Stimulation of Catalytic Activity of Transitional Metal Nitrides and Carbides

Brett John Cassidy

Submitted in fulfilment of the requirements for the Honours Degree of Engineering

In the discipline of Chemical and Metallurgical Engineering

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Author’s Declaration

I declare that the work contained in this thesis, submitted for the degree of Honours in Chemical & Metallurgical Engineering is my own account of my research except where due reference is made. The main content work has not been previously submitted for a degree at this or any other tertiary education institution.

Brett John Cassidy

Thesis Word Count

The total word count for this thesis project has included all major report chapters including the abstract; with the acknowledgements, references, appendices and contents components being omitted from the overall count. Breakdown of word count by chapter is as follows:

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Abstract

Current estimations show hydrogen production to be in excess of 55 million tonnes annually. With consumption growing globally by six percent annually, new feedstocks such as ammonia need to be explored to meet demand. Ammonia has many attractive characteristics as a source for hydrogen, such as its product stream when decomposed producing no carbon oxides or sulfurs. Research currently is limited on the decomposition of ammonia to produce hydrogen supported by transitional metal catalysts. This lack of research has suppressed the development of this technology. This thesis project is intended to develop on the original research conducted at the King Abdulaziz University where the development of high surface area molybdenum nitride was researched as a catalyst for the ammonia decomposition reaction to produce hydrogen.

The work completed in this thesis aims to capitalise on the findings in the original experiment by accurately determining the mechanisms and kinetics associated with the production of hydrogen. The modelling was separated into three distinct components which investigated the ammonia decomposition on a cobalt-molybdenum catalyst. The first component of the model was focused on optimising the surface which the mechanisms of the decomposition reaction would be situated on. The optimisation calculations found the (111) index to be the most stable of all the surfaces modelled. The data collected displayed a directly proportional relationship between the increasing number of atoms in the structure and its stability. The second component of the project modelled the ammonia decomposition mechanisms on the surface of the optimum (111) indexed surface. Multiple iterations were tested for different locations of the reacting molecule above the surface of the catalyst. The results from the optimised models found the desorption mechanisms were slightly more stable than the adsorption component of the decomposition reaction.

The concluding component of the model investigated the transient states associated with the ammonia decomposition reaction. Six transient states where identified, however only five could be modelled as a result of an atomic imbalance between the adsorption and desorption phases. Multiple transient states were calculated, with the rate limiting step determined to be the final desorption of the hydrogen molecule from the catalyst surface. From the transient state models it was determined that the Co$_3$Mo$_3$N catalyst was kinetically unsuitable for the ammonia decomposition reaction.
Acknowledgements

I would like to take this opportunity firstly to thank Dr Mohammednoor Altarawneh who has been the primary supervisor for the duration of this project. The support provided regarding training and technical issues have been vital to the success of this thesis project. The guidance and advice provided by Dr Altarawneh has been crucial in the completion of my penultimate year chemical and metallurgical engineering thesis. Associate Professor Gamini Senanayake has provided a great deal of expertise in assisting in the selection of this project and has assisted in multiple forms throughout the project, for which I am appreciative. Special thanks are due to Ibukun Oluwoye who provided the necessary modelling software programs required to complete this project. His assistance in the initial stages of the project in troubleshooting technical issues associated with the modelling software and catalyst files was vital to the timeline success of this project. Finally, to Murdoch University, particularly the Chemical Engineering department, I am indebted to for providing this opportunity to fulfil my honours requirements with this thesis project.
Contributors

Special mention has to be addressed to Mohammednoor for providing the command files for the supercomputer component of this project. The files were applied in the processing of the calculations which was of vital importance to the success of this project. Mohammednoor’s contribution to this work was critical to the development of the optimised surfaces and the transient state calculations.
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<th>Description</th>
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<tbody>
<tr>
<td>TOF</td>
<td>Turn over frequency</td>
</tr>
<tr>
<td>TPD</td>
<td>Temperature Programmed desorption</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Powder Diffraction</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon Nano Tube</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer Emmett Teller</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>STEM</td>
<td>Scanning Transmission electron microscopy</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy dispersive X-ray</td>
</tr>
<tr>
<td>CIF</td>
<td>Crystallographic Information File</td>
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</table>
Chapter 1

Introduction

The innovation of technology has played a critical role in the development and evolution of the energy sector we know today\[1\]. However, currently, the world still verges on crisis point concerning adequacy in supply at a low cost while mitigating the adverse environmental impacts. In the pursuit to combat climate change, cleaner methods in production and consumption of energy sources are required. The significant challenges prevalent require further innovation in areas such as research and development. The global energy deficit resides majorly on the substantial variation in country industrialisation, and as a result of this funding levels are skewed\[1\]. With the current situation of the energy sector yields the demands for newer, more sustainable sources of energy.

Hydrogen possesses the desired properties and has an adequate sized supply to resolve the current global energy demands. With hydrogen presenting itself as the future of energy, the only issue impeding its widespread use is finding a cost-effective method of producing it on a global scale. Hydrogen is currently produced for fuels and fertilisers on an industrial scale and is a crucial component to oil refining processes\[2\]. Hydrogen has an inability to exist in a free form; this is a result of its outer electron shell requiring another atom to fill it\[3\]. This physical characteristic of hydrogen results in the need for external intervention to remove the bound atoms to attain a combustible fuel source.

Conventional processing methods of hydrogen have been plagued with issues such as expense, efficiency, heavily polluting or a combination. As a result of supply and environmental concerns, fossil fuels can no longer be used in the production process of hydrogen; which leads to questions arising concerning how hydrogen can be produced efficiently enough to adequately quench the worlds energy needs\[4\]. Ammonia decomposition presents many advantages over more conventional hydrogen-producing techniques as the reaction does not produce CO\_2\[5\]. The reaction for the ammonia decomposition reaction is summarised as:

\[
2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2 \quad \Delta H = 11 \text{ kcal/mol.} \quad (1)
\]
The primary disadvantage of the ammonia decomposition method is the reliance on depleting catalyst supplies. The optimisation of catalyst performance through research is critical to the development of the ammonia decomposition method for producing hydrogen. The research conducted in the original experiment by S. Podila, S. Zaman, H. Driss, Y. Alhamed, A. Al-Zahrani and L. Petrov, investigated the optimisation of low-cost traditional metal nitrides for hydrogen production\[6\]. The research completed in this thesis aims to expand on the experimental information, through accurately replicating the result using modelling techniques.

Three distinct research components will take place in this project, the first being surface optimisation of the Co$_3$Mo$_3$N catalyst. The optimisation will investigate different surface cleavages of the catalyst, and use the modelling software packages; calculations were run using the supercomputer to determine their stability. The second component of this project investigates the mechanisms of the ammonia decomposition reaction by selecting the optimum surface derived from the previous component of the project. The mechanisms were optimised using the modelling software to be suitable for the transient state calculations in the final component of the project. The penultimate component to the project is the determination of the transient states of the mechanisms, where the results will be compared to literature, and used to determine the rate limiting step of the ammonia decomposition reaction from the activation energy data obtained.

1.1 Experimental Background

The research conducted in this thesis project seeks to expand on the information attained in an experiment conducted at the King Abdulaziz University in Saudi Arabia by [6]. The primary aim of the experiment was to develop a new method for the preparation of high surface area molybdenum nitride. Four high surface area bulk molybdenum nitride samples were prepared, with three samples containing 1, 3 and 5 by weight percent cobalt. The cobalt-containing catalysts were designated as 1CoMoN, 3CoMoN and 5CoMoN, respectively.

Catalytic activity measurements were taken from the sample using a quartz fixed bed reactor. The activity tests were conducted at atmospheric pressure with a 0.1 gram sample. Prior to the ammonia decomposition reaction, the catalyst samples were activated at 500°C under pure nitrogen flow for one hour. Once the activation phase of the
preparation was complete, the samples were then reduced with hydrogen for five hours, then flushed with nitrogen for an hour once again using the same conditions. Pure ammonia gas was fed into the reactor at 300°C, where the temperature was then increased stepwise at 50°C until steady state was achieved. The step changes occurred from 300°C to 600°C where steady-state conditions were achieved each time before the next step occurred. The determination of steady-state reaction conditions was achieved by conducting a percentage difference gas analysis. When the relative percentage difference remained less than 5 percent for two consecutive runs, the reaction was deemed at steady state.

The results from the experiments above show by adding controlled amounts of cobalt (1, 3, and 5 weight percent) during the catalyst preparation, resulted in no significant alteration to the surface area of the samples when compared to the untreated sample. Results from the data also indicated that the addition of cobalt promotes the formation of both γ-Mo₂N and Co₃Mo₃N phases simultaneously in the product of the reaction. BET surface area and XRD analysis on the samples showed an overall increase in the crystal sizes of the reduced and spent catalysts. The bulk MoN structure showed no new formation of phases in the catalyst structure, and the structure overall was maintained when comparing the used and fresh samples. The MoN sample diffractogram results show mainly γ-Mo₂N and MoO₂ formation. The MoO₂ crystalline phase was observed to slightly increase in the bulk sample. However, this increase was highly likely to be a result of the samples being exposed to air at the conclusion of the experiment.

SEM images of the 1CoMoN, 3CoMoN and 5CoMoN samples confirm an overall increase in the amount of γ-Mo₂N phase when compared to the bulk sample. The bulk MoN sample shows bigger MoO₂ crystals formed as determined by XRD analysis from the experiment. STEM-EDX results identified a uniform distribution of Co₃Mo₃N throughout the platelet; as the concentration of cobalt increased from zero to one percent, increases were also seen in the Co₃Mo₃N phase. When the concentration of cobalt increased from three to five percent, the Co₃Mo₃N and Mo₂N began to agglomerate. The activity at the higher temperatures did not impact the ammonia decomposition efficiency, as MoN at 600°C was found to be 99% effective. However, the 1CoMoN sample at 450-500°C saw a 10% increase in reaction conversion. The catalytic activity and conversion of NH₃ over the catalyst samples can be observed in Figures 8.1 and 8.2 in Appendix A. The activation
energies of the bulk, 1CoMoN, 3CoMoN and 5CoMoN samples was found to be 131.2, 99.7, 92.8 and 102.6 kilojoules per mole respectively. A promotional effect by the smaller dosages of cobalt was noticed in the samples. The TEM and SEM data shows the addition of cobalt reduces Co$_3$Mo$_5$N and γ-Mo$_2$N crystal formation and promotes the growth of γ-Mo$_2$N. These results are in agreement with the XRD results presented in Table 8.1 located in Appendix A, suggesting that the particle sizes of Co$_3$Mo$_5$N and γ-Mo$_2$N in the 5CoMoN sample are larger.

As no change was observed in the bulk γ-Mo$_2$N structure, this indicates a high level of stability of the γ-Mo$_2$N during the ammonia decomposition process. The increase in conversion was associated with the formation of Co$_3$Mo$_5$N species in the cobalt-containing samples. The 5CoMoN sample saw no changes in conversion when compared to the bulk MoN sample which can be attributed to larger Co$_3$Mo$_5$N crystals and γ-Mo$_2$N platelets. The 5CoMoN sample had a high activation energy as a result of the excess cobalt causing elevated active site blockages on the surface of the catalyst. The positive effect of cobalt has been associated with an increase in the Co$_3$Mo$_5$N and γ-Mo$_2$N active site formation. It was concluded that the introduction of cobalt increased the formation of both γ-Mo$_2$N and Co$_3$Mo$_5$N species. The results showed the sample with the addition of three weight percent cobalt had the most uniform distribution of γ-Mo$_2$N and Co$_3$Mo$_5$N structures in the product.

1.2 Modelling Background

Modelling and computer simulation has been utilised for scientific experimentation as far back as 1942, where it was applied in the Manhattan project[7]. Modelling of chemical reactions displays multiple advantages over physical experimentation processes. Modelling is not bound to the same set of conditions as a physical experiment is, which allows the model to include all the conditions without any simplification or scaling down[8]. A model of the reaction allows for a more significant number of samples to be processed at a lower cost as physical samples do not have to be prepared.

Concerning catalyst research, micro-kinetic models are an efficient and relatively inexpensive way to investigate catalysts[9]. Micro-kinetic modelling is a set of elementary reactions which depict an overall transformation. Screening of catalysts can be expensive and time-consuming. Modelling shows significant advantages with the ability to screen catalysts effectively for processes such as ammonia decomposition. Models can assist in
gaining significant information and insight, to help develop more suitable catalysts for reaction processes\cite{9}. Past micro-kinetic modelling of ammonia decomposition has been targeted at optimisation of the NH$_3$ conversion and how catalysis impacts this. The models developed have provided credible information to efficiently determine different catalysts suitability to a specific reaction. Such research has been conducted in \cite{10} where a Pt/Au(1 1 1) catalyst was modelled in comparison to pure platinum. Properties of catalysts used in the decomposition process have been investigated such as the turn over frequency and the interactions between the particles involved in the reactions\cite{10}.

Past modelling investigations have shown credibility in their results, which has opened opportunities for projects such as this one. The model being created for this project has the ability to confirm and elaborate on physical experimental data. The model used in this project can be utilised to determine multiple attributes of a catalyst. Models of the ammonia decomposition reaction are generally limited by simplicity, however, this model's primary advantage in this instance is its ability to assess multiple variations of the same catalyst, providing a significant level of detail to the project.

### 1.3 Research Scope

This thesis is intended to expand the research completed by S. Podila, S. Zaman, H. Driss, Y. Alhamed, A. Al-Zahrani and L. Petrov. The project will be investigating catalysis in the ammonia decomposition reaction for the purpose of hydrogen production. The project initially focuses on carbide and nitride catalysis in the ammonia decomposition reaction; however, the research is targeted towards the Co$_3$Mo$_3$N catalyst, as this catalyst was used in the original experiment conducted.

The scope of the modelling component of this thesis project has been restricted to just the Co$_3$Mo$_3$N catalysts over the (1 0 0), (1 1 0) and (1 1 1) index planes. The scope of the literature review will cover the hydrogen production field on a large scale and then become more targeted towards carbide and nitride catalysis in the ammonia decomposition reaction. The review will cover all relevant information on the catalysts, and research into their optimisation.
1.4 Research Aims

The primary aim of this project is to expand on the experimental results from [6] by accurately modelling the experiment using the Dmol³ (Materials Studio) and VASP software packages. The aim of the constructed model is to accurately determine the mechanisms and kinetics associated with the production of hydrogen from the ammonia decomposition reaction using the Co₃Mo₃N catalyst. The results from the model will be used to determine the rate limiting step of the ammonia decomposition reaction.

1.5 Research Objectives

The primary objectives of this thesis project have been summarised into the following:

• Assess the suitability of Co₃Mo₃N as a catalyst for the ammonia decomposition reaction, comparing the efficiency of the catalyst against relevant benchmarks in literature.
• Design an accurate and robust model which effectively provides credible results on the catalysed production of hydrogen from ammonia decomposition.
• To establish the reaction mechanisms operating in the conversion of ammonia over 4-d based catalysts.
• Improve the understanding of the key factors in which influence the ammonia decomposition reaction regarding catalyst performance.

1.6 Structure of Thesis

The thesis is structured into the following chapters:

• Chapter 1: Introduction - This section provides an overview of the topic and reasoning into the motives for the research.
• Chapter 2: Literature Review - Investigates areas of relevance to this thesis project looking specifically at the catalysis of the ammonia decomposition reaction
The review summarises the most up to research data in catalytic performance in hydrogen production.

- **Chapter 3: Experimental** - This section will contain technical details regarding the reaction modelling and processes used for this project.

- **Chapter 4: Surface Optimisation** - Develops surfaces through cleavage to be optimised. The energies of the surface specimens are then analysed and interpreted, where the results are then built on in later chapters of the project.

- **Chapter 5: Mechanism Optimisation** - This chapter builds on the data collected from the previous section and then provides details on the results used to optimise the mechanisms in the ammonia decomposition reaction.

- **Chapter 6: Transient State** - This chapter seeks to develop transient states by using the data from the previous Mechanism and surface optimisation sections. The models using the mechanisms are developed and interpreted in this section.

- **Chapter 7: Conclusions & Future Work** - Summarises the work modelling work which has been completed and draws conclusions from the previous chapters. The chapter then identifies areas from this project which can be further investigated and discusses areas of improvement on the research.

- **Chapter 8: Appendices** - Contains the majority of the figures and data tables from the modelling process, calculations related to the model and results from the original experiment.

### 1.7 References


Chapter 2

Literature Review

2.1 Abstract

Hydrogen poses significant potential in becoming a necessary tool in solving the world's clean energy issues. The industry has displayed steady growth over previous years and shows positive signs of continuing the trend into the future on the back of new technologies and research surrounding the industry. The current processes are limiting to the industry with pollutants being the major drawback for hydrogen being used more extensively in everyday energy applications. The ammonia decomposition method is relatively new to literature for hydrogen production. Ammonia decomposition methods offer significant advantages over more conventional hydrogen synthesis methods with many papers discussing catalysis as the main area of optimisation. Catalysis for ammonia decomposition is still extensively researched with experimental catalyst surfaces such as carbon nanotubes providing positive results in early stages of development. Scientific literature shows substantial evidence that in ammonia decomposition, carbide and nitride catalyst applications have real potential to replace the more expensive and commonly used platinum metal group catalysts. Current research shows the effectiveness of carbide and nitride catalysts in similar processes such as ammonia synthesis. Of the nitride and carbides; Mo₂N, Mo₂C, W₂C and Co₃Mo₃N show the most significant promise. However, ternary nitrides such as Co₃Mo₃N perform at a higher level and present as a suitable substitute for platinum metal groups.

