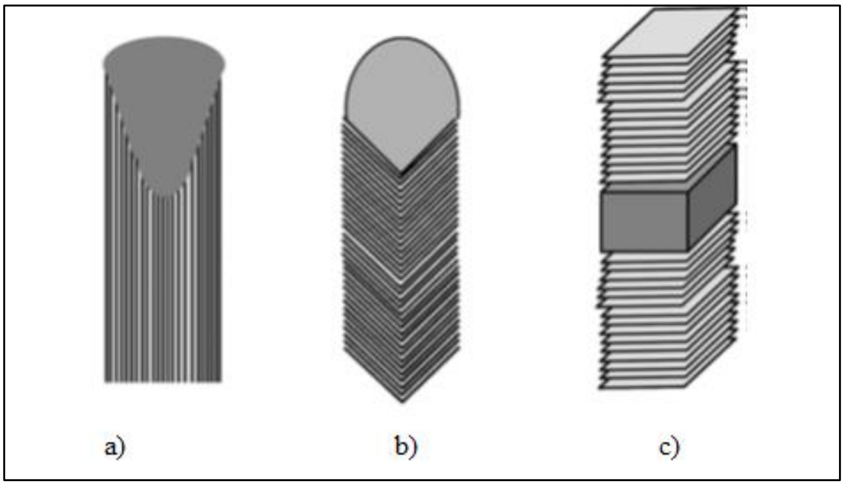


Figure 2.4 Different carbon nanostructures produced by catalytic chemical vapor deposition: (a) ribbon-carbon nanofibers (r-CNFs); (b) fishbone-carbon nanofibers (h-CNFs); and (c) platelet-carbon nanofibers (p-CNFs) (Kim, Hayashi, & Dresselhaus, 2013).

CNF is identified as a potential carbon support for many reasons. One of them is because they can be produced at relatively low costs with a high yield and are therefore suitable as catalyst support material. They can also be prepared in a reproducible manner, with tunable properties, making these fibers a support with great potential (Toebes, 2004).

The potential of CNF as catalyst support is further supported by many authors due to its characteristics (Dias, Alvim-Ferraz, Almeida, Rivera-Utrilla, & Sanchez-Polo, 2007; Ioannidou & Zabaniotou, 2007; Chen, et al., 2011): (i) their good metal/support interaction caused by the presence of the prismatic planes on the nanofibers surface, (ii) their high specific surface area that offers a better contact reactants/active sites and (iii) absence of the ink-bottled pores that reduces the diffusion phenomena, mainly in liquid phase reactions or high mass and heat transfers reactions.

Futhermore, CNF combines the advantage of both active carbon and graphite (Bitter, 2006). The material does not contain micropores, has graphitic structure, stable, they are pure and do not contain impurities (such as sulfur or other inorganic impurities), has a relatively high surface area (100 - 200 m2/g) and can be tuned to steer catalytic reactions (Bitter, 2006; Toebes, 2004).

CNF is also claimed to have a semi-conducting behaviour (Liu, Ren, & Cheng, 2009) as well as having chemically active end planes on both the inner and outer surfaces of the nanofibers (Endo, et al., 2003) resulted from its unique structure which can be visualized as regularly stacked truncated conical or planar layers along the filament length (Rodriguez, Chambers, & Baker, 1995; Endo, et al., 2002; Yoon, et al., 2004).

A related study has shown that CNF is more stable than activated carbon as a catalyst support and methanation reaction is greatly inhibited compared to activated carbon. The high level of graphitization of the support is probably the reason for the resistance toward the methanation reaction, even at high temperature. (Serp, 2009)

2.5 Density Functional Theory

Density Functional Theory (DFT) is a computational quantum mechanical modelling method used to study the electronic structure of many-body systems, in particular atoms, molecules, and the condensed phases. The name density functional theory was derived from the use of functionals of the electron density. It derives properties of the molecule based on a determination of the electron density of the molecule. Unlike the wavefunction, which is not a physical reality but a mathematical construct, electron density is a physical characteristic of all molecules. A functional is defined as a function of a function, and the energy of the molecule is a functional of the electron density. The electron density is a function with three variables – x-, y-, and z-position of the electrons. Unlike the wavefunction, which becomes significantly more complicated as the number of electrons increases, the determination of the electron density is independent of the number of electrons. Argaman and Makov (1999) stated that DFT "is one of the most widely used methods for "ab initio" calculations of the structure of atoms, molecules, crystals, surfaces, and their interactions."

