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The Role of Composition on the Ammonia Synthesis Activity of Nitrides, Carbonitrides, Carbides and Osmium Based Compounds

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Abstract

The industrial route for producing ammonia is via the Haber-Bosch Process and requires high temperatures and pressures. When considered in its entirety, including the production of the necessary feedstreams, the process is stated to account for 2% of the world’s energy demand and 1.6% of global anthropogenic CO₂ emissions. If a more active ammonia synthesis catalyst was developed, it may prove possible to operate under more moderate conditions, facilitating localised and sustainable production. One potential approach to the development of catalysts with enhanced activity by-passing the limiting scaling relationship invoked for metal catalysts is ammonia production via the Mars-van Krevelen mechanism, as possibly exhibited by some metal nitrides, such as Co₃Mo₃N.

The role composition and crystal structure type have on the ammonia synthesis activity of mixed metal nitrides, carbonitrides and carbides was investigated within this thesis. Fe₃Mo₃C, Ni₆Mo₆C, Ni₃Mo₃C and Ni₂Mo₃CxNy have been tested for their ammonia synthesis capabilities, to discover if the presence of lattice nitrogen was required. Fe₃Mo₃C was found to be inactive for ammonia synthesis at 400°C. However, when the temperature was increased to 500°C, the material became active, which may be related to the substitution of lattice carbon with nitrogen. Ni₆Mo₆C and Ni₃Mo₃C were inactive for ammonia synthesis at 400°C and 500°C, respectively. When Ni₆Mo₆C and Ni₃Mo₃C were investigated at 700°C, an induction period occurred before the two materials developed activity for ammonia synthesis; during this period, nitridation of the lattice occurred eventually leading to the formation of Ni₂Mo₃N. Ni₂Mo₃C could not be synthesised via a topotactic route from Ni₂Mo₃N and the carbonitride phase which was formed was active for ammonia synthesis at 400°C.

The lattice nitrogen in the filled β-Mn structured Ni₂Mo₃N and η-carbide structured Ni₂GaMo₃N was observed to exhibit different behaviour to that in the filled β-Mn structured Co₂Mo₃N and η-carbide structured Co₃Mo₃N and Fe₃Mo₃N. For Ni₂Mo₃N and Ni₂GaMo₃N, the bulk lattice nitrogen appeared to be relatively unreactive at 900°C, whereas Co₂Mo₃N, Co₃Mo₃N and Fe₃Mo₃N decomposed under these conditions. This suggests that both composition and crystal structure type may have an impact on the lattice nitrogen reactivity.

The potential structure sensitivity of osmium for ammonia synthesis was examined and it was found that the metal was more active when it was more highly dispersed. Supported mixed metal carbonyl clusters were also tested and were observed to have different activities to the supported monometallic equivalents.
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Author’s Declaration

I declare that this thesis is the result of my own work, except where reference is made to the contribution of others. This work has not been submitted for any other degree at the University of Glasgow or any other institution.
Publications


## Definitions/Abbreviations

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<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy Dispersive X-ray Spectroscopy</td>
</tr>
<tr>
<td>BET Surface Area</td>
<td>Brunauer-Emmett-Teller Surface Area</td>
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<tr>
<td>PXRD</td>
<td>Powder X-ray Diffraction</td>
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<td>CHN</td>
<td>Carbon, Hydrogen, Nitrogen</td>
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<tr>
<td>TGA</td>
<td>Thermogravimetric Analysis</td>
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<td>TPO</td>
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<td>IR</td>
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<tr>
<td>ToF SIMS</td>
<td>Time of Flight Secondary Ion Mass Spectroscopy</td>
</tr>
<tr>
<td>TPR</td>
<td>Temperature Programmed Reduction</td>
</tr>
<tr>
<td>JCPDS</td>
<td>Joint Committee on Powder Diffraction Standards</td>
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<tr>
<td>a.u.</td>
<td>Arbitrary units</td>
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<td>TOF</td>
<td>Turnover Frequency</td>
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1. Introduction

1.1 Fixation of N\textsubscript{2} in Nature

Nitrogen is essential to sustain the life of animals and plants. Many biomolecules, including nucleotides and amino acids, contain nitrogen and are necessary for producing the proteins in muscle and the skin [1]. Nitrogen is widely available, with almost 80% being present in air [1]. However, due to the strong nitrogen triple bond making N\textsubscript{2} relatively inert, plants and many life forms cannot uptake nitrogen in this form. Instead, plants obtain nitrogen when N\textsubscript{2} is converted into ammonia or nitrate [2]. In nature, nitrogen fixation can occur by two methods. The first is the transformation of N\textsubscript{2}, oxygen and water to nitrate by lightening [3]. The second is by the enzyme, nitrogenase, found in a small number of prokaryotes [2]. Nitrogenase forms ammonia at ambient temperature and pressure according to the following equation:

\[
N\textsubscript{2} + 8e^- + 8H^+ + 16 ATP \rightarrow 2NH_3 + H_2 + 16 ADP + 16P_i
\]

Equation 1: Formation of ammonia by nitrogenase [2]

Nitrogenase contains two main proteins, the iron protein and the molybdenum-iron protein [2] [4]. There also exist nitrogenases with vanadium or iron in place of molybdenum [5]. The structure of the Mo containing nitrogenase is presented in Figure 1. Three clusters exist within this structure, the F, P and M clusters. The F cluster consists of the iron protein and is responsible for hydrolysis of adenosine triphosphate (ATP) to adenosine diphosphate (ADP) [4]. The electrons formed by this process are transferred to the FeMo cofactor (M cluster) through the P cluster [2]. The M cluster is the active site for binding of the nitrogen and reduces H\textsuperscript{+} and N\textsubscript{2} to H\textsubscript{2} and NH\textsubscript{3} [2].

It was originally thought that the M cluster contained an interstitial nitrogen atom that could be exchanged during dinitrogen reduction [6]. However, later studies revealed that the atom was not exchangeable [7] and was instead carbon [2] [8]. The active site for this process is Fe\textsubscript{7}MoS\textsubscript{9}C [2]. It has been proposed that the formation of ammonia by nitrogenase occurs through an associative mechanism in which protonation of N\textsubscript{2} occurs prior to its dissociation [2] [9]. Through nitrogenase catalysed nitrogen fixation, 110 Tg of nitrogen is fixed per year on land and 140 Tg of nitrogen per year in the ocean [10].

However, not enough nitrogen is fixed by the enzyme to sustain the current human population. The biological process contributes 50% of the fixed nitrogen required for current agricultural production [2] [10]. When nitrogen levels are low in the soil, plant growth becomes limited and food production is low. This problem can be solved by adding
fixed nitrogen to the soil in the form of fertiliser. Therefore, it was necessary that an industrial process was developed to produce the synthetic fertiliser and support the growing population.