2.2 Introduction

In the pursuit to combat climate change by finding cleaner and greener methods to use and produce fuels for energy, hydrogen has presented itself as the future of energy. Industrial production of hydrogen is a crucial component of many other industries such as fertilisers and the aerospace industry. Accounting for approximately 75 percent of the mass of the universe hydrogen is an essential part of our world as we know it. In recent years
the hydrogen industry has shown significant sign of expansion and grow due to the recent push in finding cleaner sources of fuels and reducing our reliance on hydrocarbons. Due to hydrogen's attractive combustive attributes, significant research has been undertaken to produce it on an industrial scale better. Hydrogen processing can exist in a variety of methods whom of which have been notoriously expensive, inefficient or heavily polluting. With a heavy reliance on fossil fuels for production, the industry has had to look for new methods and technologies to maintain the longevity of the industry. The majority of production methods will not be review extensively as the scope of this review will only focus on the ammonia decomposition methods.

Ammonia is an essential storage medium of hydrogen as it has a significantly high weight percent of hydrogen and when decomposed only H₂ and N₂ gases are produced. Scientific literature highlights the significant need for more research into decomposition methods of ammonia for hydrogen production in pilot plant or full-scale reactor scenarios as currently the industry is lacking credible information in this area. A vital component of the decomposition process is the catalysis involved which currently is significantly decreasing the growth and applications of the process. Carbides and Nitrides such as Mo₂N, Mo₂C and W₂C have been used extensively in many other industries to significant effect, with the universal application catalysis in the ammonia decomposition reaction is through platinum metals which come with a high cost making economic viability challenging to justify. Transition metal catalysts present with a lower cost and a higher effectiveness as a result of new research in tailor-made catalysts for the process being extensively conducted. There are a large number of studies still being currently conducted into catalysis optimisation using platinum group metals which will not be included in this review as metal nitrides and carbides are the main components.

The most substantial findings from research and literary works into catalysis for ammonia decomposition is produced from ternary metal nitride applications. Co₃Mo₃N has provided increasingly positive results in investigations with the addition of cobalt providing significant advantages over the standard two-component metal nitride and carbide catalyst. Limitations have been found with the addition of cobalt to the catalyst compound with an elevated sensitivity to change; however, the majority of results show the performance of the catalyst to be far superior others.
2.3 Molecular Modelling of Hydrogen Production

Molecular modelling’s purpose is to model or replicate the behaviour of molecules through theoretical and computational methods. The purpose of modelling is to study molecular systems without having to physically interact with them. These molecular systems can range from large biological assemblies through to small chemical systems. Modelling and simulation tools have great value as they reduce the overall number of physical test cases, significantly reducing the cost associated with test work\(^1\). The bridging of the gap between theoretical and experimental approaches is critically important in investigation and experimentation settings\(^2\).

At present, theoretical studies involving ammonia, a feedstock for the production of hydrogen, are limited\(^3\). Studies involving ammonia decomposition modelling have only been focused on the removal of the toxic ammonia traces which are deemed as a pollutant\(^4\). It has also been noted in literature that major gaps exist in terms of ammonia decomposition modelling/theoretical studies involving reactors, specifically multi-stage membrane reactors\(^5\). Currently, efforts are being made to develop and improve the performance of catalysts used in ammonia reaction processes such as decomposition and synthesis\(^6\). The catalyst materials being targeted for these investigations using models have been iron, nickel and ruthenium\(^7\)\(^8\). Studies into catalyst optimisation however is limited, with areas of expansion in terms of numerical simulation showing promising results\(^3\).

2.4 Hydrogen Production in Industry

The simplest and most abundant element on earth, hydrogen is always found as a part of another substance for example water. To date, the largest source of which hydrogen is produced from is fossil fuels via steam reforming which is explained later in this literature review. Estimations show that hydrogen production exceeds 55 million tonnes per annum with its overall consumption increasing by approximately 6 percent annually, as illustrated in \([9, \text{ Fig } 2.1]\) a linear increase in demand and supply for hydrogen both in domestic and international markets driven by the petroleum industry\(^9\). The figure also displays incremental increases specifically in hydrogen being supplied by industry; where hydrogen being produced internally by refineries themselves is holding steady.
Hydrogen, being used primarily as a reactant has fundamental importance industrially today, it is used to manufacture Methanol one of the most important compounds industrially. Its popularity is a direct result of its reactivity, which is why it has applications as an O₂ scavenger or in hydrogenation processes where the hydrogen atom can be used to lower the molecular weight of compounds and remove unwanted atoms such as nitrogen or sulfur\(^\text{[10]}\). This removal of undesired atoms is completed by inserting hydrogen to cleave the atoms away from the molecule. Its physical properties, however, are also favoured too in applications such as coolants in electrical generators and in combustion reactions where it is used as a fuel\(^\text{[10]}\). As a fuel, hydrogen is primarily utilised in the Aerospace industry as a hydrogen/oxygen mixture releases the highest energy to weight ratio as a propellant\(^\text{[11]}\).

The majority of hydrogen is used as a reactant in the chemical and petroleum industries where chemical production processes such as ammonia synthesis and hydrocarbon processing account annually for approximately 57 and 37 percent respectively; the consumption of hydrogen are displayed in [13, Fig 2.2]\(^\text{[12]}\). Due to tightening of environmental regulations the petroleum industry is anticipated to increase exponentially, thus increasing the demand for hydrogen. The primary source of the regulation tightening comes as a direct result of unit emissions and product specification as demand for lighter more concentrated hydrogen fuels is rapidly increasing.

**Figure 2.1:** U.S refinery demand for Hydrogen (2008-14)
Processing can be conducted in a hydrotreating unit, where typically preheated hydrocarbon and hydrogen feeds are reacted in the presence of a metal oxide catalyst, such as CoMo which is then converted to a metal sulfide\cite{14}.

![Figure 2.2: World consumption of Hydrogen by country in 2014 (%)\cite{12}](image)

### 2.4.1 Future of the hydrogen industry

Progressing into the future, as the world continues to transition towards a fossil fuel free future, demand for hydrogen technologies will increase as renewable resources are virtually inexhaustible\cite{15}. In its first widespread application, hydrogen is likely to supplement hydrocarbons in the transport industry as combustion fuels. This application is a result of hydrogen burning three times more efficiently than gasoline and produces fewer pollutants. The fossil fuel systems the new technology would be replacing emit pollutants such as CO, CO₂, SOₓ and NOₓ which are more damaging than those produced by renewable hydrogen systems in automobiles\cite{16}. Alternate industries where hydrogen could potentially find application is in the housing market providing energy for heating and cooling. The target for the Department of Energy in America is to substitute ten quads of energy annually by 2030, with one quad equalling the power consumption of one million households\cite{17}. In industry air pollution is a severe environmental and health issue.
throughout first world countries, but is especially acute in developing countries. For consideration of Hydrogen to be used as a viable replacement for fossil fuels it has to not only match the physical performance of fuels, it has to be financially feasible. Currently, financial feasibility is the most significant barrier for substitute fuels progressing in development and entering the marketplace\[18\].

Concerning performance, hydrogen releases approximately 2.75 times more energy than hydrocarbon fuels but is far less economical\[19\]. The increased expense is a direct result of hydrogen being a secondary energy source. Similarly to electricity, hydrogen it has to be manufactured and hence comes at an increased cost\[20\]. With the current technologies we have today for the production of Hydrogen, widespread use is approximately 15 years away before people will be able to economically justify it as a viable substitution fuel for hydrocarbon sources.

Globally the hydrogen market is worth over 40 billion US dollars with approximately 96 percent of all production coming from fossil fuel base reactants and undergoing conversion\[21\]. Referring to [20, Table 2.1], there is a significant dependence on fossil fuels and it is evident that renewable methods of production are lagging behind; accounting for only 4 percent of the market share. The main alternative methods of hydrogen production are listed below in figure [22, Fig 2.3] where it displays different combinations of primary energies which are compatible with production technologies\[20\].

Three hydrogen synthesis processes dominate the industry globally. Currently the most widespread method for low-cost mass hydrogen production is steam reforming with its principal advantage over other methods being its high efficiency with low operational and production costs\[23\].

**Table 2.1:** Annual global hydrogen production sources\[20\].

<table>
<thead>
<tr>
<th>Source</th>
<th>Billion Cubic Metres / year</th>
<th>Share (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural Gas</td>
<td>240</td>
<td>48</td>
</tr>
<tr>
<td>Oil</td>
<td>150</td>
<td>30</td>
</tr>
<tr>
<td>Coal</td>
<td>90</td>
<td>18</td>
</tr>
<tr>
<td>Electrolysis</td>
<td>20</td>
<td>4</td>
</tr>
<tr>
<td>Totals</td>
<td>500</td>
<td>100</td>
</tr>
</tbody>
</table>
Figure 2.3: Alternative methods of hydrogen production from energy sources.

The process entails two distinct stages, the first involving the blending of raw hydrocarbons with steam in the presence of a tubular catalytic reactor. The second stage extracts the cooled product gas which hydrogen and carbon dioxide gases are produced\textsuperscript{[24]}. A network of reforming reactions occur over the two process stages which are as seen in the below equations\textsuperscript{[25]}:

\begin{align*}
C_mH_n + mH_2O(g) & \rightarrow mCO + (m + 0.5n)H_2 \\
C_mH_n + 2mH_2O(g) & \rightarrow mCO_2 + (2m + 0.5n)H_2 \\
CO + H_2O (g) & = CO_2 + H_2 \\
CH_3OH + H_2O (g) & = CO_2 + 3H_2
\end{align*}

Two catalysts are employed for the process; these are classed as non-precious metals typically nickel and the precious metals such as platinum. Due to the kinetics of the process, the reaction is rarely limited by catalysis, which accounts for approximately five percent and so the cheaper nickel alternative is usually employed in most instances\textsuperscript{[25]}. 
One of the less popular, however still commonly used production methods is through Partial Oxidation known as POX. Concerning pollution, when compared and contrasted with the more conventional steam reforming; triple the amount of CO\(_x\) pollutants produced for the same volume of hydrogen gas produced. The non-catalytic POX process works by gasifying raw material in the presence of oxygen and/or steam at high temperatures, with the critical reaction progressions as follows\(^\text{[26]}\):

\[
\begin{align*}
\text{CH}_4 + \text{O}_2 & \rightarrow \text{CO} + 2\text{H}_2 \quad (5) \\
\text{CH}_4 + 2\text{O}_2 & \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \quad (6) \\
\text{CH}_4 + \text{H}_2\text{O} \,(g) & \rightarrow \text{CO} + 3\text{H}_2 \quad (7)
\end{align*}
\]

The POX process operations of the reactor are less expensive, however, the conversion which occurs post production makes the technology more expensive than steam reforming with a decreased yield. The process typically averages around a 60-75 percent conversion rate under normal operating conditions\(^\text{[27]}\). A variation of the POX process uses the addition of a catalyst commonly known as CPOX. The addition of a catalyst is targeted at lowering the overall operating temperature of the process. Temperature control is required as the nature of the reaction is exothermic and this can result in hot spot formation or other undesired anomalies\(^\text{[27][28][29][30]}\). Typically the catalyst used in the process is based around nickel or rhodium, however, due to rhodium’s high-cost and lack of financial viability, nickel is more commonly applied.

The final major method for hydrogen synthesis is Autothermal Reforming or ATR. This method consists of a hybrid between the CPOX and the steam reforming methods. The pairing of the two approaches forms a combination of endothermic and exothermic properties\(^\text{[31]}\). This combination provides an advantage over the other methods as the process does not require any external heat making it attractive from a cost-benefit perspective however its conversion efficiency is only 60-70 percent\(^\text{[32]}\). One last advantage over the other methods is its flexibility while operating as it has the ability to produce a significantly higher volume of hydrogen than the POX method while being able to start up and shut down very rapidly compared to the other methods\(^\text{[33]}\).
2.5 Ammonia Decomposition

Ammonia used as an alternative to fuels such as methane and other hydrogen-bearing compounds is preferred. The use of ammonia is attractive due to its eco-friendly burning capabilities. This preference is due to no CO\textsubscript{x} being produced from the combustion reaction, and any unconverted NH\textsubscript{3} from the initial reaction can be subsequently reduced significantly with the utilisation of an absorber\textsuperscript{[34]}. More conventional methods such as partial oxidation or steam reforming result in significant amounts of CO\textsubscript{x} being formed as a by-product of the reactions. Ammonia decomposition is a method where the resulting products from the reactions are hydrogen, nitrogen and some leftover ammonia reactant\textsuperscript{[35]}.

The decomposition proceeds by dehydrogenation initially, which is then followed by a recombination period where the nitrogen and hydrogen atoms combine to form H\textsubscript{2} and N\textsubscript{2} respectively. The overall binding energy of the nitrogen atom is paramount to the processes success as it must be sufficient enough to render the dehydrogenation successful but not overpowering. The nitrogen atom will otherwise not be able to recombine at the conclusion of the reaction to form N\textsubscript{2}\textsuperscript{[36]}. The decomposition process is a slightly endothermic reaction, with the following equations\textsuperscript{[35]}:

\begin{equation}
2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2 \quad \Delta H = 11 \text{ kcal/mol.} \quad (8)
\end{equation}

\begin{equation}
\text{NH}_3 \rightarrow \text{NH}_2 + \text{H} \rightarrow \text{NH} + \text{H} \rightarrow \text{N} + \text{H} \quad (9)
\end{equation}

The product stream from the reaction yields no carbon oxides or sulfurs making the Hydrogen produced free of difficult to remove impurities. The resultant products also bear a strong odour making leak identification/location relatively straightforward\textsuperscript{[37]}.

The main catalysts currently being researched are transition metal carbides and nitrides such as CO\textsubscript{3}Mo\textsubscript{3}N and W\textsubscript{2}C. Other transition metals such as nickel, iridium and ruthenium are also being extensively investigated to determine their effectiveness. The focus of all research in catalysts is directed at finding economical transition metal alternatives over the more expensive platinum group metal catalysts. Multiple investigations into these new technologies for catalysing reactions have occurred as currently, catalysts are at the
forefront of process improvements. The central theme coming from the literature/research being conducted is a demand for innovative catalysts in Ammonia Decomposition.

Ammonia contains more than any other organic carrier of hydrogen with 17.5 mass percent. It also possesses attractive characteristics such as a high energy density; and an abundant supply with fewer shortage issues and simple storage solutions[38]. Economics plays a vital role in the overall decision for choosing which methods to obtain hydrogen. Ammonia production is approximately one US dollar per kilogram, compared to hydrogen where it can be as expensive as five and a half US dollars per kilogram[39]. The general trend of scientific research into the Ammonia Decomposition method has been directed towards catalytic improvements and the removal of toxic ammonia traces as a pollutant released after the reaction[40][41].

Due to such a focused trend in research, a significant gap exists in studies which investigate using ammonia as a feedstock for hydrogen production[41][42]. The industry also requires more studies researching full-scale reactors and pilot plants as information on reactors is scarce. Research conducted by M. Abashar displays significant differences in the effectiveness of reactor choice in Ammonia Decomposition. Results show that the difference between a single fixed bed reactor (FBR) and a single fixed bed membrane reactor (FBMR) is 39.57 percent concerning exit ammonia conversion. Schematic representations of the FMBR reactor is shown in [43, Fig 2.4].

The Ammonia Decomposition reaction is reversible and endothermic. Chemical equilibrium according to the Le Chateliers principle is controlled by alterations in temperature, pressure and concentration. The research determined that when applying this principle, the ammonia conversion increases with increased temperatures, decreased pressures and removal of products[43]. Increases in temperature also resulted in improved kinetics, and hence increases in the rate ammonia being decomposed (rate of reaction)[43]. These conclusions mean that for FBR’s temperature control must be maintained as exceedingly high temperatures can result in catalyst destruction[43].
Figure 2.4: Two dimensional model produced for the theoretical modelling of Ammonia decomposition.

For the FMBR, an increase in pressure will cause an equilibrium shift to the right and left due to an increased permutation of hydrogen while simultaneously decreasing the number of moles to form ammonia\cite{43}. The following [43, Fig 2.5-2.8] display different configurations of reactors for comparison.

As displayed in Figure 2.5, the performance of the FMBR and FBR comparatively regarding exit ammonia conversion with the FMBR reactor significantly outperforming its counterpart\cite{43}. Figure 2.6 displays the relationship between reactor volume and temperature which results in reduced reaction kinetics when the reactor volume increases\cite{43}. In Figure 2.7, the hydrogen concentration profiles are displayed showing significant decreases in the concentration in the FBMR as the reaction proceeds through the length of the reactor\cite{43}. Polar to the FMBR, the FBR increases significantly due to its inefficient removal of hydrogen from the reaction media\cite{43}.
Figure 2.5: Conversion profiles of NH$_3$

Figure 2.6: Temperature profiles of reactors
Figure 2.7: Concentration profiles of H$_2$ in different reactors.

Figure 2.8: Effectiveness (reaction conversion) profiles of reactors.
Polar to the FMBR, the FBR increases significantly due to its inefficient removal of hydrogen from the reaction media\textsuperscript{[43]}. The effectiveness factors are displayed in Figure 2.8 which show at the beginning of the reaction both reactors have low effectiveness which indicates that the intra-particle diffusion has a significant impact on the overall reaction rate\textsuperscript{[43]}. This finding demonstrates that the reaction is diffusion limited.