The application of DFT method is widely used in order to solve problems in atomic and molecular physics e.g. calculation of ionization potentials and vibration spectra, the study of chemical reactions, and the nature of active sites in catalysts (Argaman & Makov, 1999).

2.5.1 Density Functional Theory (DFT) Methods

There are three types of DFT methods which are:

1) Local density approximation (LDA) methods:
   LDA methods assume that the density of the molecule is uniform throughout the molecule.
2) Gradient corrected (GC) methods:
   GC methods look to account for the non-uniformity of the electron density.
3) Hybrid methods:

Hybrid methods incorporate some of the more useful features from ab initio methods with some of the improvements of DFT mathematics. An example of the most commonly used methods for computational chemistry practitioners is the B3LYP.

2.5.2 Advantages of DFT method

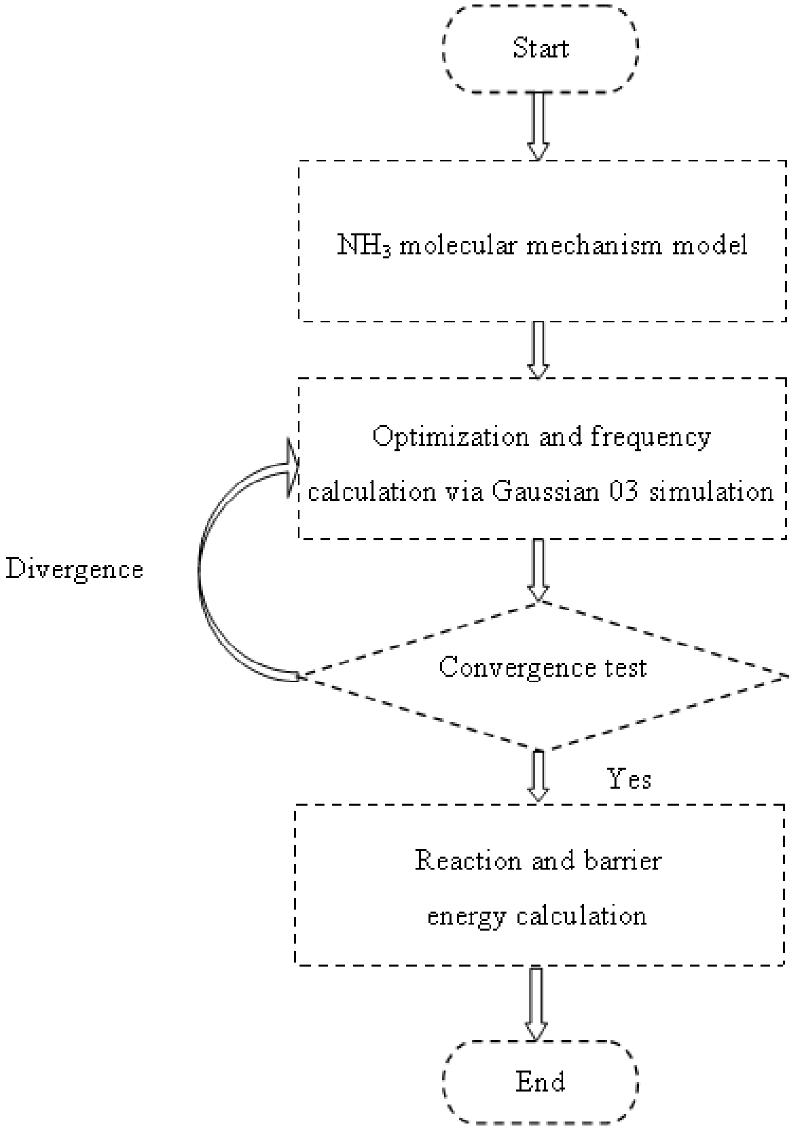
The most significant advantage to DFT methods is a significant increase in computational accuracy without the additional increase in computing time. DFT methods such as B3LYP/6-31G(d) are oftentimes considered to be a standard model chemistry for many applications. The challenge is to determine the most appropriate method for a particular application. In choosing a DFT method, it is important to determine the suitability of choice for DFT methods for a particular problem or application. However, generally, the B3LYP/6-31g(d) model chemistry is considered by most to be a good general-purpose choice.