![Figure 1: Structure of Mo nitrogenase. [2]](image)

### 1.2 Industrial Processes for Producing Ammonia

#### 1.2.1 Haber-Bosch Process

The development of the Haber-Bosch Process was one of the most important achievements of the twentieth century. It allowed the production of ammonia from the direct combination of nitrogen with hydrogen. This reaction is possible by the use of an iron catalyst doubly promoted with Al₂O₃ and K₂O. The reaction takes place at a moderate temperature of between 400-500°C and high pressures of approximately 200 atmospheres [11] [12]. The reaction is as follows:

\[
N_2 + 3H_2 \leftrightarrow 2NH_3 \quad (\Delta H^0 = -92 \text{ kJ/mol})
\]

**Equation 2: Reaction of nitrogen and hydrogen to produce ammonia**

As the reaction is exothermic and equilibrium limited, thermodynamically it is favoured at low reaction temperatures. However, higher temperatures are used industrially to achieve satisfactory reaction kinetics. As suggested in a patent by Haber and Rossignol, the
ammonia in the gas leaving the reactor is removed by cooling it to a liquid state [13]. The unreacted nitrogen and hydrogen are then recycled to increase the percentage conversion to ammonia from 15% to an overall conversion of 97% on subsequent passes [14].

Mittasch and co-workers studied a wide range of metals for the process, including iron, molybdenum, osmium, uranium and nickel [15]. Iron metal was found to initially have a good activity for ammonia synthesis but was observed to deactivate quickly [16]. Therefore, iron was originally removed from contention as the catalyst for the process. However, Mittasch discovered that mixing the iron oxide (Fe₃O₄) precursor with metal oxides, such as Al₂O₃ and K₂O enhanced the activity and stability of the resultant iron based catalyst [16]. The alumina acts as a structural promoter and prevents the sintering of α-iron, which is formed after reduction of the iron oxide [17]. Potassium increases the activity of the catalyst by donating electron charge to the iron, resulting in a weakening of the N₂ bond upon adsorption [18]. The reduced iron catalyst has a network of pores with diameters of 25 – 50 nm [19].

The process facilitated the formation of ammonia on an industrial scale. Ammonia has many uses but the most significant, is as a synthetic fertiliser and ammonia is also gaining interest as a potential fuel. The fertiliser formed from ammonia is necessary for sustaining crops and for providing food for a large fraction of the world’s population. Almost 130 million tonnes of ammonia was produced in the year 1999 [20], with more than 80% of this being converted to fertilizers. However, there are some disadvantages to this process. The production of ammonia from the Haber-Bosch Process requires 1 – 2% of the world’s manmade energy demand when the process is considered in its entirety including feed gas generation [11] [21]. Furthermore, the hydrogen feedstream obtained from natural gas, results in 2.2 tonnes of CO₂ being generated per tonne of ammonia being produced [22]. When coal is used as the source of hydrogen, 16.7 tonnes of CO₂ per tonne of ammonia is formed [22]. This results in ammonia production accounting for 1.6% of global manmade CO₂ emissions [21].

If a more active catalyst than the one used in the Haber-Bosch Process was developed, it may prove possible to operate under more moderate conditions, facilitating localised and sustainable production where the H₂ feedstream is derived from renewable hydrogen generated via electrolysis from electricity sources derived from wind, solar or tidal power. The reduction in temperature would allow the possible increase in percentage per-pass yield due to more favourable equilibrium conditions. This would require the discovery of a
new catalyst. However, it is important to consider that iron, as is currently used on the large scale, is inexpensive and abundant, although it is highly susceptible to poisoning. Any new catalyst must be highly active and, ideally, be less susceptible to poisoning.

1.2.2 Kellogg Advanced Ammonia Process (KAAP)

One alternative process that has been developed is the Kellogg Advanced Ammonia Process, which uses a promoted ruthenium on graphite catalyst [23]. The catalyst is stated to be 10 – 20 times more active than the iron-based one used in the Haber-Bosch Process. This high activity of the ruthenium catalyst has been explained in relation to its nitrogen binding energy [24]. Ruthenium was shown to have close to optimal adsorption energy for nitrogen chemisorption, resulting in high ammonia turnover frequencies.

Aika and Ozaki focused on studying ruthenium based catalysts for ammonia synthesis [25] [26] [27]. They showed that promoting the ruthenium with both Cs⁺ and Ba²⁺ resulted in a highly active catalyst [28]. It is proposed that the promoters transfer charge to the ruthenium, acting similarly to the potassium component in the Haber Bosch catalyst in enhancing N₂ activation. The choice of support was also shown to affect the rate, with carbon and alumina supported ruthenium having the highest activity [27]. The authors suggested that the support acts as a medium for the electron transfer. Due to the interest generated by Aika and Ozaki in ruthenium catalysts, BP developed a doubly promoted ruthenium catalyst supported on methanation resistant high surface area graphitised carbon (Ru/Cs/Ba/HSAG) for ammonia synthesis [29].

The Ru/Cs/Ba/HSAG catalyst contains an 8 wt.% loading of ruthenium and high loadings of the two promoters [29]. The HSAG is formed by a three stage heat treatment up to approximately 2000°C. The resultant material has a mesoporous structure that stabilises the ruthenium particles and is resistant to methanation at high pressures of hydrogen [29].

As the Ru/Cs/Ba/HSAG catalyst is more active than the Haber Bosch catalyst, the KAAP can be operated at lower pressures, which results in a lower operational cost [30]. The process can also retain a high activity at lower temperatures and higher ammonia concentrations than the Haber Bosch Process. The catalyst can operate with a range of hydrogen to nitrogen feedstream ratios. The Haber-Bosch Process operates with 3:1 H₂/N₂, whereas for the ruthenium based catalyst, the optimum ratio is lower than stoichiometric [30]. This is due to ruthenium being strongly inhibited by hydrogen and thus, the catalyst has a higher activity when higher nitrogen pressures are used [31]. The first KAAP plant was in operation by 1992 as part of the Ocelet project [29] and by 2004, there were 7
plants in operation [32]. However, there is further interest in producing a highly active catalyst operative under even less severe conditions which are more applicable to localised sustainable ammonia synthesis.