In [35] the study focused on the metal catalyst used to enhance the reaction as a key finding was the profound role in which catalysis plays in the Ammonia Decomposition reaction. A quote from the paper describes the current state of research of catalysts in the Ammonia Decomposition process\textsuperscript{[35]}:

“Unfortunately, there has been no investigation that has systematically catalogued catalytic decomposition of ammonia on various supported metal catalysts for hydrogen production.”

Individual supports such as Silica and Alumina were used during the experimentation for the transition metal catalysts to be coupled together. Tests without the catalyst supports were also conducted, this added breadth to the experiment and baseline data for comparison purposes. For the reaction not to be mass-transfer limited at the high temperature of the experiment, the catalysts were ground to a 5 - 250 nm size range\textsuperscript{[35]}.

Referring to [35, Table 2.2], it displays the overall conversion of the decomposition and the formation rate of hydrogen with each catalyst paired with silicon oxide. The results clearly indicate ruthenium is the superior catalyst used in the experiment. Ruthenium is seen to have the advantage over the other sample for all temperatures tested in conversion and production rate. Furthermore, the ruthenium catalyst is also presented graphically by [35, Fig 2.9] displaying the ruthenium and its support iterations to determine the best support for the catalyst regarding turn over frequency (TOF). The figure shows the Silicon Oxide support significantly outperforms the alumina support once above 675 Kelvin. The worst performing catalyst in the experiment was nickel with only a maximum of 70 percent conversion in contrast to 99 percent of ruthenium.
Table 2.2: Conversion and formation rates for silica containing catalysts[35].

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>10% Ni/SiO₂</th>
<th>65% Ni/SiO₂/Al₂O₃</th>
<th>10% Ir/SiO₂</th>
<th>10% Ru/SiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conv. (%)</td>
<td>Rate(H₂) (mmol/min g_cat)</td>
<td>Conv. (%)</td>
<td>Rate(H₂) (mmol/min g_cat)</td>
</tr>
<tr>
<td>673</td>
<td>1.4</td>
<td>0.44</td>
<td>3.5</td>
<td>1.1</td>
</tr>
<tr>
<td>723</td>
<td>4.2</td>
<td>1.3</td>
<td>9.3</td>
<td>2.9</td>
</tr>
<tr>
<td>773</td>
<td>10.5</td>
<td>3.3</td>
<td>21.7</td>
<td>6.8</td>
</tr>
<tr>
<td>823</td>
<td>21.6</td>
<td>6.8</td>
<td>48.7</td>
<td>15.2</td>
</tr>
<tr>
<td>873</td>
<td>36.4</td>
<td>11.4</td>
<td>79.5</td>
<td>24.9</td>
</tr>
<tr>
<td>923</td>
<td>70.0</td>
<td>21.1</td>
<td>97.0</td>
<td>30.3</td>
</tr>
<tr>
<td>973</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The paper shows credible research into its conclusions from its investigation into transition metals being used as catalysts for hydrogen production. The main finding of the experimentation was that ruthenium significantly outperformed the nickel and iridium catalysts. One other significant discovery was that the catalyst supports played a crucial role in determining the activity of the catalysts. This paper provides many areas for further research such as; new catalyst materials, surface cleavage iterations, increased testing parameters for temperature and incorporating the cost of the material as an influence on its overall effectiveness.

Figure 2.9 Catalyst turnover frequency as a function of temperature
The article provides strong baseline information into the effectiveness of transition metals being used as catalysts in the Ammonia Decomposition process. It provides reliable depth of research conceding the variations of catalyst support, with three for each transition metal, being; Silicon Dioxide, Alumina and a control sample. The experiment also provides a reliable amount of data iterations at different temperatures which provide substantial credibility to the results and allowing clear distinctions to be made about the integrity of each catalyst. The experiment procedure, however, lacks breadth in its temperatures chosen to conduct the research, and catalyst variations which detract from the effectiveness of the results. This lack of range in the temperatures tested prevents determination of the temperature range from which the optimum amount of conversion occurs. The shortcoming prevents the sensitivity of the catalyst to the temperature change from being determined. Temperature determination is incredibly useful for industrial applications as temperatures commonly fluctuate. The literature also failed to explore the variations of the catalyst surfaces and materials, which could potentially further improve the catalyst potential. Other catalysts such as molybdenum nitrides, carbides and tungsten based catalysts could be extensions on for further experimentation and comparison. The only surface explored was (1 0 0), this limits the results but allows the potential for follow-up studies to occur relating to how the surface cleavage could be a means for further optimisation.

Research conducted by [44] investigates the suitability of monolayer bimetallic catalysts in the Ammonia Decomposition reaction. The research is being carried out on this specific type of catalyst as there was a hole in literature where there was no rational method for producing these specific kinds of catalysts. For the experiment the overall ammonia decomposition process was deconstructed and modelled with 12 reaction steps, these elementary steps are as follows;

\[
\begin{align*}
    \text{NH}_3 + \ast & \rightarrow \text{NH}_3^\ast \quad \text{(10)} \\
    \text{NH}_3^\ast & \rightarrow \text{NH}_2 + \ast \quad \text{(11)} \\
    \text{NH}_3^\ast + \ast & \rightarrow \text{NH}_2 + \text{H}^\ast \quad \text{(12)} \\
    \text{NH}_2 + \text{H}^\ast & \rightarrow \text{NH}_3^\ast + \ast \quad \text{(13)} \\
    \text{NH}_2 + \ast & \rightarrow \text{NH}^\ast + \text{H}^\ast \quad \text{(14)} \\
    \text{NH}^\ast + \text{H}^\ast & \rightarrow \text{NH}_2 + \ast \quad \text{(15)} \\
    \text{NH}^\ast + \ast & \rightarrow \text{N}^\ast + \text{H}^\ast \quad \text{(16)}
\end{align*}
\]
The bimetallic catalysts consist of a monolayer of an admetal on the top layers of the host metal which makes up the bulk of the structure. The admetal has two variations where it can be found on the surface or below the initial layer of the structure when it forms a subsurface. The two structure variations investigated in the experiments, with findings showing different properties from one another when attached to the same parent metal. Results from the research show that ruthenium outperforms the other catalysts with approximately 10% conversion of ammonia and is closely followed by the cobalt and rhodium catalysts\[45\]. The peak nitrogen binding energy was found graphically to be approximately 134 kcal mol\(^{-1}\) in the research, where the value is then used to identify surfaces with desirable catalytic activities. The data was then used in a sensitivity analysis which found the rate determining step to be the removal of the second hydrogen from equation (14) when the nitrogen binding energy was less than 125 kcal mol\(^{-1}\). When the energy was above 125 kcal mol\(^{-1}\), the rate determining step was also found to be equation (14).

The paper also diverges its focus towards the configuration of the catalyst, and the effects it incurs on the bond length and the binding energy. [44, Table 2.3] depicts the difference between different catalyst constructions on a \((1 1 1)\) surface and their impacts on bond length and binding energy.
Table 2.3: DFT binding energies and bond lengths of nitrogen atoms on monolayer bimetallic surfaces

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Metal (111) surface</th>
<th>$N_2$ binding energy (kcal.mol$^{-1}$)</th>
<th>Bond Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Subsurface</td>
<td>Pt-Ti-Pt</td>
<td>70.7</td>
<td>1.975</td>
</tr>
<tr>
<td></td>
<td>Pt-V-Pt</td>
<td>81.0</td>
<td>1.975</td>
</tr>
<tr>
<td></td>
<td>Pt-Cr-Pt</td>
<td>76.3</td>
<td>1.965</td>
</tr>
<tr>
<td></td>
<td>Pt-Mn-Pt</td>
<td>77.6</td>
<td>1.968</td>
</tr>
<tr>
<td>Single Metal</td>
<td>Pt-Co-Pt</td>
<td>83.4</td>
<td>1.964</td>
</tr>
<tr>
<td></td>
<td>Pt-Ni-Pt</td>
<td>87.5</td>
<td>1.941</td>
</tr>
<tr>
<td></td>
<td>Pt</td>
<td>102.1</td>
<td>1.954</td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>113.8</td>
<td>1.770</td>
</tr>
<tr>
<td></td>
<td>Ni-Pt-Pt</td>
<td>130.7</td>
<td>1.761</td>
</tr>
<tr>
<td>Surface</td>
<td>Co-Pt-Pt</td>
<td>126.5</td>
<td>1.780</td>
</tr>
<tr>
<td></td>
<td>Fe-Pt-Pt</td>
<td>134.1</td>
<td>1.864</td>
</tr>
<tr>
<td></td>
<td>Mn-Pt-Pt</td>
<td>207.2</td>
<td>1.854</td>
</tr>
<tr>
<td></td>
<td>Ti-Pt-Pt</td>
<td>176.1</td>
<td>1.918</td>
</tr>
</tbody>
</table>

The data displays a significant spread of energies from 70.7 kcal mol$^{-1}$ from the Pt-Ti-Pt formation to 207.2 kcal mol$^{-1}$ from the Mn-Pt-Pt catalyst. The experimental results from [44] show that the surface is still active at temperatures as low as 325 Kelvin, and highlights the reduction in $\theta N$ as the temperature decreases. The experiment's findings were able to support the first computational framework proposed, which was that bimetallic catalysts were able to be screened using binding energies from DFT calculations. The calculations used were on first principles from microkinetic models. The experimental component of the research found that the Ni-Pt-Pt catalyst was more active than the Ru-based structure, based on a lower nitrogen disruption temperature and a lower dehydrogenation barrier. The modelling concluded that Ammonia Decomposition could occur at temperatures at or below 600 Kelvin. Finally, the paper was able to sufficiently predict how active the Ni-Pt-Pt surface was using TPD and HREELS (High-Resolution Electron Energy Loss Spectroscopy) to collect measurements for confirmation.

The article provides a comprehensive view of bimetallic catalysts and their appropriateness for use in producing hydrogen from Ammonia. The modelling and physical
experimenting, supported by past data provided a robust and well-developed collection of results. The article has a few areas for future research and elaboration such as; surface development and process kinetics as the study failed to venture further into that domain. The cleavage of the surfaces could be altered in future works looking at the effect on bimetallic catalyst performance. A shortcoming with the experimentation was the reliance on platinum for the surface compounds used, as 15 of the 16 surfaces contained the metal. Other transition metals should have also been trialled to provide more breadth to the metal surfaces used. The method given by the article was underdeveloped as it lacks specific details critical for replication. The missing information in the method makes a possible replication of the experiment challenging to achieve. 

In early 2004 several research papers were released using Ammonia for Hydrogen production. Article [46] attempts to address current gaps found in the literature relating to catalyst activity in Ammonia Decomposition when the reaction temperature is under 600˚C. The research is targeted at identifying catalysts which are stable and have a high activity at lower than typical temperatures for hydrogen production from Ammonia. The results of the experiments found that using the carbon nanotube (CNT) as a catalyst support outperformed all the other metal oxide supports examined. The CNT had the highest activity as a combined result of high dispersion of Ru and the low impurities found in the CNT.

**Table 2.4:** NH\textsubscript{3} decomposition over supported 5wt.\%-Ru catalysts data
The high dispersion of the Ru was found to be a direct result due to the large surface area caused by the CNT as the size of the Ru particles in the tubes are restricted. The stability of the CNT was also proven experimentally with the performance of the Ru/CNTs and K–Ru/CNT’s remaining steady over the ten hour period. Visible structural differences can be noted between the catalysts, especially the CNT when compared to the other metal oxides.

Table 2.4 displays the Ammonia conversion percentages at varying temperatures from the experiment\textsuperscript{[46]}. The tables show that the K-Ru/CNT ‘hybrid’ catalyst was the best performing with 97.3 percent conversion at 450˚C, 53.6 percent more conversion than the next best catalyst which was another CNT support. It is evident from this results table that the CNT supports provide a much higher conversion than that of the metal oxide supports. Of the stand-alone Ruthenium catalysts, the CNT supported specimen was the best performing across the board due to the large surface area caused by the support which is demonstrated by the increased activity and hence a better conversion percentage. XRD data from the research indicates the CNT support has no high levels of dispersion, this is a result of the high purity of the support and the high graphitisation.

![NH3 Conversion Graph](image)

**Figure 2.10:** Comparison of the effect of KOH modification on the catalysts.
The addition of Potassium to form the K-Ru/CNT ‘hybrid’ catalyst significantly improves the performance of the catalyst. [46, Fig 2.10] graphically supports the data found in Table 2.3 which shows the K-Ru/CNT’s significantly outperforming other catalyst supports, even at temperatures under 450°C where typically the conversion is not high. The high level of graphitisation results in a high efficiency of electron transfer from the promoter to Ruthenium atom. Due to the increased efficiency, it is thought one of the slower kinetic steps in nitrogen atom desorption is increased[47]. The graph shows the increasing trend of Ammonia conversion which is directly proportional to the temperature of the reaction. The literature provides information and answers on catalyst supports which did not exist in the scientific community. The work conducted shows that catalyst supports have many avenues to explore in the sense that CNT’s provide significant opportunities for improvement in catalyst stability and activity. The paper fails, however, to link theoretical information with the physical information presented. The Potassium modification made of the Ru/CNT catalyst forming the K-Ru/CNT ‘hybrid’ lacks a theoretical explanation as to why such a large performance improvement is recorded.

The research also requires follow-up experimentation as the data points for temperature are very small for each catalyst support and as a result has a high uncertainty value. The future research should look more specifically at the K-Ru/CNT and other ‘hybrids’ and focus on ways to gain increased performance at lower temperatures. The literature also has a shortcoming in explaining why there is an increase in stability of the CNT catalysts and how the stability compares with the other metal oxide catalysts. In further work, exploration of other transition metals such as molybdenum are avenues for exploration due to the high cost of Ruthenium. The price of ruthenium in a large scale setting is not sustainable, and substations need to be found.

2.6 Catalysis of Metal Nitrides & Carbides

Metal Nitrides & Carbides in recent years have been identified as the key research area for replacing conventional catalysts in reactors[48]. Over the last decade, major strides have been taken in developing technologies for the hydroprocessing industry. Molybdenum-based solids have received the most attention by researchers however limited experimental evidence is available to show that nitrides or carbides provide any advantage over one another. [49, Fig 2.11a & 2.11b] displays the crystallographic structure
of Mo$_2$N & Mo$_2$C catalysts where they share many similarities with one another. When compared to other molybdenum-based catalysts such as Mo$_2$S they show no resemblance at all. In [50, Fig 2.12a & 2.12b] it indicates that the heat of formation of both metal carbides and nitrides from group IV to VIII decreases significantly as the group increases. The figure shows that Mo$_2$N & Mo$_2$C have significantly lower formation energies than the majority of the other compounds with Mo$_2$N being approximately double that of Mo$_2$C. Both catalysts provide resistance against reduction with Mo$_2$N being the more stable catalyst of the pair. However, both structures are susceptible to sulfidation as there is a significant driving force present. Concerning [51, Table 2.5] the sulfidation can be minimised significantly if hydrogen gas is present due to it being produced by reactions (3) and (4),
hence reducing the driving force. Table 2.5 also displays the sulfidation may be reduced due to the presence of NH₃ and hydrocarbons. The table also suggests that in reaction five the combination of NH₃ and H₂ could result in the Mo₂C catalyst being converted into Mo₂N. For this to occur in a real-life situation, a sufficient amount of nitrogen-containing compound would have to be present in the feed for conversion of the catalyst to be feasible.

The paper [52] investigates two main areas, the first being carbon monoxide hydrogenation over different surfaces of Mo₂C(hcp), Mo₂C(fcc) and Mo₂N(fcc) catalysts. The three catalysts were characterised after three main stages of the experiment; synthesis, pretreatment and exposure to reaction conditions. The characterisation methods/techniques employed were as follows; XRD, elemental analysis, transmission electron microscopy, BET surface area measurement and CO chemisorption. When
observing [52, Fig 2.13] it shows a relatively slow approach to the steady state value for the MoN$_2$ catalyst, whereas the other carbide catalysts approach the steady state activities more aggressively and with more energy. For the Mo$_2$N catalyst, it achieved steady state kinetics after 16 hours, a notable difference is that the Mo$_2$N catalysts activity does not go through a maximum before reaching steady state like the other catalysts did.

![Graph showing steady state activity approach](image)

**Figure 2.13:** Steady state activity approach for CO hydrogenation over Mo$_2$N(fcc)

Referring to [52, Table 2.6] it is evident in the results that the Mo$_2$C(hcp) structure is half as active as the Mo$_2$C(fcc) and MoN$_2$(fcc) surfaces. MoN$_2$ was the most active catalyst with a value of 50.1 s$^{-1}$ and throughout all the results had almost identical selectivity values to the Mo$_2$C(fcc) catalyst.