CHAPTER 3

METHODOLOGY

3.1 Project Methodology

The project methodology can be simplified as shown in the flow chart below:



3.1.1 NH_3 Mechanism Model

The ammonia reaction mechanism chosen for the simulation is taken from Hwang and Mebel (2004) where the ammonia reaction takes place in three consequent steps:

$$N_2 + H_2 \rightarrow N_2H_2 \qquad (1)$$

$$N_2H_2 + H_2 \rightarrow N_2H_4 \qquad (2)$$

$$N_2H_4 + H_2 \rightarrow 2NH_3 \qquad (3)$$

3.1.2 Geometry Optimization

Based on the reaction mechanism, geometry optimization was carried out for each elementary reaction. The intermediate molecules were optimized to a transition state. This is done by drawing several initial guess structures for N_2H_2, N_2H_4 and $2NH_3$ molecules in GaussView 3.07 followed by the optimization calculation using DFT (B3LYP) method with basis set of 3-21G.

The information obtained from geometry optimization calculation are:

1) Atomic coordinates of optimized molecule

2) Optimized Parameters: atomic distances and angles

3.1.3 Frequency Analysis

Frequency analysis is carried out after geometry optimization for the optimized molecules. This calculation type keyword computes force constants and the resulting vibrational frequencies. Vibrational frequencies are computed by determining the second derivatives of the energy with respect to the Cartesian nuclear coordinates and then transforming to mass-weighted coordinates. The same combination of theoretical model and basis set should be used for both the Optimization and Frequency calculations.

The goal of the frequency calculation are:

1) To determine if the optimized structure is a minimum, a transition state (1 imaginary frequency), or a saddle point (2 or more imaginary frequencies).

2) To predict the quantum mechanical zero-point energy, the entropy, and the temperature-dependent vibrational, rotational, and translational energy terms.

3) To yield theoretical harmonic vibrational frequencies as well and IR and Raman intensities.

The information that can be obtained from frequency calculation are:

1. Atomic coordinates of optimized molecule
2. Optimized parameters: atomic distances and angles
3. HOMO/LUMO eigenvalues (hartree)
4. Mulliken atomic charges (short)
5. Dipole moments
6. Single Point energy
7. Harmonic frequnecies (wavenumbers)
8. Reduced masses (amu)
9. Force constants
10. IR intensities
11. Raman intensities (not default)
12. Thermochemistry
    (a) Temperature
    (b) Pressure
    (c) Isotopes used
    (d) Molecular mass
    (e) Thermal energy: E (Thermal)

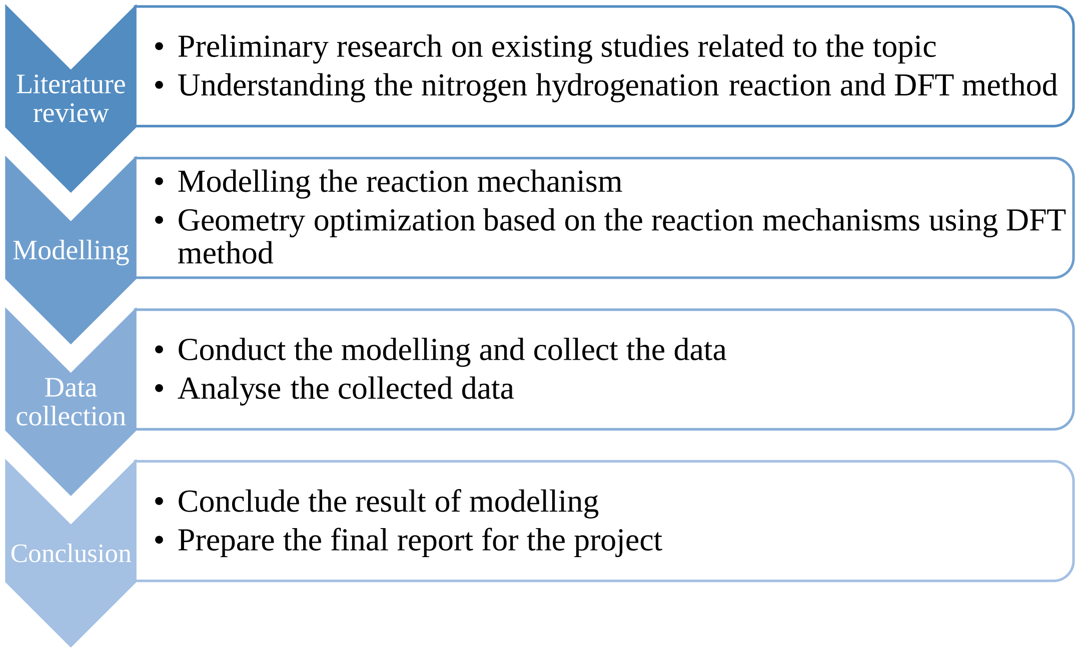
(f) Constant volume molar heat capacity (CV)