1.3 Metal Nitrides

Another alternative being considered is the use of binary and ternary nitrides as catalysts for ammonia synthesis. Mittasch discovered that molybdenum nitride and uranium nitride were particularly active for ammonia synthesis [15] [16]. Uranium nitride was one of the early contenders for the Haber Bosch Process before the iron catalyst was discovered [33]. The uranium could be promoted with certain metals to provide an ammonia yield of between 1% and 2.5% at 550°C and 100 atmospheres pressure [15]. However, the uranium catalyst was expensive and, therefore, it was necessary to find an alternative that was as effective and more commercially acceptable [15].

During the search for a catalyst for the Haber Bosch Process, Mittasch observed that molybdenum formed a nitride under the ammonia synthesis conditions [15] [16]. The molybdenum had an advantage over pure iron as it was less easily poisoned. Mittasch also stated that molybdenum was the most efficient of the easily obtainable materials [15]. As the molybdenum was transformed into the nitride, the activity increased and therefore, it was proposed that the nitride was the active form of the catalyst [16]. Molybdenum nitride was observed to have an ammonia synthesis yield of 1.5% at 550°C and 100 atmospheres pressure [15]. The activity of the material could be increased by combining molybdenum with cobalt, nickel or iron and promoting molybdenum with alkali metals. However, oxides of the alkali metals were observed to have a negative impact. The promoted molybdenum material had an ammonia yield of up to 4% at 550°C and 100 atmospheres pressure [15].

Kojima and Aika also studied molybdenum nitride ($\gamma$-Mo$_2$N) for ammonia synthesis and obtained a rate of 48 µmol h$^{-1}$ g$^{-1}$ at 400°C and atmospheric pressure [34]. Generally, ternary molybdenum nitrides, such as Co$_3$Mo$_3$N, Ni$_2$Mo$_3$N and Fe$_3$Mo$_3$N, are reported to be more active [35] [36]. This supports the observations made by Mittasch that alloying the molybdenum with one of these metals increases the activity. It has been shown that the Co$_3$Mo$_3$N has high activity for ammonia synthesis and even exceeds the activity of the iron based industrial catalyst, particularly when doped with Cs$^+$ [37].

Materials that have recently been developed which show promise with respect to the commercially applied promoted iron and ruthenium based systems are CoRe$_4$ and Cs$^+$ on
Co₃Mo₃N. CoRe₄ has an extremely high activity of 943 ± 44 µmol h⁻¹ g⁻¹ at 400°C and ambient pressure [38]. However, the high cost of rhenium is a disadvantage to using this material. A disadvantage to the Cs⁺ on Co₃Mo₃N is that phase instability can occur [39]. Therefore, any material that is prepared has to be highly active, stable and reasonably cost effective, as well as being suitable for application under transient operation and in addition less harsh reaction conditions than the Haber Bosch Process.

1.4 Sustainability for Ammonia Synthesis

Finding ways to produce ammonia in a sustainable way has grown in importance over the years [11] [22] [40]. One possible solution is to use renewable sources, such as solar, tidal or wind energy, instead of fossil fuels to form the H₂ feedstream via electrolysis of water. Localised production, where the fertiliser is formed near the crop growing fields where it would be applied, would also be desirable. However, for this to occur, a more active catalyst would need to be developed, in order that more moderate conditions suitable for ammonia production on a farm could be utilised.

One proposed method related to catalysis is chemical looping [40] [41]. This process requires multiple steps in order to produce ammonia via the intermediacy of a metal nitride as seen in Figure 2. Either H₂O or H₂ can be used in the looping process. For the H₂O cyclic looping, the first reaction step involves oxidising a metal nitride with water to form ammonia and a metal oxide. Then, the metal oxide is reacted with a reducing agent, such as carbon, and then N₂ to generate the recycled metal nitride [41] [42]. In order to remove the oxygen from the metal oxide to produce the metal nitride, energy has to be supplied. This energy could be supplied from solar power using parabolic mirror devices to attain the high temperatures necessary to make this process sustainable. Another advantage of this process is that it can be applied at ambient pressure [40]. However, the need for reducing agents containing carbon and the formation of carbon monoxide are drawbacks to this process. The regeneration of the metal nitride from the metal oxide can occur by thermal treatment but requires high temperatures (above 1200°C) [41] [43].

![Figure 2: Chemical looping processes to produce ammonia](image)

One potential cycle for this process involves AlN/Al₂O₃, where AlN is produced from Al₂O₃ by carbothermal reduction under N₂ and is subsequently, hydrolysed to form
ammonia and Al₂O₃ [44]. The procedure was performed at ambient pressure and the energy required for the reduction step was provided by thermal radiation [45]. Michalsky and Pfromm studied a range of metals for this process and observed that Mg₃N₂ had a rate of $1.1 \pm 0.2 \times 10^{-3}$ mol$_{NH_3}$ mol$_{metal}^{-1}$ s$^{-1}$ at 500°C, with 69.9 mol. % of lattice nitrogen converted to ammonia [12]. However, Mg₃N₂ generates a large amount of heat during the hydrolysis stage. The authors suggested that Mo₅N was a more suitable material. Manganese nitrides have also shown promise for this process [42] [43].

For the hydrogen-based cyclic looping to produce ammonia, the first stage is the same as the H₂O cyclic looping, where a metal is nitrided with N₂ to form a metal nitride. However, H₂ is used to reduce the metal nitride to form ammonia and the starting metal [41]. The use of a carbothermal reduction agent would therefore, not be required. The hydrogen applied in this process could be generated from, for example, solar powered electrolysis of water. Michalsky et al examined a range of binary nitrides for this process [46]. The ammonia production rates for Sr₃N₂ and Ca₃N₂ under H₂ at 1 atmosphere and 550°C were stated to be 2.1 ± 0.2 and 1.3 ± 0.4 μmol NH₃ (mol metal x s)$^{-1}$, respectively. The nitrides were observed to transform into SrH₂ and Ca₂NH. The authors concluded that the insertion of hydrogen increased the formation of ammonia from the lattice nitrogen [46]. Other studies have shown that manganese based materials are active for this process, with Li-Mn-N having a high activity at 400°C under 1:3 N₂/H₂ [47].

However, the materials produced so far are somewhat unstable and have unsatisfactory reactivities. Finding a material for this sustainable process is of importance and is the next challenge for the ammonia synthesis process.

As the aim is to reduce the pressure and temperature that the ammonia synthesis process occurs, this would make the materials more environmentally friendly than those currently used in industry.