**Table 2.6:** Activities and selectivities of Mo$_2$C(hcp), Mo$_2$C(fcc), and Mo$_2$N(fcc) for CO hydrogenation

<table>
<thead>
<tr>
<th></th>
<th>Mo$_2$C(hcp)</th>
<th>Mo$_2$C(fcc)</th>
<th>Mo$_2$N(fcc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_{CH4} \times 10^3$ (s$^{-1}$)</td>
<td>27.4</td>
<td>46.0</td>
<td>50.1</td>
</tr>
<tr>
<td>$S_{CH4}$ (%)</td>
<td>76.9</td>
<td>83.7</td>
<td>83.5</td>
</tr>
<tr>
<td>$S_{C2H4}$ (%)</td>
<td>5.2</td>
<td>1.2</td>
<td>1.5</td>
</tr>
<tr>
<td>$S_{C2H6}$ (%)</td>
<td>15.6</td>
<td>14.3</td>
<td>14.0</td>
</tr>
<tr>
<td>$S_{C3H6}$ (%)</td>
<td>1.1</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>$S_{C3H8}$ (%)</td>
<td>1.3</td>
<td>0.9</td>
<td>1.0</td>
</tr>
</tbody>
</table>
At the conclusion of the experiment, the catalysts were sampled with the Mo$_2$N structure showing no loss of nitrogen due to contact with the synthesis gas; the findings were determined to utilise an elemental analysis. The results indicate however oxygen and carbon accumulation is occurring, but the X-ray diffraction pattern suggests that the bulk of the structure continues to remain as MoN$_2$ with no new phases forming. The two carbide catalysts increase substantially over time as a direct result of oxygen being removed progressively from the lattice as the reaction progresses. Of the carbide structures, the (hcp) surface is almost 200 fold more active than the ccc surface over the duration of the reaction than the (fcc) surface. This difference is attributed to the principal surface present in each of the phases through the process.

The article is one of the first major research works contributed to the scientific community relating to nitrides and carbides being used for catalytic applications. The literature provides well-represented data using multiple methods to gain accurate findings. The work convincingly provides substantial evidence towards the case of the ability of carbides and nitrides to be used as catalysts. Of the carbide surfaces from the data and arguments provided it is straightforward to conclude that the Mo$_2$C(fcc) catalyst for the carbides was superior in carbon monoxide hydrogenation. In the C$_2$H$_6$ hydrogenolysis, the Mo$_2$C(hcp) was the preferred catalyst after displaying it was multiple times more active in the reaction. The major shortcoming from the paper was the failure to include a second MoN$_2$ catalyst surface to compare the results to the (fcc) surface used in the experiments. With the addition of the other surface, strong correlations could be made between the two classes of catalysts in carbides and nitrides. The optimum catalyst class could be then determined for the two different reactions included in the experiment, and better comparisons could be made in catalyst performance. Another area of research-extension could be experimenting with more than just the (fcc) and (hcp) surfaces, allowing for more variation in the catalyst surface. Varying the transition metal in which the nitride and carbide are bonded to could also be another domain of exploration with investigations to see if Molybdenum is the best-suited metal in the compound.

Similarly to platinum, molybdenum nitride shares many characteristics as a catalyst with many critical applications, including NO$_x$ reduction, hydrogenation and hydro-desulphurisation$^{[53]}$. Applications have been found in hydrogen production from ammonia decomposition where research is finding it can outperform platinum group catalysts while
being more economical. Recent studies [54] have found that the most stable facet was a nitrogen truncated surface which was along the (111) index. The research details the optimised geometry of the y-Mo$_2$N(111) surface which is composed of four layers of two by two unit cells with five distinct adsorption sites being determined by the work[54]. The article [54] presents that total hydrogen uptake from the y-Mo$_2$N catalyst is approximately 10 percent of the total surface area and that the method of adsorption is via the homiletic disassociation pathway. Once the y-Mo$_2$N surface becomes covered in nitrogen atoms, the catalytic reactivity will decrease significantly.

Due to the high bond strength which N$_2$ posses bonds with it highly unlikely that y-Mo$_2$N will de-catalyse when exposed to nitrogen in the atmosphere. The catalyst can be converted into an oxynitride in the form of Mo$_2$N$_x$O$_y$ when y-Mo$_2$N is exposed to the atmosphere, in particular, atmospheric oxygen[54]. It has been extensively reported in the literature that the surface terminations are a vital determinate of the products and the reaction rates[55]. Results from the article highlight y-Mo$_2$N(111) having a high affinity for oxygen which can bond to the vacant nitrogen site and ultimately hindering the overall performance of the catalyst. Future developments of y-Mo$_2$N research are extending into experimental proof of the effects of surface termination on the activity of the catalyst[53].

2.6.1 Catalysis featuring Mo$_2$N, Mo$_2$C and W$_2$C structures

It has been documented in the literature of the important role played by metal nitrides in the decomposition of ammonia. The importance is a result of the adsorption and desorption of nitrogen is a rate-limiting step in the decomposition reaction[56]. Theoretical calculations were conducted in [57] which showed that nitrogen had a more significant affinity towards the edges for the surfaces. The two rate-limiting steps in the ammonia decomposition reaction; ‘synthesis’ (N$_2$ dissociation) and ‘decomposition’ (nitrogen recombination) are related to the interactions which occur between the active surface site on the catalysts and the N atoms[58].

It has also been reported that the performance of a bimetallic surface in the decomposition reaction can be accurately predicted from the binding energies from DFT calculations. The calculations are supported/guided from the first principle based microkinetic models[59]. From the theoretical calculations in [57], the binding energy of N was stronger over MoN
than it is over Mo$_2$C, this finding then supports the conclusion that the Mo$_2$C catalyst will be more active than the former due to more active sites being present during the reaction. The findings showed that the Mo$_2$C tended to form MoN under a pure ammonia atmosphere at high temperatures. This formation occurred after the NH$_3$ molecule was cracked and resulted in a significant drop in the surface area of the catalyst$^{[57]}$. A central finding in the literature was that nitrogen atoms usually take a position on the subsurface of the Mo$_2$C catalyst, which results in the progressive formation of Mo$_2$N. The EELS analysis supports this finding, which MoN is more dominant on the surface than the bulk$^{[57]}$. 

Tungsten carbide was first discovered in the early nineteen seventies to have platinum like properties$^{[60]}$. When used as a catalyst, W$_2$C exhibits favourable properties such as; a high electrical conductivity of 10$^5$ S cm$^{-1}$ at 20ºC, and strong conductive displacing attributes. When paired to another catalyst can improve the overall electrical conductivity, the ion diffusion performance and the electrochemical properties of the final catalyst hybrid$^{[61]}$. In the article [62], tungsten carbides being used as a catalyst for the decomposition of hydrazine for space applications were found to be efficient in the decomposition of the hydrazine compound. The graph [62, Fig 2.14] displays that the WC$_x$O$_y$ catalyst (1) outperforms the conventional iridium catalyst (2) in catalytic decomposition. Figure 2.14

![Figure 2.14: Thrust comparison between tungsten (1) and iridium (2)](image-url)
also indicates that as time extends in the reaction, the discrepancy in the two catalysts performances increases with tungsten performing better for longer. Tungsten carbide materials since the discovery of their attractive properties for catalysing reactions have shown great potential to act as a substitute for noble metals as catalysts in chemical processes[63].

When acting as a catalyst support tungsten carbides low surface area assists in significantly improving the hydrogen productions activity, which was found in [64] where the activity of MoS$_2$ increased abundantly. The results of the experiment also found when W$_2$C was incorporated as a catalytic support the activity increased due to more active sites being present for the hydrogen evolution to occur. The activity also increased secondly due to the promoted electron transfer rate which was directly attributed to the addition of the tungsten[64].

2.6.2 Catalysis featuring Co$_3$Mo$_3$N

In recent years, it has been reported that ternary metal nitrides such as Co$_3$Mo$_3$N have displayed high activity traits experimentally[65]. This high activity has attracted significant attention from researchers, which has found that the activity from Co$_3$Mo$_3$N is greater than the conventional iron-based Haber-Bosch catalyst[65]. [66, Table 2.7] presents data from ammonia synthesis where different Co$_3$Mo$_3$N based catalysts are used. The results are compared to the iron-based Haber-Bosch catalyst, which performed worst overall concerning the rate of Ammonia Synthesised. The tables also presents evidence to support that specific variations of the Co$_3$Mo$_3$N catalyst resulted in vast improvements in the production of Ammonia such as Co$_3$Mo$_3$N-Cs$_2$ with 652 $\mu$mol h$^{-1}$ g$^{-1}$ 986 $\mu$mol h$^{-1}$ g$^{-1}$ rates respectively. The increase in catalyst production can be attributed to Cs$^+$ as it has been found to be a promoter. The promoter characteristics, however, only exist up to an absolute limit as once reached the catalyst will begin to decompose[65].

In [66], Norskov's work on the Co$_3$Mo$_3$N catalyst explains the increased activity as a result of the binding energies of the compound. The theory suggests that the average N$_2$ binding energies for cobalt occur too weakly, where the molybdenum atoms in the compound are bound too strongly. The dissociation of N$_2$ is often referred to as the rate-limiting step, and it is argued in the literature, that for the catalyst to be effective, the components must be
nearby regarding binding energy. The (1 1 1) surface plane of the catalyst exhibits a consistent mixture of molybdenum and cobalt sites. The theory gained support from microkinetic studies provided by the authors, where the activation energy between the molybdenum and cobalt atoms was discovered to be intermediate.\[67\]

Table 2.7: Various Catalyst Data For Ammonia Synthesis

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Rate (μmol h(^{-1}) g(^{-1}))</th>
<th>Surface area (m(^2) g(^{-1}))</th>
<th>Specific activity (μmol h(^{-1}) m(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-K(_2)O-Al(_2)O(_3)</td>
<td>330</td>
<td>14</td>
<td>24</td>
</tr>
<tr>
<td>Co(_3)Mo(_3)N</td>
<td>652</td>
<td>21</td>
<td>31</td>
</tr>
<tr>
<td>Co(_3)Mo(_3)N-K5</td>
<td>869</td>
<td>17</td>
<td>51</td>
</tr>
<tr>
<td>Co(_3)Mo(_3)N-K30</td>
<td>364</td>
<td>8</td>
<td>46</td>
</tr>
<tr>
<td>Co(_3)Mo(_3)N-Cs2</td>
<td>986</td>
<td>16</td>
<td>62</td>
</tr>
<tr>
<td>Co(_2)Mo(_2)N-Cs10</td>
<td>586</td>
<td>10</td>
<td>59</td>
</tr>
</tbody>
</table>

Co\(_3\)Mo\(_3\)N is suggested in the literature as one of the most dominant active phases of Co-Mo catalysts.\[68\] As described in the article [3], catalysts are commonly used in the presence of hydrogen with such cases being desulphurisation where cobalt-molybdenum catalysts are preferred. From thermodynamic calculations on ammonia decomposition, it is theoretically possible to achieve 99 percent conversion with one atmosphere of pressure at 400°C.\[69\] Co\(_3\)Mo\(_3\)N being used as a catalyst in ammonia decomposition is a relatively new concept as ternary nitride systems have only recently themselves attracted attention to areas such as ammonia synthesis.

In the article [68], investigations are undertaken looking specifically at optimisations of Co\(_3\)Mo\(_3\)N, MoN (Mo\(_2\)N) catalysts involved in ammonia decomposition. Findings show that the introduction of cobalt in the formation of the molybdenum catalysts promotes the formation of both y-Mo\(_2\)N and Co\(_3\)Mo\(_3\)N simultaneously.\[68\] It has also been discovered that the cobalt introduction leads to substantial increases in the intensity of the molybdenum catalysts.\[68\] XRD analysis images from [68] shows an increase in the concentration of cobalt from one percent, through to 5 percent which has a significant impact on the structure of the compound. The experiments conducted using Co\(_3\)Mo\(_3\)N and MoN showed that the former slightly outperformed the later with 98.3 and 97.2 percent conversion of ammonia respectively at 600°C. The addition of cobalt to the compounds saw a significant decrease in the activation energies and suggest promotion influences from the cobalt.\[68\] A
threshold for the addition of the cobalt was discovered as the activation energy of the three percent structure was 92.8kJ mol⁻¹, and the five percents sample was 102.6kJ mol⁻¹ [68]. The increase in activation energy was directly attributed to the increase in cobalt concentration as the excess addition caused an increase in the crystal size.

Concerning the data in [68, Table 2.8] it collates data from a significant portion of experiments relating to catalysts in ammonia decomposition looking at the conversion effects each has. The Co₃Mo₃N catalyst features as one of the more promising compounds as it is in the upper quartile of conversion results. The results from [68] found that the best performing concentration was three percent cobalt regarding conversion and H₂ formation rate. All the samples apart from the five percent sample had reached equilibrium by the one hour mark of the reaction, whereas the five percent sample continued to react for the full thirty hours of the experiment. The increased cobalt lead to the decrease in catalytic performance due to the resulting agglomeration which was noted on the XRD images. The agglomeration resulted in the deactivation of the catalyst and hence resulting in decreased conversion and production rate [68].

### Table 2.8: Catalytic Activities of Different Catalysts For NH₃ Decomposition

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Metal Loading (wt%)</th>
<th>GHSV, h⁻¹</th>
<th>Temperature (°C)</th>
<th>NH₃ Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru/CNT</td>
<td>5</td>
<td>30000</td>
<td>500</td>
<td>100</td>
</tr>
<tr>
<td>CoMo/Al₂O₃</td>
<td>5</td>
<td>36000</td>
<td>600</td>
<td>99.0</td>
</tr>
<tr>
<td>Co₇Mo₉/MCM-41</td>
<td>5</td>
<td>36000</td>
<td>600</td>
<td>99.2</td>
</tr>
<tr>
<td>MoN/Al₂O₃</td>
<td>12</td>
<td>3600</td>
<td>600</td>
<td>75.2</td>
</tr>
<tr>
<td>MoN/SBA-15</td>
<td>12</td>
<td>15800</td>
<td>650</td>
<td>100</td>
</tr>
<tr>
<td>Co₃Mo₃N/Mg(Al)O</td>
<td>10</td>
<td>7600</td>
<td>600</td>
<td>-</td>
</tr>
<tr>
<td>Co₃Mo₃N/CNT</td>
<td>10</td>
<td>11000</td>
<td>600</td>
<td>71.5</td>
</tr>
<tr>
<td>La-CoMoN₂/CNT</td>
<td>10</td>
<td>11000</td>
<td>600</td>
<td>97.6</td>
</tr>
<tr>
<td>Mo₂C</td>
<td>Bulk</td>
<td>36000</td>
<td>600</td>
<td>71.0</td>
</tr>
<tr>
<td>Mo₂N</td>
<td>Bulk</td>
<td>15000</td>
<td>600</td>
<td>70.1</td>
</tr>
<tr>
<td>MoN</td>
<td>Bulk</td>
<td>6000</td>
<td>600</td>
<td>97.2</td>
</tr>
<tr>
<td>3CoMoN</td>
<td>Bulk</td>
<td>6000</td>
<td>600</td>
<td>98.3</td>
</tr>
</tbody>
</table>
2.7 Conclusions

Hydrogen’s properties such as molecular weight and reactivity historically have made it an essential component for the refining of other compounds like Ammonia and methanol. Hydrogen is not a primary energy source as no natural reservoirs exist, this is due to its inability to exist as a stand-alone atom. As the world continues to progress in transitioning towards a fossil fuel free society the demand for alternative fuels such as hydrogen will continue to increase. Future progression of hydrogen technologies are leading towards fuel replacement in machines and automobiles which are reported in the literature to be 15 years away. Currently production of hydrogen is too expensive, and produces large volumes of pollutants as only four percent of hydrogen used in the industry comes from renewable sources. The literature highlights the need for research into more efficient and cost-effective methods for producing hydrogen. The necessity of research to fill gaps in the industry comes as environmental regulations are getting tighter and the current production methods will struggle to continue to adhere to the pollution regulations.

Ammonia decomposition presents many advantages over other hydrogen-producing processes as the reaction does not produce CO₂ as seen in reactions (8) and (9). Ammonia as a compound can hold 17.5 percent hydrogen by mass, making it a useful hydrogen storage facilitator. Research has shown that the choice of the reactor in which the reaction takes place has a significant impact on the effectiveness of the decomposition. The evidence shows that under the same reaction conditions an FBR and FMBR can differ by as much as 40 percent regarding conversion. Research into reactor composition also highlights that reactor the volume is a significant factor, affecting the temperature, concentration, conversion and overall effectiveness of the reaction. From the effectiveness data collected, it has been determined that the kinetics of the reaction are diffusion limited due to the low values at the beginning of the reaction. Efforts into improving the ammonia decomposition technology have been focused towards catalyst optimisation as the current platinum group catalysts not being financially viable. Early research into catalysis in the ammonia decomposition reaction highlighted the need for increased investigations on various metal supported catalysts are the platinum metal groups were not sustainable heading into the future demand for hydrogen-related fuels. Table 2.2 showed ruthenium to have the advantage in early catalysis experimentation with conversion results above 500°C yielding the best conversions. However, the current
demand is for greater than 90 percent conversion at temperatures under 400ºC which current catalysts are failing to achieve.

Tailor-made catalysts for the hydrogen decomposition reaction is the new trend in research with metal carbides and nitrides showing strong results in other similar processes such as ammonia synthesis. Compounds such as W_2C, Mo_2N, Mo_2C are beginning to be investigated vigorously as they are showing the most promising results. Of the three catalysts named, Mo_2C theoretically possess the ability to perform the best due to it having a more considerable amount of active sites found on the structure. Ternary Nitrides such as Co_3Mo_3N in recent research has also shown strong signs as an appropriate substitute for platinum metal catalysts with recent experimentation with cobalt improving the performance of the catalyst regarding activity due to the binding energies of the compound. Norskov’s theory which is supported in literature explains that N_2 dissociation is the rate-limiting step of the reaction and when the Co_3Mo_3N catalyst is implemented this is significantly reduced. Another new technology which needs further researching is carbon nanotubes (CNT’s) as early experimentation has shown capabilities of achieving higher than 90 percent conversion at 450ºC.