(g) Entropy (S)

(h) Free Energy (sum of electronic and thermal Free Energies)

(i) Enthalpy (sum of electronic and thermal Enthalpies)

3.2 Project Flow Chart



- Preliminary research on existing studies related to the topic
- Understanding the nitrogen hydrogenation reaction and DFT method

- Modelling the reaction mechanism
- Geometry optimization based on the reaction mechanisms using DFT method

- Conduct the modelling and collect the data
- Analyse the collected data

- Conclude the result of modelling
- Prepare the final report for the project

3.3 Gantt chart and Key Milestones

No	Detail Work	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	Project Work continues	🟦	🟦	🟦	🟦	🟦	🟦	🟦								
2	Submission of Progress Report								🟨							
3	Project Work Continues									🟦	🟦	🟦	🟦			
4	Pre-SEDEX											🟨				
5	Submission of Draft Report											🟨				
6	Submission of Dissertation (Soft Bound)												🟨			
7	Submission of Technical Paper												🟨			
8	Viva Oral Presentation													🟨		
7	Submission of Project Dissertation															🟨

🟦 Process 🟨 Suggested milestone

3.4 Computational Details

All computations were carried out using the Gaussian 03 Revision-B.03 suite of programmes implemented on a Dell computer. DFT calculations were performed by using a combination of the Becke’s three parameter hybrid exchange potential with the correlation functional of Lee et al. (B3LYP). The basis sets used were uniformly 3-21G.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Geometry Optimization

Job type: Optimization (TS Berny)
Method: DFT
Basis set: B3LYP 3-21G

The geometry for initial guess structure and the optimized geometry is shown in the table below. The output from optimization provides the optimized parameters i.e. bond length (R) and bond angle (A).

4.1.1 Geometry Optimization result for N_2H_2

Table 4.1 Geometry Optimization result for N_2H_2

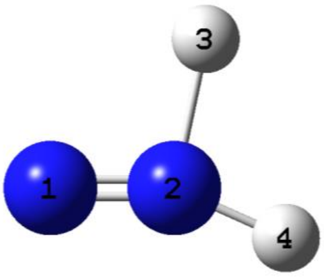
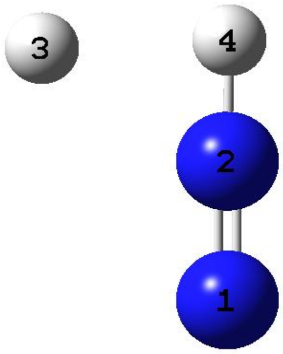
<table>
<tr><th colspan="2">Elementary step: $N_2 + H_2 \rightarrow N_2H_2$</th></tr>
<tr><td>Initial Guess Structure</td><td>Optimized Geometry</td></tr>
<tr><td>
</td><td>
</td></tr>
</table>

Table 4.2 Guess Parameters and Optimized Parameters (N_2H_2)