1.5 Aims

The influence of composition and structure type on the ammonia synthesis activity of ternary and quaternary molybdenum materials and Group 8 metals will be investigated within this thesis. Nitrides (Ni₂Mo₃N, Ni₂GaMo₃N, Co₂Mo₃N and Fe₃Mo₃N) with different metal compositions and either a η-carbide structure or a filled β-manganese structure will be tested for ammonia synthesis activity and lattice nitrogen reactivity. This will be performed in order to study the effect metal composition and crystal structure type may have on the activity. The performance of ternary carbides (Ni₆Mo₆C, Ni₃Mo₃C and
Fe₃Mo₃C and a carbonitride (Ni₂Mo₃CₓNᵧ) will also be examined and compared with their corresponding nitrides, in order to gain an insight into the effect the interstitial carbon/nitrogen may have on the activity. In Chapter 6, the possible structure sensitivity of osmium for ammonia synthesis will be investigated and compared with the other Group 8 metals and possible structure-activity relationships will be explored. Supported mixed metal clusters will also be prepared and tested for ammonia synthesis activity, in order to try and optimise the activity of the Group 8 cluster materials.
2. Experimental

2.1 Materials Preparation

2.1.1 Preparation of Ni$_2$Mo$_3$C$_x$N$_y$

Nickel molybdenum oxide precursor (Ni$_2$Mo$_3$O$_x$) was prepared as described elsewhere by Bion et al. [36], who applied a modified form of the Pechini method. The necessary amounts of ammonium molybdate tetrahydrate ((NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O, Fluka Analytical, puriss. p.a., ACS reagent, ≥ 99.0%), nickel nitrate hexahydrate (Ni(NO$_3$)$_2$·6H$_2$O, Janssen Chimica) and citric acid monohydrate (C$_6$H$_8$O$_7$·H$_2$O, Sigma Aldrich, ACS reagent, ≥ 99.0%), were dissolved in a 10% aqueous solution of nitric acid. The mixture was stirred at room temperature, until a clear solution was obtained. Then, the solvent was evaporated off at 70 °C, until a green coloured gel had formed. The gel was calcined in air at 500°C (60°C/min) for 2 hours to form the oxide.

Nickel molybdenum nitride (Ni$_2$Mo$_3$N) was prepared by nitridation of the oxide precursor by using a 3:1 ratio of 60 mL/min H$_2$/N$_2$ gas mixture (BOC, H$_2$ 99.998%, N$_2$ 99.995%) at 700°C for three hours. A ramp rate of 10°C/min was used to reach 700°C. The material was then cooled after the three hours under H$_2$/N$_2$.

The carburised material (Ni$_2$Mo$_3$C$_x$N$_y$) was prepared by carburisation of Ni$_2$Mo$_3$N with a 20% CH$_4$/H$_2$ gas mixture (BOC, 99.98%) at a flow rate of 12 mL/min. The ramp rate used was 6°C/min until the reactor had reached 350°C and was then changed to 1°C/min up to 560°C. The reactor was kept at 560°C for 2 hours and then the sample was cooled down at a ramp rate of 10°C/min under CH$_4$/H$_2$.

2.1.2 Preparation of Ni$_6$Mo$_6$C

Nickel molybdenum oxide precursor (Ni$_3$Mo$_3$O$_x$) was prepared by using a similar method to the one described in section 2.1.1. Stoichiometric amounts of nickel nitrate hexahydrate (Ni(NO$_3$)$_2$·6H$_2$O, Janssen Chimica) and ammonium molybdate tetrahydrate ((NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O, Fluka Analytical, puriss. p.a., ACS reagent, ≥ 99.0%) were dissolved in 200mL of 10% nitric acid. Then, 26.547g of citric acid monohydrate (C$_6$H$_8$O$_7$·H$_2$O, Sigma Aldrich, ACS reagent, ≥ 99.0%) was added to the mixture and this was stirred until the solution was clear. The mixture was heated at 70°C, until a gel had formed. The gel was then dried in an oven for 12 hours at 120°C. The material was not calcined.

Nickel molybdenum carbide (Ni$_6$Mo$_6$C) was prepared by reducing the uncalcined oxide precursor under a 3:1 ratio of H$_2$/Ar gas mixture (BOC, 99.98%) at a flow rate of
60 mL/min. The citric acid was used as the source of carbon. The material was reduced at either 700°C or 750°C for 6 hours. The ramp rate used was 10°C/min until the reactor had reached 350°C and then it was changed to 5°C/min until the required temperature was attained. The sample was cooled down under H<sub>2</sub>/Ar to room temperature.

2.1.3 Preparation of Ni<sub>3</sub>Mo<sub>3</sub>C

Two methods were used in attempting to prepare nickel molybdenum carbide (Ni<sub>3</sub>Mo<sub>3</sub>C):

1) The first method used a similar process as described by Regmi and Leonard [48]. Uncalcined oxide precursor (Ni<sub>3</sub>Mo<sub>3</sub>O<sub>x</sub>) and excess activated charcoal (0.0156g, British Drug Houses Ltd., powder, washed with acid) were ground together for 20 minutes using a pestle and mortar to obtain a homogeneous mixture. Subsequently, the material was prepared under a 60 mL/min flow rate of Ar gas (BOC, 99.998%) at 1000°C. The ramp rate used for heating was 1°C/min. Once the furnace reached 1000°C, the furnace was cooled down to room temperature under Ar.

2) The second method prepared the material by using the carburisation reactor described in section 2.1.11. Ni<sub>6</sub>Mo<sub>6</sub>C was carburised in 20% CH<sub>4</sub>/H<sub>2</sub> (BOC, 99.98%) at a flow rate of 12 mL/min. The material was loaded into a quartz reactor tube and placed into the microreactor. The material was heated to either 560°C or 800°C at a ramp rate of 50°C/min. After 5 hours at the required temperature, the sample was cooled down to room temperature under 20% CH<sub>4</sub>/H<sub>2</sub>.

2.1.4 Preparation of Ni<sub>2</sub>GaMo<sub>3</sub>N

Nickel gallium molybdenum oxide precursor (Ni<sub>2</sub>GaMo<sub>3</sub>O<sub>x</sub>) was prepared using a modified Pechini method as described in section 2.1.1. Stoichiometric amounts of nickel nitrate hexahydrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Janssen Chimica), gallium (III) nitrate hydrate (Ga(NO<sub>3</sub>)<sub>3</sub>·xH<sub>2</sub>O, Sigma Aldrich, 99.9% metals basis) and ammonium molybdate tetrahydrate ((NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O, Fluka Analytical, puriss. pa., ACS reagent, ≥99.0%) were dissolved in 100mL of 10% nitric acid. Then, 13.226g of citric acid monohydrate (C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>·H<sub>2</sub>O, Sigma Aldrich, ACS reagent, ≥ 99.0%) was added to the mixture and this was stirred until the solution was clear. Following this, the mixture was evaporated off at 70 °C, until a gel had formed. The gel was dried in an oven overnight at 150°C and then, was calcined in air at either 500°C, 600°C or 650°C (60°C/min) for 2 hours to form the oxide.
Nickel gallium molybdenum nitride (Ni$_2$GaMo$_3$N) was prepared using the ammonolysis reactor (as described in section 2.1.9). Ni$_2$GaMo$_3$O$_x$ was nitrided with 95 mL/min of NH$_3$ (BOC, 99.98 %) at 785°C for 5 hours. The temperature was increased from room temperature to 357°C at a ramp rate of 5.6°C/min, then, to 447°C at a ramp rate of 0.2°C/min. Finally, the ramp rate was increased at 2.1°C/min until the final temperature had been reached. After 5 hours at 785°C, the material was cooled down to room temperature under 95 mL/min of NH$_3$. The reactor was then flushed with nitrogen for 30 minutes to remove any residual NH$_3$. Subsequently, the material was passivated for 1 hour by using a mixture of 25 mL/min 2% O$_2$/Ar diluted with nitrogen.