When comparing all the catalysts with the research to date, the carbon nano tube support technology presents the most promise as a catalyst in the ammonia decomposition reaction. If the CNT’s are removed from the comparison due to the relatively conceptual nature of their development, the Co_3Mo_3N compound shows the most promise as it has the greatest conversion when compared to the W_2C, Mo_2N, Mo_2C catalysts which can be seen in Table 2.8. The Co_3Mo_3N catalyst also outperforms in terms of activity and rate at which the reaction takes place. The limited number of articles in this field highlight the need for increased research in the area of catalysts for ammonia decomposition, with specific mention in the field of full scale and pilot plant process development. Future work in this area will significantly assist the development of catalyst to optimise the ammonia decomposition process further.
2.8 References


Chapter 3

Experimental Methodology

The modelling techniques and methods applied in this project are described in detail throughout this chapter. The techniques used are for various aspects of the project such as catalyst surface characterisation, transient state calculations, catalyst optimisation and mechanism modelling for the ammonia decomposition reaction. The techniques were applied to various software programs allowing the modelling and data collection to occur for the different aspects of the investigation.

3.1 Software Methodology

The primary software programs used in this project were Materials studio v6.0.0 and VESTA 3.4.0 (Visualisation for Electronic Structural Analysis). The software packages were used to manipulate an original bulk file of the catalyst for calculations to be performed using the Raijin Supercomputer. The files were then observed before and after the calculation requests were received by the supercomputer to determine any differences in the original file and the calculated file.

3.1.1 Raijin Supercomputer

Installed in 2012, through funding from the Australian government, the Raijin Supercomputer’s primary application is for processing data for earth and atmospheric sciences. It also utilised for multiple other areas of science such as astrophysics and chemistry[1]. The Raijin Supercomputer was used in the project to perform calculations concerning catalyst surface optimisation, transient state calculations, reaction mechanism energies and catalyst energy values. The super computer received files from the Materials Studio software with pending calculations which were solved and sent back to a shared drive.
3.1.2 Materials Studio v6.0.0

The Materials Studio software by BIOVIA is a simulation and materials modelling program compatible with CIF files. The software has application in advanced research of materials such as catalysts which was the primary application for materials studio in this project[2][3]. Materials studio was used in this project to manipulate the original catalyst bulk file and request calculations to be conducted on the various sample files created. The calculation request files was delivered to the Raijin Supercomputer, with the completed files being reconstructed back on Materials Studio, where they are viewed for alterations done by the optimisation process.

3.1.3 VESTA 3.4.0

Visualisation for Electronic Structural Analysis, more commonly known as VESTA is a 3D visualisation program being used the analysis of the catalyst surfaces in this project[4]. The VESTA software provided high-quality graphic images of the catalyst molecules for observation and allow the data files to be exported into various formats comparable with the other programs used in the project.

3.2 Catalyst Surface Optimisation

This first component of this project was surface optimisation of the Co₃Mo₃N bulk file. This section of research was concerned with the determination of the optimum catalyst surface by comparing energies received from optimisation calculations by the Raijin Super computer. The optimisation of the catalyst in the ammonia decomposition reaction has been broken down into critical steps which are found in the subsequent sections of this section.

3.2.1 Catalyst Preparation

The catalyst bulk structure chosen for the project was the first significant step in order to expand on the information from the original physical experiment by [5]. The
catalyst samples used in the original experiment were variations of the CoMoN catalyst; to expand on this, the decision was made to use a Co$_3$Mo$_3$N bulk structure for this investigation. The bulk structure file was selected from [6], with the file being in CIF format, where it could be later transferred to the Materials Studio v6.0.0 software to have the surface cleaved. The CIF file which the original bulk structure was received in a standard text file containing the crystallographic information, where modelling software programs such as Materials Studio are compatible with it$^7$. The CIF file for the catalyst bulk structure was opened in Materials Studio where the catalyst was displayed as an empty cell as seen in Figure 3.1. The figure displays the catalyst with not atoms, only the lattice outline.

![Figure 3.1: Co3Mo3N Bulk model development; initial CIF file from [6], to ball and stick bond display after bond contraction.](image)

For characterisation, the catalyst’s bonds were generated by utilising Material Studio’s bond generation function where information from the CIF file is used to create the bonds for the catalyst. After creating the bonds, the image format of the bonds is changed to the “ball and stick” setting with the resulting model displayed in Figure 3.1. The size of the ball radius of the atoms was set to 0.4, and the sticks were set to 0.1 in the display style editor, these settings were uniform across all the models in Materials Studio for this project.

3.2.2 Catalyst Surface Preparation

With the catalyst bulk file prepared, the final step to the characterisation of the catalyst was to cleave the sample in systematic variations of the surface, to determine the optimum surface. This surface was determined by using the inbuilt cleave function in
materials studio, where for this project the cleavage lines for the bulk structure were chosen to be (1 0 0), (1 1 0) and (1 1 1) generating three iterations to be optimised. The three cleaved surfaces were then modelled into two different vacuum arrangements as depicted in Figure 3.2 below.

![Diagram of vacuum arrangements](image)

**Figure 3.2:** Cleaved (1 0 0) Surface In Vacuum 1 & 2

The first vacuum was characterised as a 1 sample and had the catalyst slab arranged in the middle of a 20 Angstrom (Å) vacuum. The second vacuum arrangement was 10 Angstrom (Å) with the catalyst slab beginning at the edge of the vacuum and was characterised as the 2 sample. Please refer to Appendix B for the remaining figures for the cleaved surfaces (1 1 0) and (1 1 1). Once inside the vacuum, the thickness of the catalyst structure was altered by adjusting the number of atoms. Adjusting the thickness manipulated the structures making them more symmetrical. Symmetry was achieved by increasing the thickness, so the same number of atoms of each element were present on the surface. The thickness of the catalyst slab was restricted to be less than 15 Angstrom (Å) to ensure the supercomputer could perform calculations promptly. The files were then
converted to a VASP format to allow the files to be transferred to the VESTA 3.4.0 software.

The VESTA software allowed the structures to be observed in high detail and provided information on the physical characteristics of the different surface iterations such as bond length. A total of four bond length points were recorded for later comparison between original and optimised surfaces. For the bond length measurement, two atoms bonded together were selected in the program where selected, and the length of the bond was generated by the VESTA software as seen in Figure 3.3 below. The final formatting step of the file was then converted it into a POSCAR format, allowing the surface to be optimised using the Raijin Supercomputer.

![Figure 3.3: Bond Length Measurement of Co$_3$Mo$_3$N Bulk Specimen Example](image)

3.2.3 Surface Optimisation

The files containing cleaved surfaces in the 1 and 2 vacuums were transferred from the VESTA software back to the Materials Studio program where they were uploaded onto a shared drive which is accessible to the Raijin Supercomputer. The surfaces had the geometry optimisation calculation initiated with the Dmol$^3$ calculation parameters were...
mostly unchanged. Two alterations were made, the first was the smearing value and the second the Max SCF Cycles. The Max SCF Cycles was increased to 100, and the smearing was decreased to 0.05. The calculation parameters were kept constant for each calculation. Once the optimisation calculation was initiated and saved, the file was uploaded to the supercomputer along with four other files which were provided by Mohammednoor Altarawneh to assist with the calculations. These files were named INCAR, KPOINTS, P and POTCAR and were collectively known as the command files, which are not altered during this project. The command files perform the calculations at the supercomputer and were kept constant for each surface optimisation calculation. The folder containing the five files was then sent to the super computer for processing.

When the supercomputer completed the calculations, multiple files were added back to the original specimen folder. The OUTCAR and CONTCAR files where then extracted from the folder for analysis. The OUTCAR file contained the energy information of the system. The CONTCAR file contained the number of atoms of each element in the optimised file. The desired data from the files was recorded for analysis. The process of initiating the optimisation calculation and adding the file to the control files in a folder was repeated for each cleaved surface, known as a specimen. The OUTCAR and CONTCAR files were extracted for each specimen with the energy and element count data collected.

### 3.2.4 Catalyst Surface Area Energy

The information from the surface optimisation calculations was also applied to determine the catalyst surface area energies. Bulk files for nitrogen, cobalt and molybdenum were collected from the crystallography database to compare their unit energies against the manipulated bulk Co$_3$Mo$_3$N catalyst specimens individual atom energies. This was achieved by extracting the overall energy from the OUTCAR file of each specimens individual elements i.e. cobalt, molybdenum and nitrogen. The bulk files of the elements which made of the Co$_3$Mo$_3$N catalyst also had energy calculations conducted by performing the same geometry optimisation calculation used in the surface optimisation component in Chapter 3.2 of this report. The sum bulk elements energies were compared to the energies of the same number of specimen atoms by subtracting the bulk energy value to find the difference.
3.3 Mechanism Optimisation

Is the second major research area of this project is investigating the catalyst - molecule location optimisation between Co₃Mo₃N and the ammonia molecule. From the literature review in chapter 2 of this report, the 12 mechanism steps supported by [8] were able to be modelled in this component of the project. Seven distinct mechanism steps where identified after the removal of the non-critical steps. The seven mechanism steps are as follows;

$$\text{NH}_3 + \ast \rightarrow \text{NH}_3^\ast \quad (1)$$
$$\text{NH}_3^\ast + \ast \rightarrow \text{NH}_2 + H^\ast \quad (2)$$
$$\text{NH}_2 + \ast \rightarrow \text{NH}^\ast + H^\ast \quad (3)$$
$$\text{NH}^\ast + \ast \rightarrow \text{N}^\ast + H^\ast \quad (4)$$
$$\text{N}^\ast + \ast \rightarrow H^\ast \quad (5)$$
$$\text{N}^\ast + \text{N}^\ast \rightarrow \text{N}_2 + \ast \quad (6)$$
$$H^\ast + H^\ast \rightarrow H_2 + \ast \quad (7)$$

(* Represents an adsorbed surface species.)

The first four steps in this project were the adsorption steps of the ammonia atom onto the surface of the catalyst. The final three steps of the reaction were the desorption of the hydrogen and nitrogen atoms forming H₂ and N₂ molecules. For this modelling to occur, the original bulk file of the Co₃Mo₃N catalyst was chosen, and the first mechanism step was replicated by locating an NH₃ atom within bonding distance to the Co₃Mo₃N catalyst in the Materials Studio software. Different bonding zones were trialled by locating the NH₃ molecule at different areas above the catalyst surface; this was to increase the data points collected for comparison.

The mechanism model then had the optimisation calculation initiated, with the same parameters used in the surface optimisation calculations in section 3.2.3. The model file was then uploaded onto the shared drive in a folder with the command files where it was then sent to the supercomputer for the calculation to be completed. This process of placing the molecule above the catalyst surface to replicate the reaction step was repeated for the six remaining mechanism steps. Different locations were trialled for each mechanism step.
to increase the scope of the research. Figures 3.4 & 3.5 display an example of the seven mechanism steps on materials studio which were sent to the supercomputer. The figure shows the decomposition of the ammonia molecule and the adsorption of the H\textsubscript{2} and N\textsubscript{2} molecules. All the remaining unoptimised mechanism steps with different molecule locations pre-calculation figures can be found in chapter five.

![Mechanism 1 and Mechanism 2]

(Dark Blue: Nitrogen, Aqua: Molybdenum, Red: Cobalt)

![Mechanism 3 and Mechanism 4]

**Figure 3.4:** Ammonia Adsorption Mechanism Step models Pre-Optimisation
The completed files from the supercomputer were received back in the original folder on the shared drive. The POTCAR file was examined for the energy value of the calculation, the energies of each mechanism step trial were tabulated for comparison. The POSCAR file was opened in the Materials Studio software to observe if the optimised file displayed a successful bond between the molecule and the catalyst, where the molecule above the surface was determined by the mechanism being modelled. Figures 3.6 & 3.7 display an example of the seven mechanism steps with a successful bond/optimisation calculation, all the completed mechanism calculation figures can be found in chapter five.
When the POSCAR file is opened in the Materials studio after being processed by the supercomputer, the optimisation is completed by using the analysis - structure function to update the optimised structure to what the supercomputer calculated the optimum structure to be. Once the structure has been updated, the bonds need to be recreated by selecting the generate bond function, similarly to section 3.2.1. The surface is then observed with any distinct characteristics or abnormalities being recorded.
3.4 Transient State

The transient state calculations are the final component of this project’s experimental method. The transient state calculations develop on the mechanism optimisation work conducted in the previous section. The optimised mechanism specimens from section 3.3 are utilised in this section to by pairing up subsequent mechanisms in the following steps:

**Table 3.1: Transient State Mechanism Steps**

<table>
<thead>
<tr>
<th>Transient State</th>
<th>Mechanism Steps</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Mechanism 1 &amp; Mechanism 2</td>
</tr>
<tr>
<td>2</td>
<td>Mechanism 2 &amp; Mechanism 3</td>
</tr>
<tr>
<td>3</td>
<td>Mechanism 3 &amp; Mechanism 4</td>
</tr>
<tr>
<td>4</td>
<td>Mechanism 4 &amp; Mechanism 5</td>
</tr>
<tr>
<td>5</td>
<td>Mechanism 5 &amp; Mechanism 6</td>
</tr>
<tr>
<td>6</td>
<td>Mechanism 6 &amp; Mechanism 7</td>
</tr>
</tbody>
</table>

Referring to Table 3.1, six transient states have been identified from this project. In Materials Studio six folders are created where the two optimised mechanism files are copied into them. The reaction editor is then opened in Materials Studio, where the earlier reaction mechanism is selected as the reactant, and the following mechanism is denoted as the product. The atoms of each element are matched between the two mechanisms; the file is then saved, producing one reaction file. The Transient State search calculation or TS search, was then initiated on the reaction file, with the same parameters used in the surface optimisation calculations in section 3.2.3. The TS search calculation file was then uploaded to the supercomputer shared folder with the command files and was sent away for processing.

When the calculations completed were sent back to the shared folder the OUTMOL file was opened where the energy value was recorded for comparison against other iterations of the same transient state using the different mechanism specimens. The same transient state process was used for the other iterations of the mechanisms and was repeated to attain the energy values.
3.5 References

1. P. Mahony, "Raijin supercomputer cooks up a storm", ECOS, 2013.
Chapter 4
Surface Optimisation

The first component of this project was the optimisation of the $\text{Co}_3\text{Mo}_3\text{N}$ surface. The rationale for the optimisation calculations was to find the most stable catalyst surface to support the ammonia decomposition reaction. The specimens have been characterised by their cleavage and vacuum iterations, for example, a specimen with the name 100 describes that its surface has been cleaved along the (1 0 0) plane of the catalyst. The 1 or 2 at the end of the specimen title represents the type of vacuum the surface has been applied to. Specimens with ‘a’ or ‘b’ as an extension to their title denote that the same catalyst cleavage has been used, but a different thickness has been employed to make to catalyst more symmetrical.

A fundamental assumption applied to this component of the project is that the final energy is independent of the parameters entered into the software. This directly relates to the thickness and the symmetry of the catalyst which were assumed to have no impact on the results. The thickness and symmetry of each catalyst tested were assumed to be equal and have not been recorded in this project. The surface optimisation calculations had vital importance to the project, as the most stable surface derived from this work was then used moving forward in the mechanism calculations and transient state development.

4.1 Surface Optimisation Data

The energy of optimised specimens was used to determine the stability of the catalyst surfaces sent to the supercomputer. A total of seven surfaces were cleaved and optimised with the bulk structure being optimised for comparison. The energy results from the optimised surfaces and energy of the constituents have been summarised in Table 4.1, which includes calculations for the surface area from tables 4.2 and 4.3 found in Appendix B. The table also includes the difference by surface area results for the optimised surfaces. The optimised energy values of the specimens show the 110_2 and the 111_2 specimen to
be the most stable and unstable of the cleaved surfaces. Additional data can be found in Appendix B related to the surface optimisation.

Table 4.1: Surface Optimisation Energy & Calculation Results

<table>
<thead>
<tr>
<th>Surface</th>
<th>Specimen Code</th>
<th>Energy of Constituents (eV)</th>
<th>Optimised Energy (eV)</th>
<th>Unit Surface Area Energy (eV/Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk (Co₃Mo₃N)</td>
<td>000_</td>
<td>-275.637</td>
<td>-303.258</td>
<td>-0.55877</td>
</tr>
<tr>
<td>Co₃Mo₃N (100)</td>
<td>100_1</td>
<td>-612.369</td>
<td>-660.319</td>
<td>-0.90690</td>
</tr>
<tr>
<td>Co₃Mo₃N (100)</td>
<td>100_2</td>
<td>-612.369</td>
<td>-660.425</td>
<td>-0.90890</td>
</tr>
<tr>
<td>Co₃Mo₃N (110)</td>
<td>110_1</td>
<td>-608.644</td>
<td>-643.472</td>
<td>-0.57048</td>
</tr>
<tr>
<td>Co₃Mo₃N (110)</td>
<td>110_2</td>
<td>-596.061</td>
<td>-629.652</td>
<td>-0.55021</td>
</tr>
<tr>
<td>Co₃Mo₃N (111)</td>
<td>111_1a</td>
<td>-795.751</td>
<td>-839.212</td>
<td>-0.82202</td>
</tr>
<tr>
<td>Co₃Mo₃N (111)</td>
<td>111_1b</td>
<td>-866.838</td>
<td>-881.938</td>
<td>-0.28559</td>
</tr>
<tr>
<td>Co₃Mo₃N (111)</td>
<td>111_2</td>
<td>-866.838</td>
<td>-882.677</td>
<td>-0.29958</td>
</tr>
</tbody>
</table>

In general, the (111) surface iterations had the most negative optimised energy values, making them the most stable of all the surfaces optimised. The results for the difference by surface area was calculated from the energy of constituents and the optimised energy values. By observation, it can be seen that the (100) samples have the most negative results of -0.9069 and -0.9089 eV/Å². The constituent energy values were calculated using the unit energies from the optimised individual element bulk models. The individual elements were sent to the supercomputer for optimisation using the same technique as for the specimens. The number of atoms, of each element in the catalyst used was determined by the supercomputer in the optimisation calculations. Of all the surfaces optimised, the (111) surface planes are the most negative. Full calculations for the energies and surface area can be found in Appendix C.