Name	Definition	Guess Geometry	Optimized Geometry
R1	R(1,2)	1.0920 Å	1.1622 Å
R2	R(2,3)	1.3400 Å	1.7714 Å
R3	R(2,4)	1.0800 Å	1.0139 Å
A1	A(1,2,3)	102.0000°	122.3053°
A2	A(3,2,4)	156.0000°	58.5559°
A3	L(1,2,4,3,-2)	180.0000°	180.0000°

4.1.2 Geometry Optimization result for N_2H_4

Table 4.3 Geometry Optimization result for N_2H_4

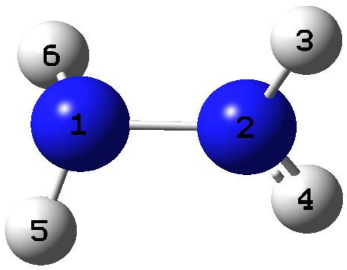
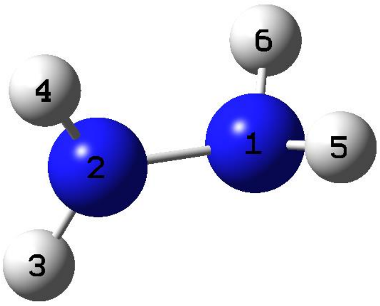
Elementary step: $N_2H_2 + H_2 \rightarrow N_2H_4$	
Initial Guess Structure	Optimized Geometry
	

Table 4.4 Guess Parameters and Optimized Parameters (N_2H_4)

Name	Definition	Guess Geometry	Optimized Geometry
R1	R(1,2)	1.4000Å	1.4150 Å
R2	R(1,5)	1.0000 Å	1.0243 Å
R3	R(1,6)	1.0000 Å	1.0243 Å
R4	R(2,3)	1.1300 Å	1.0062 Å
R5	R(2,4)	0.9100 Å	1.0121 Å
A1	A(2,1,5)	109.4710°	112.7523°
A2	A(2,1,6)	109.4170°	112.7524°
A3	A(5,1,6)	109.4170°	111.1521°
A4	A(1,2,3)	120.0000°	116.8875°
A5	A(1,2,4)	120.0000°	122.5488°
A6	A(3,2,4)	120.0000°	120.5636°
D1	D(5,1,2,3)	-150.0000°	-116.5599°
D2	D(5,1,2,4)	30.0000°	63.4401°
D3	D(6,1,2,3)	90.0000°	116.5564°
D4	D(6,1,2,4)	-90.0000°	-63.4436°

4.1.3 Geometry Optimization result for $2NH_3$

Several guesses of NH_3 transition state geometry were built for geometry optimization of $2NH_3$. However, all of the geometries could not be optimized. According to Hwang (2003), before the process can occur one of the hydrogen atoms has to be moved from one NH_2 group in hydrazine to another, thus releasing some room for the H_2 molecule to attack.

4.2 Frequency Analysis

Table 4.5 Thermochemistry data

	N_2H_2	N_2H_4
Zero-point vibrational energy	48884.4 (Joules/Mol) 11.68365 (kcal/Mol)	133907.1 (Joules/Mol) 32.00456 (Kcal/Mol)
Zero-point correction	0.018619 (Hartree/Particle)	0.051003 (Hartree/Particle)
Thermal correction to Energy	0.021649	0.054142
Thermal correction to Enthalpy	0.022593	0.055086
Thermal correction to Gibbs Free Energy	-0.003191	0.028484
Sum of electronic and zero-point Energies	-109.864051	-111.174243
Sum of electronic and thermal Energies	-109.861021	-111.171103
Sum of electronic and thermal Enthalpies	-109.860077	-111.170159
Sum of electronic and thermal Free Energies	-109.885861	-111.196761

CHAPTER 5

CONCLUSION AND RECOMMENDATION

This project research is carried out to discover the reaction mechanism of ammonia synthesis. Optimization and frequency were done for each elementary step proposed by Hwang and Mebel. Optimization to a transition state however is a bit challenging compared to minimum. To obtain a true transition state, it is important to have the correct initial guess for a molecule. A true transition state is indicated by having only one imaginary frequency. Therefore, it is also important to understand the geometry of the molecule studied.

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