2.1.5 Preparation of Fe$_3$Mo$_3$C

Iron molybdenum oxide (FeMoO$_4$) was prepared by following the procedure outlined by Bem et al. [49]. A green 0.25 M aqueous solution of 37.1 mL of iron (II) chloride tetrahydrate (FeCl$_2$.4H$_2$O, Sigma Aldrich, ReagentPlus, 98%) was added dropwise to a 0.66 M aqueous solution of 14 mL of sodium molybdate dihydrate (Na$_2$MoO$_4$.2H$_2$O, Hopkin and Williams, Analar, 99.0 - 102.0%). FeCl$_2$.4H$_2$O was weighed out in a glovebox. A solid formed immediately when the solutions were mixed together. Once all the aqueous solution of iron (II) chloride tetrahydrate was added, the mixture was left to stir for 1 hour. A brown precipitate was acquired after vacuum filtration and this was washed twice with distilled water and once with ethanol. The solid was dried overnight in an oven at 150°C. Then, it was calcined under 60 mL/min of nitrogen at 500°C (10°C/min) for 6 hours. The solid was cooled down to room temperature under nitrogen.

Iron molybdenum nitride (Fe$_3$Mo$_3$N) was formed by ammonolysis of approximately 0.6 g of FeMoO$_4$ with 95 mL/min of NH$_3$ (BOC, 99.98 %) at 785°C for 5 hours. The ammonolysis reactor was used as described in section 2.1.9. The temperature was increased from room temperature to 357°C at a ramp rate of 5.6°C/min. Then, to 447°C at a ramp rate of 0.2°C/min and finally, the ramp rate was increased at 2.1°C/min until the final temperature had been reached. After 5 hours at 785°C, the material was cooled down under 95 mL/min of NH$_3$. At room temperature, the reactor was flushed with nitrogen for 30 minutes to remove any NH$_3$. Then, the material was passivated for 1 hour by using a mixture of 25 mL/min 2% O$_2$/Ar diluted with nitrogen.

Iron molybdenum carbide (Fe$_3$Mo$_3$C) was prepared from Fe$_3$Mo$_3$N, which was carburised by using a 12 mL/min flow of 20% CH$_4$/H$_2$ gas mixture (BOC, 99.98%) at 560°C for 2 hours. The ramp rate used was 6°C/min until the reactor had reached 350°C and was then
changed to 1°C/min up to the final temperature. After 2 hours, the sample was cooled down to room temperature at a ramp rate of 10°C/min under CH₄/H₂.

2.1.6 Preparation of Co₂Mo₃N

Cobalt molybdenum oxide was synthesised by using three different methods:

1) The first method used a modified form of the Pechini method as described by Bion et al. [36]. To give a 2:3 ratio of Co:Mo, the necessary amounts of cobalt (II) nitrate hexahydrate (Co(NO₃)₂·6H₂O, Alfa Aesar, ACS, 98.0 – 102.0%, crystalline) and ammonium molybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O, Fluka Analytical, puriss. p.a., ACS reagent, ≥ 99.0%) were dissolved in a 10% aqueous solution of nitric acid. Then, citric acid monohydrate (C₆H₈O₇·H₂O, Sigma Aldrich, ACS reagent, ≥ 99.0%) was added. The mixture was stirred at room temperature, until a clear solution was obtained. Then, the mixture was treated at 70°C, until a red coloured gel had formed. The gel was dried in an oven overnight at 120°C. Subsequently, the gel was calcined in air at 500°C (60°C/min) for 2 hours to form the oxide.

2) 2.22 g of ammonium molybdate tetrahydrate (NH₄)₆Mo₇O₂₄·4H₂O, Fluka Analytical, puriss. p.a., ACS reagent, ≥ 99.0%) and 3.64 g of cobalt (II) nitrate hexahydrate (Co(NO₃)₂·6H₂O, Alfa Aesar, ACS, 98.0 – 102.0%, crystalline) were dissolved separately in 100 mL of deionised water. The solution containing cobalt was added dropwise to the solution of molybdenum under stirring. Then, the solution was heated to 85°C and left at this temperature until approximately 75 mL of deionised water remained. A purple precipitate was obtained after vacuum filtration and this was washed twice with deionised water and once with ethanol. The solid was dried overnight in an oven at 150°C and was then calcined in air at 500°C (10°C/min) for 3 hours.

3) A similar method was used as outlined by Hunter et al. [50]. 4.00 g of ammonium molybdate tetrahydrate (NH₄)₆Mo₇O₂₄·4H₂O, Fluka Analytical, puriss. p.a., ACS reagent, ≥ 99.0%) and 4.40 g of cobalt (II) nitrate hexahydrate (Co(NO₃)₂·6H₂O, Alfa Aesar, ACS, 98.0 – 102.0%, crystalline) were dissolved in 200 mL of deionized water. The solution was then heated to 85°C and left at this temperature until approximately 75 mL of deionised water remained. The resulting purple precipitate of CoMoO₄·nH₂O was vacuum filtered and then, washed twice with deionised water and once with ethanol. The sample was dried overnight in an oven at 150°C. The material was not calcined.
Cobalt molybdenum nitride (Co₂Mo₃N) was prepared by nitridation of the oxide precursor by using a 3:1 ratio of 60 mL/min H₂/N₂ gas mixture (BOC, H₂ 99.998%, N₂ 99.995%). The material was prepared at different temperatures of either 600°C, 650°C or 700°C for one, two or three hours. A ramp rate of 10°C/min was used to reach the required temperature. The material was then cooled after the reaction time under H₂/N₂.

2.1.7 Preparation of Osmium
The osmium metal sample was purchased from Acros Organics (99.9%, trace metal basis) and was used as provided.