Of the specimens tested, all saw an increase in stability per Ångström squared with the (100) specimens having the most substantial stability increase, with an average of 3.77 percent excluding the bulk structure. The bulk structure saw the most significant change in its stability. However the bulk Co₃Mo₃N catalyst remained the most unstable surface. Regarding Figure 4.1, a directly proportional relationship is recognised between the number of atoms in the catalyst and the overall stability of the catalyst. The figure contains data from Table 4.3 in Appendix B, which summaries the calculated surface areas of the
specimens and the elemental atomic totals. By observation, the results display a connection between the surface area of the catalyst and its stability.

## 4.1.1 Bond Length Data

The physical change of the catalyst from the optimisation process can be examined by measuring specific bond lengths from the modelled catalyst before and after the optimisation calculations were conducted by the supercomputer. Details of the method can be located in Chapter 3 section 3.2.2, where Figure 3.3 displays an example of how the bond lengths are measured. The bond length data comes from a series of specimens being optimised by the supercomputer where the catalyst surfaces were physically altered. The length values taken from the modelled specimens were collected from the same locations for the four bond data points. Table 4.4 summarises the changes made to each specimen as a result of the optimisation calculations. The bond location with the most significant average change for all the specimens measured was location one, with an average of 4.317 percent. The average change was calculated by taking the absolute value all the percentage changes and then taking their sum. The full calculations for the average change and net change for the bonds can be located in Appendix C. The specimen to have the largest change in a bond length was the 110_2 bond four with a 9.14 percent increase from its original length to its optimised length, this shows a significant change in the bond length as a result of optimisation.

### Table 4.4 Summary of Bond Length Changes Resulting From Optimisation

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Bond 1</th>
<th>Bond 2 (Å)</th>
<th>Bond 3 (Å)</th>
<th>Bond 4 (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Length Change (Å)</td>
<td>% Change</td>
<td>Length Change (Å)</td>
<td>% Change</td>
</tr>
<tr>
<td>000_a</td>
<td>-0.062</td>
<td>-1.472</td>
<td>-0.062</td>
<td>-1.472</td>
</tr>
<tr>
<td>100_1</td>
<td>-0.219</td>
<td>-5.409</td>
<td>0.219</td>
<td>5.406</td>
</tr>
<tr>
<td>100_2</td>
<td>-0.096</td>
<td>-2.307</td>
<td>0.219</td>
<td>5.406</td>
</tr>
<tr>
<td>110_1</td>
<td>-0.206</td>
<td>-5.068</td>
<td>0.201</td>
<td>4.952</td>
</tr>
<tr>
<td>110_2</td>
<td>-0.208</td>
<td>-5.128</td>
<td>0.209</td>
<td>5.144</td>
</tr>
<tr>
<td>111_1a</td>
<td>-0.193</td>
<td>-4.730</td>
<td>0.193</td>
<td>4.738</td>
</tr>
<tr>
<td>111_1b</td>
<td>-0.254</td>
<td>-6.348</td>
<td>0.060</td>
<td>1.425</td>
</tr>
<tr>
<td>111_2</td>
<td>-0.167</td>
<td>-4.073</td>
<td>0.027</td>
<td>0.630</td>
</tr>
</tbody>
</table>
A summary of the bond length calculations conducted in this project is below in Table 4.5. The results show the most considerable average change of 5.406 percent occurred in the 110_1 specimen. This finding expected as it also had the largest bond change out of all the specimens optimised. The average length change in the surface was 0.395Å with an overall net change of plus 12.917Å in the bonds measured. The 111_2 specimen was the only surface to decrease in bond size over the measurement points with an overall net change of -2.453Å for the surface; the surface also saw the smallest overall percentage change of 2.172 percent.

Table 4.5 Summary of Bond Change Calculations

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Average Length Change (Å)</th>
<th>Average % Change</th>
<th>Net Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>000_</td>
<td>0.078</td>
<td>1.472</td>
<td>0.001</td>
</tr>
<tr>
<td>100_1</td>
<td>0.383</td>
<td>5.406</td>
<td>10.807</td>
</tr>
<tr>
<td>100_2</td>
<td>0.215</td>
<td>3.498</td>
<td>9.379</td>
</tr>
<tr>
<td>110_1</td>
<td>0.344</td>
<td>4.659</td>
<td>8.499</td>
</tr>
<tr>
<td>110_2</td>
<td>0.395</td>
<td>5.793</td>
<td>12.917</td>
</tr>
<tr>
<td>111_1a</td>
<td>0.296</td>
<td>3.712</td>
<td>4.024</td>
</tr>
<tr>
<td>111_1b</td>
<td>0.348</td>
<td>3.892</td>
<td>2.873</td>
</tr>
<tr>
<td>111_2</td>
<td>0.216</td>
<td>2.172</td>
<td>-2.453</td>
</tr>
</tbody>
</table>

Figures 4.1 - 4.8 display the top and side profiles of the optimised specimens which were received from the supercomputer and viewed in the materials studio modelling software. The different surface cleavages expose different elements to the reaction which has the potential to interact differently with the reaction taking place. When observing the optimised structures, it can be seen that the layers underneath the surface are systematically repeated and that only the top surface layers impacted by the cleavage iteration.
(Dark Blue: Nitrogen, Aqua: Molybdenum, Red: Cobalt)

**Figure 4.1:** 000_ Optimised structure side and top profiles

(Dark Blue: Nitrogen, Aqua: Molybdenum, Red: Cobalt)

**Figure 4.2:** 100_1 Optimised structure side and top profiles
(Dark Blue: Nitrogen, Aqua: Molybdenum, Red: Cobalt)

**Figure 4.3:** 100_2 Optimised structure side and top profiles

**Figure 4.4:** 110_2 Optimised structure side and top profiles
**Figure 4.5:** 110_1 Optimised structure side and top profiles

**Figure 4.6:** 111_1a Optimised structure side and top profiles
Figure 4.7: 111_1b Optimised structure side and top profiles

Figure 4.8: 111_2 Optimised structure side and top profiles
4.2 Interpretation of Results

The key information derived from the optimisation data was the most stable surface being the 111_2 specimen as the specimen had the lowest optimised energy value. All the surfaces exist as a nano-particle, which contains multiple surfaces. The most stable surface will be more prevalent than the other surfaces planes which is desirable. This means the most stable surface will have significantly more of one particular surface than any other surface present. Applying this understanding to the results, the 111_2 specimens energy value of -882.667 eV shows it to be the most stable catalyst. This result can be explained by the (111) surfaces on the nano-particle being vastly more prevalent than the other surfaces on there. When compared to the prevalence of the (110) surfaces on the 110_1, and 110_2 specimens, significantly less (110) surfaces would be present when compared categorically to the 111_2 specimen.

In general, when comparing the (111) energies of both the constituent and optimised data the surface is significantly more stable which is supported from the literature review findings in chapter two of this report which agreed that the (111) indexed surface were more stable on similar nitride catalysts[1]. The results of the physical changes in the bonds are directly related to the findings from the stability data. It was discovered in the results that the (111) surfaces experienced the smallest percentage change regarding its bond lengths when optimised by the supercomputer. These findings are reciprocated by the (110) specimens as the specimens displayed the highest average bond change which shows the largest physical alterations occurred in the optimising process to the most unstable catalyst. These results show a directly proportional relationship between the stability of the catalyst and the changes occurring during the optimisation process.

Trends from the unit surface area energy show the more stable surface to have more positive energy values per Angstrom squared than the less stable catalysts. This could be a result of an increased number of atoms providing the increased stability of the catalyst. Figure 4.9 displays a directly proportional trend between the increasing number of atoms present in the catalyst and the increased stability. The figure contains data from Table 4.3 in Appendix B, which summaries the calculated surface areas of the specimens and the elemental atomic totals.
By observation, the results display a connection between the surface area of the catalyst and its stability. The increased number of atoms is related to the thickness of the surfaces, which as been assumed in this project not to have an impact on the results. The data shows the most stable optimised energy value of -882.667 eV which has the highest number of accompanying atoms, 88. The most unstable atoms have a 25 percent reduction in the energy value with a 30 percent reduction in the number of atoms present in the catalyst.

The relationship between the stability of the catalyst and the number of atoms could be a result of the increased cobalt presence. Cobalt is more prevalent in the more stable catalysts as displayed in Figure 4.10; this supported in literature and in the original physical experiment which these models are expanding on, as the physical experiment concluded cobalt presence to be the driving force behind the improved catalyst stability[1] [2]. Similarly to Figure 4.9, the cobalt presence has a directly proportional relationship to the catalyst stability.
The data in Figures 4.9 and 4.10, provide conclusive findings that these interactions potentially could have an impact on the stability, which should be explored in further work by determining if the stability is influenced by the thickness of the catalyst or the presence of cobalt.

4.3 Summary

The data was assembled from the optimisation calculations completed by the supercomputer, which found the 111_2 specimen to be the most stable comparatively with an energy value of -882.667 eV. Optimisation process conducted on the specimens has had a significant impact on the physical properties of the catalysts, changing the physical structures on average by 3.83 percent. These changes can be attributed to the bond lengths being modified as a result of the optimisation. Alterations to the physical structure provided information on the stability of the surface which was in agreement with the stability result. A directly proportional relationship between the stability of the surface and the physical changes of the catalyst was determined from the data collected. A directly proportional relationship between the catalyst thickness and the stability was identified with
changes in one parameter being proportional reciprocated by the other. A second relationship similar to the first was determined between the cobalt presence and the stability. The findings are in support to one another, with current literature supporting the cobalt’s impacts on the stability.

The results from this components work are limited regarding breadth, as a result of the number of surface planes selected to cleave. A broader scope of surfaces could have provided more information of the most stable surface with different combinations of elements being exposed to the optimisation calculations. Another limitation of the data was to identify the driving force behind the increase in stability, with only speculative relationships determined. Further work was highlighted to elaborate on the relationships as the thickness of the catalyst was out of the scope of this project.

4.4 References


Chapter 5
Mechanism Optimisation

The second component of this project is mechanism optimisation. This work investigates the different mechanisms of the ammonia decomposition reaction and expands on the work completed in the previous surface optimisation component. The 111_2 specimen exhibited the most stability after the optimisation calculations, making it the desired catalyst to model the mechanisms for the ammonia decomposition reaction on moving forward into the project.

A total of 12 mechanism steps were found in the literature review component of this report[1]. The following seven mechanisms were modelled in materials studio after removing the reverse reactions:

1. \( \text{NH}_3 \text{ (prior to adsorption)} \)  
2. \( \text{NH}_3^* + * \rightarrow \text{NH}_2 + \text{H}^* \)  
3. \( \text{NH}_2 + * \rightarrow \text{NH}^* + \text{H}^* \)  
4. \( \text{NH}^* + * \rightarrow \text{N}^* + \text{H}^* \)  
5. \( \text{N}^* + \text{N}^* \rightarrow \text{N}_2 + * \)  
6. \( \text{H}^* + \text{H}^* \rightarrow \text{H}_2 + * \)  
7. \( \text{N}_2 + \text{H}_2 \text{ (desorbed)} \)

Mechanisms one and seven are the initial reactants and the final products. The initial reactant is the ammonia above the surface of the catalyst prior to adsorption, and the final products are the desorbed \( \text{N}_2 \) and \( \text{H}_2 \) molecules.

The rationale behind the modelling and optimisation the ammonia decomposition mechanisms is to determine the most stable variations of them to provide credible information for the transient state modelling in the next component of the model. Different iterations of the same mechanism were optimised by changing the original location of the ammonia atom above the catalyst surface. The atom bonding locations were manipulated during the decomposition to increase the sample of mechanisms optimised for
comparison. The iterations were tested for their ability to bond, and the stability of the mechanism after completing the optimisation calculation. It was assumed in this component of the model that the distance the ammonia molecule was above the surface did not change during the adsorption phase of the model. The distance above the surface was assumed to be constant over all the different iterations optimised, and any variations had no impact on the stabilities determined from the energy values.

5.1 Mechanism Optimisation Data

The energy of optimised mechanisms was used to determine their stability from the results returned from the Raijin supercomputer. A total of seven mechanisms were optimised with multiple test locations taken for comparison. The mechanisms and their iterations optimised have been summarised in Tables 5.1 & 5.2 below; the table only includes mechanisms which were valid and returned a stable energy value. Table 5.1 combines information on the energy values returned from the supercomputer and the validity of the mechanisms which can be found in Appendix B in Tables 5.3, 5.4 & 5.5.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>-143.3602</td>
<td>M2a</td>
<td>-143.3602</td>
<td>M3a</td>
<td>-143.3601</td>
<td>M4a</td>
<td>-143.3601</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M2b.2</td>
<td>-143.3602</td>
<td>M3b.2</td>
<td>-143.3601</td>
<td>M4b.2</td>
<td>-143.3601</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>M3c</td>
<td>-143.3601</td>
<td>M4c</td>
<td>-143.3601</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mechanism 5</th>
<th>Energy (kcal/mol)</th>
<th>Mechanism 6</th>
<th>Energy (kcal/mol)</th>
<th>Mechanism 7</th>
<th>Energy (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M5a1b</td>
<td>-143.4459</td>
<td>M6a2a</td>
<td>-143.4458</td>
<td>M7a2a</td>
<td>-143.4458</td>
</tr>
<tr>
<td>M5b2</td>
<td>-143.4458</td>
<td>M6a3a</td>
<td>-143.4458</td>
<td>M7a3a</td>
<td>-143.4458</td>
</tr>
<tr>
<td>M5b3</td>
<td>-143.4458</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M5c2a</td>
<td>-143.4458</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M5c3c</td>
<td>-143.4458</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The results have above have been filtered of mechanisms which were unable to be used in the transient state calculations due to being invalid or being unable to perform the optimisation calculations on it. The following Figure 5.1 displays the valid optimised mechanism for the first mechanism of the reaction.

![Original M1 Model vs Optimised M1 Model](image)

(Dark Blue: Nitrogen, Aqua: Molybdenum, Red: Cobalt, White: Hydrogen)

**Figure 5.1:** Original & Optimised Mechanism File (M1)

The second mechanism contained a variation of the surface bonding which was not anticipated prior to the supercomputer optimisations. The two mechanism iteration were then developed and re-run using a ‘flipped’ NH$_2$ compound above the surface to attain the desired result. Figures 5.2 & 5.3 display the original M2a, M2b.2 and the optimised M2a, M2b.2 figures where the variations between the surfaces can be distinguished by the locations of NH$_2$ molecule and which was done as a result of the optimised file returning which an unexpected surface bonding result. The M2b.2 image displayed in Figure 5.3 is a variation of the M2b.1 mechanism which failed.
Figure 5.2: Original & Optimised Mechanism File (M2a)

Figure 5.3: Original & Optimised Mechanism File (M2b.2)
Mechanism three contains a, b & c iterations as a result of three different possible bonding locations for the remaining NH$_2$ compound, which can occur at the cobalt site (M3a) or (M3c). The final iteration can occur at the molybdenum site (M3b.2) which has been displayed on Figures 5.4 - 5.6. The M3b.2 was edited from the original M3b iteration as the mechanism failed.

**Figure 5.4:** Original & Optimised Mechanism File (M3a)

**Figure 5.5:** Original & Optimised Mechanism File (M3b.2)
Mechanism four has three different variations as it is physically possible for the H+ atom to be bonded to three different sites. The following iterations of the fourth mechanism are illustrated in figures 5.7 - 5.9. When the NH₂ is above the cobalt two different hydrogen bonding locations are observed (M4a) and (M4c). Whereas for the NH₂ iteration above the molybdenum site the distance is too great for the H+ atom to travel beyond the empty site which M3b displays.

Figure 5.6: Original & Optimised Mechanism file (M3c)

Figure 5.7: Original & Optimised Mechanism file (M4a)
Figure 5.8: Original & Optimised Mechanism file (M4b.2)

Figure 5.9: Original & Optimised Mechanism file (M4c)
The fifth mechanism has one of the hydrogen removed as it is spectating the desorption reaction taking place. The Hydrogen atom removed from the NH compound physically cannot travel the distance to bond and therefore removed the spectator Hydrogen. A nitrogen atom is added to the model to allow for the nitrogen atoms to bond together and leave at the catalyst surface. The nitrogen atom added to the surface was arranged above different cobalt and molybdenum surface bonding sites hence the addition a, b & c iterations of the mechanism.