2.1.8 Preparation of Supported Metal Carbonyl Compounds
2.1.8.1 Preparation of 5% Os₃(CO)₁₂ on Support
Triosmium dodecacarbonyl (Os₃(CO)₁₂, Sigma Aldrich, 98%) was supported onto silica (Silica-amorphous, precipitated, Sigma Aldrich) or alumina (γ-alumina, Condea chemie, alumina extrudates) by the method outlined by Collier et al. [51]. The support was impregnated with a solution of Os₃(CO)₁₂ in dichloromethane (DCM, VRW chemicals, ≥99%, stab. with 0.2% ethanol). The volume of dichloromethane required was determined by point of wetness for each support. The material was then dried at 40°C to remove the dichloromethane to produce a yellow powder of supported Os₃(CO)₁₂. The material was prepared to target a percentage loading of 5% by weight of osmium. The silica was either used as supplied (the hydroxylated support) or was dried at 500°C (10°C/min) for 16 hours under a 60 mL/min flow of nitrogen prior to being impregnated (the dehydroxylated support).

2.1.8.2 Preparation of 5% Os₃(CO)₁₂ on Silica in Inert Conditions
Triosmium dodecacarbonyl (Os₃(CO)₁₂, Sigma Aldrich, 98%) and silica (Silica-amorphous, precipitated, Sigma Aldrich) were weighed out in a nitrogen filled glove box. These were then placed in a sealed Schlenk flask and connected to a Schlenk line. Dry dichloromethane was added to the Schlenk line and was added dropwise, by a syringe, to the silica support and Os₃(CO)₁₂. The material was prepared under nitrogen. The volume of dry dichloromethane needed was determined from the point of wetness for silica. A vacuum was applied to the material to evaporate off any excess dry DCM. The material was prepared to give a percentage loading of 5% by weight of osmium.

2.1.8.3 Preparation of 5% Os₃(CO)₁₂ on Silica and 1% KOH
5% Os₃(CO)₁₂/silica was prepared as described in section 2.1.8.1. Potassium hydroxide (KOH, Sigma Aldrich, puriss. p.a., Reag. Ph. Eur., ≥ 85%, pellets) was added to the 5%
Os$_3$(CO)$_{12}$/silica by wetness impregnation. A solution of KOH in deionised water was added to give a 1% loading of potassium. The material was dried at 100°C for 3 hours.

2.1.8.4 Preparation of 1% Fe$_3$(CO)$_{12}$ on Support
Triiron dodecacarbonyl (Fe$_3$(CO)$_{12}$, Alfa Aesar, 96% (dry wt.), stab. with 5-10% methanol) supported on either silica (Silica-amorphous, precipitated, Sigma Aldrich) or alumina (γ-alumina, Condea chemie, alumina extrudates) was prepared by the method described by Collier et al. [44]. A solution of Fe$_3$(CO)$_{12}$ in dichloromethane was impregnated onto the support. The amount of dichloromethane required to fill the pore volume of the support was determined from the point of wetness. After impregnation, the material was dried at 40°C to remove the dichloromethane. The material was prepared to give a percentage loading of 1% by weight of iron.

2.1.8.5 Preparation of 1% Fe$_2$(CO)$_{9}$ on Alumina
Diiron nonacarbonyl (Fe$_2$(CO)$_{9}$, Sigma Aldrich, 98%) was supported on alumina (γ-alumina, Condea chemie, alumina extrudates) to give a percentage loading of 1% by weight of iron. A solution of Fe$_2$(CO)$_{9}$ in dichloromethane was impregnated onto the support. The amount of dichloromethane needed was decided from the point of wetness for the support. Weighing of the Fe$_2$(CO)$_{9}$ was performed in a glove box due to the material being air sensitive.

2.1.8.6 Preparation of 2% Ru$_3$(CO)$_{12}$ on Support
Triruthenium dodecacarbonyl (Ru$_3$(CO)$_{12}$, Sigma Aldrich, 99%) was supported on silica (Silica-amorphous, precipitated, Sigma Aldrich) or alumina (γ-alumina, Condea chemie, alumina extrudates). The support was impregnated with a solution of Ru$_3$(CO)$_{12}$ in dichloromethane. The material was then dried at 40°C to remove the dichloromethane to produce a powder of supported Ru$_3$(CO)$_{12}$. The material was prepared to give a percentage loading of 2% by weight of ruthenium.

2.1.8.7 Preparation of 5% Ru on Alumina and 1% KOH
The 5% Ru/Al$_2$O$_3$ was a commercial material purchased from Sigma Aldrich (powder, reduced, dry) and was used as provided. Potassium hydroxide (KOH, Sigma Aldrich, puriss. p.a., Reag. Ph. Eur., ≥ 85%, pellets) was added by wetness impregnation. The material was treated with a solution of KOH in deionised water to produce a loading of 1% by weight of potassium. Then, the material was dried overnight at 110°C in an oven.
2.1.8.8 Preparation of 5% Os\textsubscript{3}(CO)\textsubscript{12} and 2% Ru\textsubscript{3}(CO)\textsubscript{12} on Silica

The formation of a supported bimetallic cluster was attempted by using an approach suggested by Kulkarni and Gates [52]. First, triosmium dodecacarbonyl (Os\textsubscript{3}(CO)\textsubscript{12}, Sigma Aldrich, 98%) was supported onto silica (Silica-amorphous, precipitated, Sigma Aldrich) as described in section 2.1.8.1. The resulting material was a yellow powder. Then, triruthenium dodecacarbonyl (Ru\textsubscript{3}(CO)\textsubscript{12}, Sigma Aldrich, 99%) was supported on the silica as detailed in section 2.1.8.6. The material was prepared to target a percentage loading of 5% by weight of osmium and 2% by weight of ruthenium. The material produced was an orange powder of Os\textsubscript{3}(CO)\textsubscript{12} and Ru\textsubscript{3}(CO)\textsubscript{12} on silica.

2.1.8.9 Preparation of 5% Os\textsubscript{3}(CO)\textsubscript{12} and 1% Fe\textsubscript{3}(CO)\textsubscript{12} on Silica

Initially, triosmium dodecacarbonyl (Os\textsubscript{3}(CO)\textsubscript{12}, Sigma Aldrich, 98%) was supported onto silica (Silica-amorphous, precipitated, Sigma Aldrich) as outlined in section 2.1.8.1. Then, triiron dodecacarbonyl (Fe\textsubscript{3}(CO)\textsubscript{12}, Alfa Aesar, 96% (dry wt.), stab. with 5-10% methanol) was supported onto the material as described in section 2.1.8.4. The material was prepared to target a percentage loading of 5% by weight of osmium and 1% by weight of iron. The material produced was a green powder of Os\textsubscript{3}(CO)\textsubscript{12} and Fe\textsubscript{3}(CO)\textsubscript{12} on silica.

2.1.8.10 Preparation of 2% Ru\textsubscript{3}(CO)\textsubscript{12} and 1% Fe\textsubscript{3}(CO)\textsubscript{12} on Silica

The first step involved supporting triruthenium dodecacarbonyl (Ru\textsubscript{3}(CO)\textsubscript{12}, Sigma Aldrich, 99%) onto silica, following the method described in section 2.1.8.6. Then, triiron dodecacarbonyl (Fe\textsubscript{3}(CO)\textsubscript{12}, Alfa Aesar, 96% (dry wt.), stab. with 5-10% methanol) was supported onto the material as explained in section 2.1.8.4. The material was prepared to target a percentage loading of 2% by weight of ruthenium and 1% by weight of iron. The resulting material was a green powder of Ru\textsubscript{3}(CO)\textsubscript{12} and Fe\textsubscript{3}(CO)\textsubscript{12} on silica.

2.1.9 Ammonolysis Reactor

The sample oxide was placed in a quartz reactor tube (10.5 mm internal diameter), which had a quartz sintered disk fitted halfway along the tube. A small amount of quartz wool was placed on top of the sample. The reactor tube was placed vertically inside the Carbolite furnace, which was set to go through various heating programmes by using a temperature controller. Ammonia (NH\textsubscript{3}, BOC, grade N3.8) was introduced into the reactor through ¼ inch stainless steel tubing (Swagelok). A Brooks 5850 TR mass flow controller regulated the flow rate of ammonia. The vented gas was passed through an empty conical flask, to act as a dead volume, and then, a dilute sulfuric acid solution to neutralise any unreacted ammonia. After the reaction, the reactor was cooled down to room temperature and then was flushed with nitrogen for 30 minutes to remove any residual NH\textsubscript{3}. Resultant
Nitrides were passivated at room temperature by using a gas mixture containing 2% O₂/Ar diluted with N₂. Figure 3 shows the experimental set up used for nitriding materials by ammonolysis.

2.1.10 Reactor for Nitridation with N₂/H₂

A schematic of the microreactor system applied for nitridation with the N₂/H₂ reaction gas mixture is displayed in Figure 4. The sample oxide was loaded into a quartz reactor tube (8 mm internal diameter) and was packed at each end with quartz wool. This was then positioned in the centre of the Carbolite furnace, which was used to control the temperature. A Brooks 5850 TR MFC controlled the flow rate of 3:1 H₂/N₂ and the gas was flowed through ¼ inch stainless steel tubing. The resulting nitride was cooled to room temperature under the flowing gas mixture.
2.1.11 Carburisation and Reduction Reactor

The apparatus set up for the carburisation and reduction processes is shown in Figure 5. The sample was loaded into a quartz reactor tube (8 mm internal diameter) and was packed between quartz wool plugs. The reactor tube was placed in the Carbolite furnace, which was used to control the temperature. Brooks 5850 TR MFCs controlled the flow rates for both the 3:1 H₂/Ar (BOC, 99.98 %) and 20% CH₄/H₂ (BOC, 99.98 %) gas mixtures when applied. The gases were flowed through ¼ inch stainless steel tubing. The resulting material was cooled to room temperature under the flowing gas mixture.
2.2 Materials Testing

2.2.1 Reactor for Ammonia Synthesis

The success of a material at producing ammonia was measured by the change in conductivity of a sulfuric acid solution (200 mL, 0.00108 mol/L) over time. The exit gas from the reactor was passed through the sulfuric acid solution and the conductivity decrease was measured. This decrease in conductivity corresponds to the formation of ammonium ions upon reaction of the ammonia with protons. The experimental method applied was related to the one developed by McKay [53]. A schematic of the ammonia synthesis reactor is displayed in Figure 6. The material was located in a quartz reactor tube (8 mm internal diameter) and was held in place between quartz wool plugs. This was then positioned in the centre of the Carbolite furnace, which was used to control the temperature. Reactions were performed at atmospheric pressure under either a 3:1 ratio of H₂/N₂ (BOC, H₂ 99.998%, N₂ 99.995%) or a 3:1 ratio of H₂/Ar (BOC, 99.98 %) with a gas flow rate of 60 mL/min. Flow rates were controlled by Brooks 5850 TR MFCs and the gases were flowed through ¼ inch stainless steel tubing. The conductivity was measured using a HACH HQ14d portable conductivity meter. The calibration value used to calculate ammonia synthesis rates is provided in Appendix I.

2.2.2 Experimental Method

Some of the samples were pre-treated before the reaction. Pre-treatment of these materials was performed at 700°C (except when specified otherwise) for two hours with either 1:3 N₂/H₂ or 1:3 Ar/H₂ gas mixtures. The flow rate of each gas applied was 60 mL/min. A ramp rate of 10°C/min was used to heat the furnace to the required temperature. After the two hours, the reactor was then cooled down to 400°C or 500°C and the ammonia synthesis reaction was started. All the ammonia synthesis reactions were performed at atmospheric pressure. The exit gas was passed through the sulfuric acid solution and the conductivity values were recorded periodically, every five minutes.
2.3 Material Characterisation

2.3.1 Powder X-ray Diffraction (PXRD)

XRD patterns were obtained for the materials pre- and post-reaction by using a PANalytical X-Pert Pro Diffractometer (40kV, 40mA) with a monochromatised CuK alpha radiation source (1.5418 Å). A scanning range of 5-85° 2θ with a total scan time of 51 minutes and a step size of 0.0167° was used. Identification of phases was performed by comparing the patterns with JCPDS database files.

2.3.2 CHN Analysis

Carbon, hydrogen and nitrogen (CHN) analysis for pre- and post-reaction samples was very kindly performed by Mr Gangi Reddy Ubbara at the University of Glasgow. Elemental analysis was performed by combustion by using a CE-440 elemental analyzer made by Exeter Analytical, Inc.

2.3.3 Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDX)

A Philips XL30E-Scanning electron microscope fitted with a tungsten filament and secondary electron detector was used to take SEM images. A beam of 20 kV and a spot size setting of 5 was applied. The spot size is an instrumental size and relates to the diameter of the beam on the sample. The microscope was also used to obtain Energy-Dispersive X-ray spectroscopy (EDX), which is applied to give the composition of the materials. EDX was measured by Oxford Instruments AZtec Software with X-act 10 mm² SDD detector.
The samples were placed onto carbon tabs and covered with a film of gold/palladium to reduce electron charging. This was done with a Polarn SC7640 Auto high-resolution sputter coater.