The M5a1c iteration does not exist as it is physically impossible for the hydrogen atoms to bond over such a long distance, hence why only M5a1a & M5a2b were constructed. As there are three hydrogen atoms are present, one will be a spectator to the formation of hydrogen gas. In this instance, there is a clear decision to which hydrogen atom was the spectator. This was a similar case for M5a2 and its iterations. Only two iterations were created as there was a definite spectating hydrogen atom on the surface of the catalyst. The definite spectating hydrogen The optimised models in figures 5.7 - 5.9 displays the determined spectating hydrogen atom to be removed for the fifth mechanism. With the alterations made to the previous fourth mechanism models, the following models were used for the fifth mechanism.

![Original M5a1b Model](image1.png) ![Optimised M5a1b Model](image2.png)

**Figure 5.10:** Original & Optimised Mechanism file (M5a1b)
Figure 5.11: Original & Optimised Mechanism file (M5b2)

Figure 5.12: Original & Optimised Mechanism file (M5b3)
Figure 5.13: Original & Optimised Mechanism file (M5c2a)

Figure 5.14: Original & Optimised Mechanism file (M5c3c)
The sixth mechanisms only yielded two valid optimised models as a result of most of the iterations stemming from the previous mechanism five being of an invalid trajectory. The sixth mechanism model displays the desorption of the nitrogen atoms forming N\textsubscript{2} in figures 5.15 & 5.16 Similarly for the seventh and final mechanisms modelled; only two models were produced following on from the previous models. The seventh models in Figures 5.17 & 5.18 display the two hydrogen atoms deserting from the catalyst surface, forming H\textsubscript{2}.

**Figure 5.15:** Original & Optimised Mechanism file (M6a2a)

**Figure 5.16:** Original & Optimised Mechanism file (M6a3a)
Figure 5.17: Original & Optimised Mechanism file (M7a2a)

Figure 5.18: Original & Optimised Mechanism file (M7a3a)
5.2 Interpretation Of Results

Successful optimisation calculations were completed on 18 of the 54 models sent to the supercomputer. The majority of the models provided stability data from the optimisation calculations, however, could not be applied further in this project as the trajectories were not valid for the transient state calculations in the next chapter. The data summarised in Table 5.1 shows little variation between the stabilities of the mechanisms and their intermediates. Of the adsorption steps, the average energy for the optimised mechanisms was -143.3601 kcal/mol. The desorption mechanisms were slightly more stable than the adsorption steps with an average optimised energy value of -143.4458 kcal/mol.

During the optimisation of the mechanisms, limited alterations were recognised between the surfaces of the optimised and original specimens. This is related to the previous optimisation completed on the surfaces before the mechanisms were added. The slight changes noticed on the surface of the adsorption surfaces is a result of the new bonds being formed by the decomposing ammonia molecule. The changes on the desorption surfaces of the catalyst can be attributed to the hydrogen and nitrogen molecules being formed. The high amount of unsuccessful mechanisms model can be attributed to the initial locations of the atoms replicating the mechanisms being incorrectly placed above the surface. Multiple locations were tested to increase the number of successful mechanisms optimised due to the uncertain nature of this component of the model.

The figures of the original and optimised mechanisms show in the final desorption step of the nitrogen molecule; it remains bonded to the surface instead of completely dissociating from the surface. This can be for two possible reasons, the first being the model prevents the nitrogen existing as a free molecule above the surface of the catalyst. The second explanation is the model is showing the nitrogen to have an affinity for the surface of the catalyst and will not dissociate without added stimulation. This would result in the catalyst being covered in nitrogen atoms during the decomposition reaction and result in the catalytic effect being suppressed in a physical experiment.
5.3 Summary

The work completed in this component of the model was targeted at developing models for each of the mechanisms discovered in the literature. The models of the mechanisms were then optimised using the Raijin supercomputer and reconstructed in the materials studio software. Each mechanism model shows a successful step being adsorption or desorption, in the ammonia decomposition process. Multiple iterations of the same mechanisms were tested to provide sufficient breadth for the transient state calculations in the next chapter. A total of 18 optimised models were developed, with the results finding the desorption mechanisms were slightly more stable than the adsorption component of the decomposition reaction. The only calculations conducted in this component of the work was done by the supercomputer, which determined the stabilities of the individual mechanisms.

The models developed in this component of the project have limiting factors such as a vast majority of the stable mechanisms that were modelled and optimised could not be reconstructed in the materials studio software. This restricted the availability of models to be used for comparison purposes and decreased the overall sample size. Future work on this information collected in this component of the project could be expanding on the areas of which the atoms bond to the surface of the catalyst. Finally, areas such as the influence of other species present on the behaviour of the system could also be explored further.

5.4 References

Chapter 6
Transient State

The final component of this project was the transient state development, which builds on the results collected from chapters four and five. The previous chapter developed optimised models from seven mechanisms found in literature. From the seven mechanisms, 18 different models were developed and successfully optimised to develop the transient states on in this chapter. As a result of multiple mechanisms being optimised, multiple transient states were developed to increase the breadth of the data.

The transient state calculations were achieved by pairing up subsequent mechanisms, identifying the common atoms and then performing calculations using the supercomputer. Six transient states where identified for the ammonia decomposition reaction from the optimised mechanisms. The breakdown of the transient states and their mechanisms are detailed in Table 3.1 chapter three. The calculations completed by the supercomputer are aimed at determining the rate limiting step of the ammonia decomposition reaction through the activation energy results collected.

The rational behind calculating the activation energies and the overall rate limiting step is the main modelling aim of this project, which is to determine the kinetics of the ammonia decomposition reaction on the surface of the Co₅Mo₅N catalyst. The work completed developing the transient states had a fundamental assumption applied, which was that the energies calculated were independent of the parameters entered into the software for the mechanisms. This had a carry on effect that the transient states were not impacted by the physical parameters of the mechanisms such as size. It was also assumed that if a calculation was unsuccessful or the mechanisms could not be matched in the atomic matching that the transient state for that iteration did not exist.
6.1 Transient State Data

The paired transient state files containing two optimised mechanism models (reactant & product) produced results for the activation energies and the reaction energies. From the successful transient states developed, the results returned were average over each transient state. The transient states were developed to determine the rate-limiting step for the ammonia decomposition reaction. The results found average highest activation energy to be for transient state six with a value of 96.056 kcal/mol, which contained mechanisms six and seven as the reactant and product. The highest average reaction energy was observed in both the second and third transient states with energies of 20.523 and 20.527 kcal/mol respectively.

The transient state data for the adsorption and desorption steps are tabulated in Appendix B. The activation energies could not be found by the supercomputer in each iteration when the transient was being determined. The reaction energies could be found for each of the iteration for the adsorption step with the averages summarised in Table 6.1. The average result for the activation energies for the successful calculations have been summarised. The average values were derived from the raw information from the supercomputer calculations in Table 6.3 and 6.4 for the energies from the adsorption and desorption components for the decomposition reaction.

The results from Table 6.1 show transient state four not have a transient state. During the modelling phase for the transient states, there was an atomic imbalance, where the number of atoms did not match. This issue resulted in the transient state not being found for any of the iterations. Table 6.2 contains the optimum transient state results which contain the best performing transient state iterations for each mechanism step. Transient state three exhibited the lowest activation energy, whereas the best performing transient state for the final mechanisms step was still contained the rate-limiting step for the reaction. The results have been filtered to determine the optimum energy path to show a full successful model for the whole ammonia decomposition reaction which has been displayed in Figures 6.1 - 6.7.

The data in Table 6.2 has been applied to the following figures which display the optimum activation energy results from the successful transient state calculations completed at the
supercomputer. The figures show the two mechanisms or product and reactant for each transient state and a transition image of the transient stage between the mechanisms.

**Table 6.1: Transient State Mechanism Steps Average Energies**

<table>
<thead>
<tr>
<th>State Iteration</th>
<th>Mechanism Step</th>
<th>Average Activation Energy (kcal/mol)</th>
<th>Average Reaction Energy (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transient State 1</td>
<td>Mechanism 1 &amp; Mechanism 2</td>
<td>67.645</td>
<td>0.848</td>
</tr>
<tr>
<td>Transient State 2</td>
<td>Mechanism 2 &amp; Mechanism 3</td>
<td>63.073</td>
<td>20.523</td>
</tr>
<tr>
<td>Transient State 3</td>
<td>Mechanism 3 &amp; Mechanism 4</td>
<td>24.430</td>
<td>20.527</td>
</tr>
<tr>
<td>Transient State 4</td>
<td>Mechanism 4 &amp; Mechanism 5</td>
<td>No Transient State Found</td>
<td>No Transient State Found</td>
</tr>
<tr>
<td>Transient State 5</td>
<td>Mechanism 5 &amp; Mechanism 6</td>
<td>63.543</td>
<td>3.680</td>
</tr>
<tr>
<td>Transient State 6</td>
<td>Mechanism 6 &amp; Mechanism 7</td>
<td>96.056</td>
<td>7.537</td>
</tr>
</tbody>
</table>

**Table 6.2: Filtered Transient State Mechanism Steps Average Energies**

<table>
<thead>
<tr>
<th>State Iteration</th>
<th>Mechanism Step</th>
<th>Average Activation Energy (kcal/mol)</th>
<th>Average Reaction Energy (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transient State 1</td>
<td>Mechanism 1 &amp; Mechanism 2</td>
<td>63.945</td>
<td>0.843</td>
</tr>
<tr>
<td>Transient State 2</td>
<td>Mechanism 2 &amp; Mechanism 3</td>
<td>63.703</td>
<td>7.335</td>
</tr>
<tr>
<td>Transient State 3</td>
<td>Mechanism 3 &amp; Mechanism 4</td>
<td>23.071</td>
<td>23.085</td>
</tr>
<tr>
<td>Transient State 4</td>
<td>Mechanism 4 &amp; Mechanism 5</td>
<td>No Transient State Found</td>
<td>No Transient State Found</td>
</tr>
<tr>
<td>Transient State 5</td>
<td>Mechanism 5 &amp; Mechanism 6</td>
<td>42.082</td>
<td>5.929</td>
</tr>
<tr>
<td>Transient State 6</td>
<td>Mechanism 6 &amp; Mechanism 7</td>
<td>76.614</td>
<td>3.996</td>
</tr>
</tbody>
</table>
Figure 6.1 shows the first mechanism step of the ammonia decomposition reaction. The ammonia molecule can be observed losing one of its hydrogen atoms, as it is being adsorbed onto the catalyst surface at the beginning the ammonia decomposition reaction. The optimum activation energy for this mechanism step was 63.945 kcal/mol. It can be seen from the transient model that the hydrogen bonds to the surface on the nitrogen site and there remaining NH₂ molecule bonds the cobalt & molybdenum site instead of the molybdenum site where it initially bonds too.

Figure 6.2 illustrates the NH₂ bonded to the cobalt site have a hydrogen atom adsorbed onto another nitrogen site and then become bonded to the open molybdenum and cobalt site as NH. The optimum activation energy of the reaction calculated from the supercomputer is 63.073 kcal/mol, which is almost equal to transient state one.
Figure 6.2: Transient State Two Model

Figure 6.3: Transient State Three Model
Figure 6.3 shows the final hydrogen being bonded to the surface of the catalyst on the final nitrogen site available. The lone nitrogen atom remained bonded to the cobalt and molybdenum site. The activation energy for the mechanism was 23.071 kcal/mol which is significantly lower than the previous transient states and was the lowest of all the transient states calculated.

The transient state five model displayed in Figure four shows the initial desorption step of the ammonia decomposition reaction. One of the spectating hydrogen atoms was removed from the surface, leaving two hydrogen and nitrogen atoms bonded to the surface of the catalyst. The nitrogen can be seen successfully bonding together above the surface of the catalyst. The hydrogen bond can also be seen breaking, to from H₂ in the next mechanism step. The optimum activation calculated by the supercomputer was 42.082 kcal/mol.

![Mechanism 5](image)

\[ \text{Ea} = 42.082 \text{ kcal/mol} \]

![Mechanism 6](image)

**Figure 6.4:** Transient State Five Model

The transient state six model displayed in Figure 6.5 shows the final desorption step of the ammonia decomposition reaction. The activation energy of the reaction is the highest of all the transient states calculated with a value of 76.614 kcal/mol. The final desorption step...
displays the hydrogen atoms bond above the surface of the catalyst, and the previously bonded N\textsubscript{2} molecule attaching to the surface of the catalyst again.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{transient_state_six.png}
\caption{Transient State Six Model}
\end{figure}

\section{Interpretation of Results}

The results collected from the calculations completed by the supercomputer, the rate-limiting step for the ammonia decomposition reaction modelled in this project was determined to be transient state six. This finding was based on the activation energy information which shows the average energy of the final transient state to be the highest with a value of 96.056 kcal/mol. Referring to the adsorption transient state models, the hydrogen atoms which adsorb onto the surface of the catalyst always bonded to the surface on a nitrogen site. This could be attributed to nitrogen and hydrogen having a higher affinity to one another with the nitrogen on the surface having an open spot in its electron shell, so it is much more readily bonded to than the other elements on the surface. This trend should potentially be an area of exploration in future work.
The activation energy value is related to temperature when the value is very high the reaction will not occur at low temperatures. It has been found that the activation energies discovered in this model would not find the Co₃Mo₃N catalyst suitable for the ammonia decomposition reaction as the values are generally much higher than 40 kcal/mol which was the upper limit determined during the modelling of this reaction. The aim of using bi-metallic catalysts is to be able to achieve a high level of ammonia decomposition conversion as decreased temperatures. The result for the activation energies in this experiment exceed the pre-determined upper limit.

Surfaces which returned a negative reaction energy result from the supercomputer were determined not to have a transient state, or similarly, a transient state was unable to be found due to the negative result received. As a result of this, some of the transient states were not determined and were not included in the average values determined.

6.3 Summary

The penultimate component to the modelling in this project developed six transient state models, which were identified for the ammonia decomposition reaction. However, the model could only replicate five of them due to an imbalance on the surface between the adsorption and desorption stages of the reaction. The transient state models develop the mechanism optimisation work conducted in the previous section.

One of the main limitations of the transient data is that when the supercomputer cannot calculate an activation energy for every specimen even if a transient state is determined for two mechanisms. Secondly, this work is dependent on the work completed in the previous two sections which results in the breadth of transient states being limited by this stage of the model due to various reasons as some mechanisms do not work or are not comparable with each other.

Calculations were conducted by the supercomputer to determine the activation energies of each transient state. The results from the model found five of the transient states to be possible, with the rate-limiting step for the ammonia decomposition reaction determined to be the final mechanism step during the reaction, with an average activation energy of
96.056 kcal/mol. The results from the transient state calculated from the supercomputer exceed the upper limit of the activation energies, which means the Co$_3$Mo$_3$N catalyst regarding this modelling project is unsuitable when compared to literature values for the ammonia decomposition reaction. The reaction for the mechanisms to be able to progress would have to be a higher temperature than desirable according to the models results.
Chapter 7
Conclusions & Further Work

The primary aim of this thesis project is to expand on the experimental results from [1] conducted at the King Abdulaziz University, by accurately modelling the experiment using modelling software packages. The model was targeted at accurately determining the mechanisms and kinetics associated with the production of hydrogen from the ammonia decomposition reaction using the Co$_3$Mo$_3$N catalyst. Three distinct research components were developed, the first being the optimisation of the Co$_3$Mo$_3$N catalyst and the second being the investigation of the ammonia decomposition reaction mechanisms and finally developing transient state models of the mechanisms. The overriding objective of this thesis was to develop a successful and robust model to address these research components.

The literature report covered the hydrogen production field on a large scale and then became more targeted towards carbide and nitride catalysis in the ammonia decomposition reaction. The review sought explicitly after information related to catalysis of carbides and nitrides and current research into their optimisation. The main findings from the report detailed that there have been limited investigations into the decomposition of ammonia on variously supported metal catalysts for hydrogen production[2]. The report also found that there were significant gaps in theoretical studies for the ammonia decomposition reaction[3]. The literature also showed that currently, tailor-made bimetallic catalysts such as Co$_3$Mo$_3$N and transitional metal nitrides & carbides had been gaining momentum regarding research. The literature review found the Co$_3$Mo$_3$N catalyst to be suitable for the ammonia decomposition reaction.

The opening surface optimisation component of the modelling work was to manipulate and determine the most stable surface to develop the mechanism models on. The surface development was achieved by cleaving the original bulk surface of the Co$_3$Mo$_3$N catalyst over the (100), (110) and (111) indexes and optimising them using the Raijin
supercomputer. The primary assumption which was applied throughout the project was; the final energy is independent of the parameters entered into the software.

The most stable catalyst surface optimised was the (1 1 1) surface, confirming similar physical experimental information from the literature review\([4]\). The optimum surface denoted 111_2 was the overall most stable comparatively with an energy value of -882.667 eV. This result was confirmed by the bond length analysis which showed the 111_2 specimen to undergo the smallest amount of change during optimisation. The relationships derived from the surface optimisation results show two plausible relationships with the first being between the catalyst thickness and the stability; the second being the cobalt presence and the stability. The findings are in support to one another. However, current literature supports the relationship of cobalt’s impacts on the stability.

Stable mechanisms were developed for the ammonia decomposition reaction. The mechanisms were biased over the catalyst surface where they were optimised using the supercomputer. The results from the energy values showed that the desorption mechanisms were slightly more stable than the adsorption steps. Different location placements of the ammonia molecule were tested above the surface of the catalyst to determine the most stable iteration comparatively. The most stable mechanisms where then used in the final transient state modelling of the reaction.

The findings from the transient state modelling of the optimised mechanisms determined the rate-limiting step of the ammonia decomposition reaction to be the final transient state, TS6. As there were multiple mechanisms due to the various placements of the ammonia molecule, multiple transient states were formed for each mechanism step. The activation energies from each transient state were calculated using the supercomputer and averaged. The final transient state was composed of mechanisms six and seven, had the highest average activation energy of 76.614 kcal/mol. It was determined by having the highest activation energy that the hydrogen desorption from the catalyst surface (TS6), was the rate-limiting step of the model. This finding was contrary from the literature which found the nitrogen desorption to be the rate-limiting step on similar nitride catalysts. The activation energy found has seldom reliability due to the theoretical nature of the modelling. The majority of the transient states where determined to be unsuitable for lower temperature due to their high energies. This finding deems the Co\(_3\)Mo\(_3\)N catalyst from the
model to be unsuitable at low temperature for the ammonia decomposition reaction. From the literature, the catalyst is required to perform at lower temperatures, which from this model the Co3Mo3N catalyst does not display the kinetic properties it is required to do so.

7.1 Reaction Mechanism Sensitivity Investigations

The modelling of the reactions mechanisms governing ammonia decomposition were at the centre of this project. Two areas have been identified in the project which was assumed to have no impact on the results in this project but could be investigated further to assist in the development more robust and accurate model in the future.

During the modelling and the optimisation calculations in the project, the relationship between the distance of the molecule above the surface of the catalyst and successfulness of the mechanism step was not explored. From reaction mechanism data collected in chapter five, the primary assumption was the ammonia molecule above the catalyst surface was the same for each iteration and the distance had no impact on the energy values collected. Observations were made during the modelling of the mechanisms and the transient states, that the distance between the reacting molecule and the catalyst surface had an impact on the energy values produced. Further work on from this project could investigate the sensitivity to the distance between the mechanisms of the ammonia decomposition reaction and the distance the molecules are from the surface of the catalyst. The impact of the distance on the mechanisms developed in this model is unknown; this presents many further avenues for investigation. Research into the distance relationship could assist in providing more accurate models of the ammonia decomposition reaction.

The physical properties of the surfaces used such as the thickness, and the symmetry of the catalysts used in the calculations was assumed to have no impact on the results. Referring the Figure 4.9 in Chapter four, a correlation between the number of atoms in the catalyst and the optimised energy of the catalyst was identified. The figure shows an inversely proportional trend which suggests as the thickness increases the energy value decreases, i.e. the stability of the catalyst increases. When constructing the catalysts, the thickness alteration was aimed at making the catalyst as symmetrical as possible. The impact of symmetry is not known regarding the integrity of the modelling, and the impact symmetry has on the stability of the catalyst. Future work investigating the physical properties of the Co3Mo3N catalyst and its impact on the model would be beneficial in addressing these gaps in this project. An expansion of the physical property investigation could look at the relationship between the cobalt molecules and can confirm the data trend in Figure 4.10 that the number of cobalt atoms in the catalyst impacts the stability. The further
work could then confirm if the energy is related to the cobalt atoms or the number of atoms as a result of the catalyst thickness.

7.2 Expansion of Surface Models

The model for this project explored the (1 0 0), (1 1 0) and (1 1 1) indexs, for the surface optimisation component for the mechanisms to be modelled on. In chapter four of this report, it was deemed a limitation of the results that only three different surface planes were investigated for the optimisation calculations. The cleaving of the surface allows different elements of the catalyst to be exposed to the reaction, resulting in different properties to be exhibited.

With an expansion of the surface models to be optimised, an evaluation can be made on the (1 1 1) surface iteration. An increased number of surfaces optimised will test the relationships identified between the stability of the catalyst and the thickness and the cobalt presence outlined in the above further work component. It is critical however, that more modelling work is conducted on the Co₃Mo₃N catalyst by expanding the surfaces optimised. The exploration of varying properties caused by the different surfaces will provide significant information for comparison and confirmation for the results in this work.

7.3 Development of Mo₂N & W₂C Catalyst Models

Carbide and nitride catalysts in the ammonia decomposition reaction recently have gained momentum in their research. This expanded research is to replace convention catalysts in reactor due to the advantages transitional metal nitrides and carbides present to have⁶. When comparing the two most promising non bi-metallic catalysts in literature, molybdenum nitride has been researched more extensively than tungsten carbide. Similarly to platinum, W₂C exhibits favourable catalytic properties such as high electrical conductivity and strong conductive displacing attributes⁵. Mo₂N has available information in terms of modelling in literature however direct comparisons are difficult to initiate⁷. Future work investigating catalysis in the ammonia decomposition reactions should look at building models for the Mo₂N and W₂C catalysts. Development of this models will provide points of comparison between the carbide and nitride surfaces and will allow assessment of the most suitable catalyst for the reaction.
One of the findings in the literature review for this project was that there is limited theoretical studies involving ammonia as a feedstock for hydrogen[8]. To bridge the gap in literature it is recommended future work look at replicating this project using a different catalyst such as Mo$_2$N and W$_2$C. It is paramount that the same surface parameters be used for the models with cleavage iterations used on the Mo$_2$N and the W$_2$C surfaces to be over the (1 0 0), (1 1 0) and (1 1 1) lines. The surfaces should be optimised to determine the most stable catalyst surface which can be then directly compared to the research results in tables 4.1 and 4.4. Trends can be then derived to see if this expanded research confirms that the (1 1 1) surface is the most stable across other nitride and carbide catalysts.
7.4 References


Chapter 8
Appendices

Appendix A — Original Experimental Results

8.1 Experimental Figures

Figure 8.1: Catalyst activity for ammonia decomposition using MoN, 1CoMoN, 3CoMoN, and 5CoMoN at 300-600 °C\[1\].

Figure 8.2: NH\(_3\) decomposition Arrhenius plots over MoN, 1CoMoN, 3CoMoN, and 5CoMoN catalysts\[1\].
8.2 Experimental Tables

**Table 8.1:** BET data; surface area and catalyst average size of particle crystallite

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Fresh</th>
<th>Used</th>
<th>y-Mo2N</th>
<th>y-Mo2N</th>
<th>MoO2</th>
<th>Co3Mo3N</th>
<th>MoO2</th>
<th>Mo2N</th>
<th>Co3Mo3N</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoN</td>
<td>110</td>
<td>78</td>
<td>7</td>
<td>7</td>
<td>169</td>
<td>—</td>
<td>54</td>
<td>46</td>
<td>—</td>
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<tr>
<td>1CoMoN</td>
<td>91</td>
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<td>3CoMoN</td>
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<td>10</td>
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<td>20</td>
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<td>5CoMoN</td>
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<td>59</td>
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<td>13</td>
<td>110</td>
<td>20</td>
<td>3</td>
<td>90</td>
<td>7</td>
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</table>

**Table 8.2:** Experimental Catalytic Activation Energies

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Ea (KJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoN</td>
<td>131.2</td>
</tr>
<tr>
<td>1CoMoN</td>
<td>99.7</td>
</tr>
<tr>
<td>3CoMoN</td>
<td>92.8</td>
</tr>
<tr>
<td>5CoMoN</td>
<td>102.6</td>
</tr>
</tbody>
</table>
Appendix B — Modelling Figures & Tables

8.3 Chapter 4
8.3.1 Original Catalyst Surfaces

Figure 8.1: Original (100) Unoptimised Co₃Mo₃N Surface
Figure 8.2: Original (110) Unoptimised $\text{Co}_3\text{Mo}_3\text{N}$ Surface
Figure 8.3: Original (111) Unoptimised Co₃Mo₃N Surface
### 8.3.2 Modelling Tables

**Table 4.2: Catalytic Energy Values By Element**

<table>
<thead>
<tr>
<th>Specimen Code</th>
<th>Molybdenum Energy (eV)</th>
<th>Cobalt Energy (eV)</th>
<th>Nitrogen Energy (eV)</th>
<th>Total Energy (eV)</th>
</tr>
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**Table 4.3: Physical Properties Of The Optimised Specimens**

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# Chapter 5

## 8.4.1 Modelling Tables

### Table 5.3 Adsorption Mechanisms Energy Data

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<th>Energy (eV)</th>
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### Table 5.4 Desorption Mechanisms Energy Data

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### Chapter Six

#### 8.5.1 Modelling Tables

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<th>Product Mechanism</th>
<th>Activation Energy (kcal/mol)</th>
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#### Transient State 2

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### Table 6.4 Desorption Transient State Energy Data

#### Transient State 4

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<td>-0.920</td>
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<tr>
<td>TS5.5</td>
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<td>1.439</td>
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<tr>
<td>TS5.6</td>
<td>M5a1b</td>
<td>M6a3a</td>
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</tr>
<tr>
<td>TS5.7</td>
<td>M5b2</td>
<td>M6a3a</td>
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<td>3.666</td>
</tr>
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<td>M6a3a</td>
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#### Transient State 6

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Reactant Mechanism</th>
<th>Product Mechanism</th>
<th>Activation Energy (kcal/mol)</th>
<th>Reaction Energy (kcal/mol)</th>
</tr>
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<tbody>
<tr>
<td>TS6.1</td>
<td>M6a3a</td>
<td>M7a3a</td>
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<td>TS6.2</td>
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<td>M7a2a</td>
<td>134.126</td>
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<td>TS6.3</td>
<td>M6a2a</td>
<td>M7a3a</td>
<td>N/A</td>
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<td>TS6.4</td>
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<td>M7a2a</td>
<td>77.427</td>
<td>11.077</td>
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Appendix C - Modelling Calculations

8.6 Chapter Four

The following calculations are for the summarised data in chapter five of this report. The supercomputer provided the atomic composition of each element in the surfaces optimised. This data was used in conjunction with the optimised energy values calculated by the supercomputer.

8.6.1 Energy of Constituents Calculations

Optimised Element Energies;
Molybdenum: -50.332 eV ÷ 4 atoms = -12.583 eV
Cobalt: -35.067 eV ÷ 4 atoms = -8.7667 eV
Nitrogen: -4.860 eV

Bulk Surface;
Molybdenum Energy: -12.583 eV * 12 atoms = -150.996 eV
Cobalt Energy: -8.7667 eV * 12 atoms = -105.201 eV
Nitrogen Energy: -4.860 eV * 4 atoms = -19.44 eV

Total Energy of Constituents: (-150.996) + (-105.201) + (-19.44) = -275.637 eV

100_1 Surface;
Molybdenum Energy: -12.583 eV * 27 atoms = -339.741 eV
Cobalt Energy: -8.7667 eV * 25 atoms = -219.169 eV
Nitrogen Energy: -4.860 eV * 11 atoms = -53.460 eV

Total Energy of Constituents: (-339.741) + (-219.169) + (-53.460) = -612.370 eV

100_2 Surface;
Molybdenum Energy: \(-12.583\) eV * 27 atoms = \(-339.741\) eV
Cobalt Energy: \(-8.7667\) eV * 25 atoms = \(-219.169\) eV
Nitrogen Energy: \(-4.860\) eV * 11 atoms = \(-53.460\) eV

Total Energy of Constituents: \((-339.741) + (-219.169) + (-53.460) = -612.370\) eV

110_1 Surface;
Molybdenum Energy: \(-12.583\) eV * 25 atoms = \(-314.575\) eV
Cobalt Energy: \(-8.7667\) eV * 28 atoms = \(-245.469\) eV
Nitrogen Energy: \(-4.860\) eV * 10 atoms = \(-48.600\) eV

Total Energy of Constituents: \((-314.575) + (-245.469) + (-48.600) = -608.664\) eV

110_2 Surface;
Molybdenum Energy: \(-12.583\) eV * 24 atoms = \(-301.992\) eV
Cobalt Energy: \(-8.7667\) eV * 28 atoms = \(-245.469\) eV
Nitrogen Energy: \(-4.860\) eV * 10 atoms = \(-48.600\) eV

Total Energy of Constituents: \((-301.992) + (-245.469) + (-48.600) = -596.061\) eV

111_1a Surface;
Molybdenum Energy: \(-12.583\) eV * 36 atoms = \(-452.988\) eV
Cobalt Energy: \(-8.7667\) eV * 33 atoms = \(-289.303\) eV
Nitrogen Energy: \(-4.860\) eV * 11 atoms = \(-53.460\) eV

Total Energy of Constituents: \((-452.988) + (-289.303) + (-53.460) = -795.751\) eV

111_1b Surface;
Molybdenum Energy: \(-12.583\) eV * 36 atoms = \(-452.988\) eV
Cobalt Energy: \(-8.7667\) eV * 40 atoms = \(-350.670\) eV
Nitrogen Energy: \(-4.860\) eV * 13 atoms = \(-63.180\) eV

Total Energy of Constituents: \((-452.988) + (-350.670) + (-63.180) = -866.838\) eV
111_2 Surface;
Molybdenum Energy: \(-12.583\) eV * 36 atoms = \(-452.988\) eV
Cobalt Energy: \(-8.7667\) eV * 40 atoms = \(-350.670\) eV
Nitrogen Energy: \(-4.860\) eV * 13 atoms = \(-63.180\) eV

Total Energy of Constituents: \((-452.988) + (-350.670) + (-63.180) = -866.838\) eV

8.6.2 Unit Surface Area Energy Calculations

General Equation:
(\text{Optimised Energy (eV) - Constituent Energy (eV)}) \div \text{Surface Area of Specimen (Å}^2\text{)}

Bulk Surface;
\((-303.258 - (-275.637)) \div 49.4317 = \text{0.55877 eV/Å}^2\)
100_1 Surface;
\((-660.319 - (-612.37)) \div 52.8715 = \text{0.9069 eV/Å}^2\)
100_2 Surface;
\((-660.425 - (-612.37)) \div 52.8715 = \text{0.9089 eV/Å}^2\)
110_1 Surface;
\((-643.472 - (-608.664)) \div 61.0508 = \text{0.57048 eV/Å}^2\)
110_2 Surface;
\((-629.652 - (-596.061)) \div 61.0508 = \text{0.55021 eV/Å}^2\)
110_2 Surface;
\((-629.652 - (-596.061)) \div 61.0508 = \text{0.55021 eV/Å}^2\)
111_1a Surface;
\((-839.212 - (-795.751)) \div 52.8715 = \text{0.82202 eV/Å}^2\)
111_1b Surface;
\((-881.938 - (-866.838)) \div 52.8715 = \text{0.2856 eV/Å}^2\)
111_2 Surface;
\((-882.667 - (-866.838)) \div 52.8715 = \text{0.9958 eV/Å}^2\)
Appendix D - Report Definitions

Brunauer Emmett Teller - is an analysis technique to measure the surface area of materials\textsuperscript{[2]}.  
Carbon Nano Tube - is a tube shaped material made of carbon which has a diameter measured on the nanometer scale\textsuperscript{[3]}.  
Energy dispersive X-ray - spectroscopy within the scanning transmission electron microscope (STEM) provides accurate elemental analysis with high spatial resolution\textsuperscript{[4]}.  
Reaction Rate - Is defined as how quickly a reaction occurs. i.e The speed of a reaction for a reactant or product.  
Scanning Electron Microscope - is a electron microscope which uses a technique where surfaces are scanned with a focused beam of electrons to attain an image\textsuperscript{[5]}.  
Scanning Transmission electron microscopy - is the same as TEM however allows for three dimensional images to be produced\textsuperscript{[6]}.  
Temperature Programmed desorption - is a method to observe molecules which have been desorbed from a particular surface. This occurs when the surface is heated allowing the analysis to occur\textsuperscript{[7]}.  
Transient State - Is when a system (reaction) is between two mechanisms and has not yet reached steady state.  
Turn over frequency - Measures the overall level of activity of the catalyst. It is the total number of moles transformed into the desired product by one mole of active site per unit time\textsuperscript{[8]}.  
Transmission electron microscopy - is a microscopy technique where an imaged is formed via a beam of electrons being transmitted through a sample\textsuperscript{[6]}.  
X-ray Powder Diffraction - is a technique used to primarily identify phases of a crystalline material. The method also has the ability to determine the unit cell dimensions of a sample\textsuperscript{[9]}.  

Appendices E - Literature Review

8.8 Hydrogen Physical & Chemical Properties\textsuperscript{[20]}

Table 2.9: Physical and chemical properties of Hydrogen fuel

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Weight (g/mol)</td>
<td>2.016</td>
</tr>
<tr>
<td>Mass Density (kg/Nm(^3)) @ T = 0°C, P = 1 atm</td>
<td>0.09</td>
</tr>
<tr>
<td>Boiling Point (K)</td>
<td>20.2</td>
</tr>
<tr>
<td>Higher heating value (MJ/kg)</td>
<td>142.0</td>
</tr>
<tr>
<td>Lower heating value (MJ/kg)</td>
<td>120.0</td>
</tr>
<tr>
<td>Flammability Limits (% Volume)</td>
<td>4.0-75.0</td>
</tr>
<tr>
<td>Diffusion velocity in air (m/s)</td>
<td>2.0</td>
</tr>
<tr>
<td>Ignition energy (mJ) @ stoichiometric mixture</td>
<td>0.02</td>
</tr>
</tbody>
</table>

8.9 References