2.3.4 Raman Spectroscopy
The Raman spectra of the pre- and post-reaction samples were collected by using a Horiba Jobin Yvon LabRAM High Resolution spectrometer. A Ventus 532 nm green laser at 100 mW was used as the excitation source. The samples were focused by using a 50x objective lens. The laser was focused for 10 seconds, with a repetition of 3 and a grating of 600 cm\(^{-1}\). The spectral region measured was from 50 - 3000 cm\(^{-1}\). The Raman spectra were collected at room temperature on a glass slide.

2.3.5 Thermogravimetric Analysis with Mass Spectrometry (TGA-MS)
A TA Instruments SDT Q600 coupled to an ESS evolution mass spectrometer was used to perform thermogravimetric analyses on the materials. Mass spectrometry was performed in multiple ion detection mode (MID mode). The sample was heated from room temperature to 1000°C at a ramp rate of 10°C/min under a gas flow comprising either 3:1 H\(_2\)/Ar or 5% H\(_2\)/N\(_2\). TGA-MS was very kindly performed by Mr Andrew Monaghan at the University of Glasgow.

2.3.6 Temperature Programmed Oxidation (TPO)
Thermogravimetric analysis of the uncalcined and calcined nickel gallium molybdenum oxide was performed on a TA Instruments TGA Q500. The samples were heated from room temperature to 900°C at a ramp rate of 10°C/min under 90 mL/min of air. TPO was very kindly performed by Mr Andrew Monaghan at the University of Glasgow.

2.3.7 Infrared Measurement
Infrared spectroscopy was performed on the materials derived from organometallic clusters. Infrared analysis for the samples was performed with a 10 mm KBr cell inserted into a Shimadzu IR Affinity-1S instrument. A background was taken before each sample and was subtracted to give the IR spectra for the corresponding metal carbonyl complex. The spectra were collected in the carbonyl region of 1500 – 2800 cm\(^{-1}\), the resolution was 4 cm\(^{-1}\) and the number of scans undertaken was 50.

2.3.8 BET Surface Area
Surface areas of the pre- and post-reaction materials were measured from a Quadrasorb evo Gas Sorption Surface Area and Pore Size Analyzer manufactured by Quantachrome.
Before each measurement, approximately 0.1 g of sample was degassed overnight under vacuum at 110°C with a Flovac degasser. The programme used to analyse the data was Quadrawin software.

2.3.9 Time of Flight Secondary Ion Mass Spectroscopy (ToF SIMS)
A ToF-SIMS ION-TOF was used to characterise iron molybdenum and nickel molybdenum carbides and carbonitrides. The equipment has a bismuth ion gun and a time of flight mass analyser. Secondary ion mass spectra and depth profiles were recorded using Bi\(^{3+}\) as primary ions. The bismuth pulse duration was 1 ns with an AC current. For depth profiling, Cs was used for sputtering in the negative mode. The sputtering area was 300 µm x 300 µm and the area of analysis was 100 µm x 100 µm. The sputter current was 42.79 nA and the Cs primary ion beam energy was 0.5 keV. The analysis was performed at the Unite de Catalyse et Chimie du Solide (UCCS) in Lille with the very kind help of M. Nicolas Nuns. The placement of the samples in the sample holder is shown in Figure 7 and images of the ToF-SIMS V ION-TOF instrument are provided in Figure 8.

![Figure 7: Images showing the samples placed in the sample holder, a) nickel molybdenum samples and b) iron molybdenum samples.](image)
Figure 8: Images showing the ToF-SIMS V ION-TOF instrument, a) the overall ToF-SIMS V ION-TOF instrument, b) chamber where the samples are located during measurements and c) arm used to place the samples in the chamber.
3. Nickel Molybdenum Materials

3.1 Introduction

Nickel molybdenum nitride is a known ammonia synthesis material with relatively high activity of \(395 \pm 6 \text{ µmol h}^{-1} \text{ g}^{-1}\) at 400°C and atmospheric pressure [36] [39]. \(\text{Co}_3\text{Mo}_3\text{N}\) has been shown to have the highest activity of the nitrides at atmospheric pressure, with a rate of \(652 \text{ µmol h}^{-1} \text{ g}^{-1}\) at 400°C [39] and \(489 \pm 17 \text{ µmol h}^{-1} \text{ g}^{-1}\) at 500°C [54]. The ternary nitrides tend to have higher rates than the binary nitrides as seen for \(\gamma\text{-Mo}_2\text{N}\) having a rate of \(195 \pm 7 \text{ µmol h}^{-1} \text{ g}^{-1}\) at 500°C [55].

Molybdenum carbide promoted with nickel has also been investigated as a catalyst for the hydrodesulfurization of dibenzothiophene (DBT) [56]. It was reported that \(\text{Ni-Mo}_2\text{C}\) had 96.25% conversion, with this being 1.57 times higher than for unpromoted \(\text{Mo}_2\text{C}\). \(\text{Ni-Mo}_2\text{C}\) could be carburised at 50°C lower than \(\text{Mo}_2\text{C}\) and, therefore, had a higher BET surface area.

\(\text{Ni}_3\text{Mo}_3\text{C}\) has been examined for use as an anode electrocatalyst for high performance microbial fuel cells and was found to be 19% more active than \(\text{Mo}_2\text{C}\) and 62% as active as a Pt anode [57]. \(\text{Ni}_3\text{Mo}_3\text{C}\) and \(\text{Ni}_6\text{Mo}_6\text{C}\) mixed with Ketjen carbon were also found to have a good activity for anodic hydrogen oxidation, with the \(\text{Ni}_6\text{Mo}_6\text{C}\) containing catalyst having 15% of the activity of Pt catalyst and the \(\text{Ni}_3\text{Mo}_3\text{C}\) containing catalyst having a current density of 21 mA/cm² at 0.6 V [58]. These results suggest the potential of nickel molybdenum materials for electrochemistry.

The ammonia synthesis activity of ternary nitrides has tended to focus on \(\text{Co}_3\text{Mo}_3\text{N}\), with \(\text{Ni}_2\text{Mo}_3\text{N}\) receiving less attention. This work focuses on the influence of phase composition and crystal structure on the ammonia synthesis activity.

3.1.1 Synthesis of Nickel Molybdenum Nitride

When trying to form the nickel molybdenum nitride (\(\text{Ni}_2\text{Mo}_3\text{N}\)) from its oxide (\(\text{NiMoO}_4\)), issues arise due to the difference in metal ratios between the precursor and the nitride. This causes impurities to form along with the required product [59] [36]. The presence of nickel metal in this material results in a lower catalytic activity for ammonia synthesis. The \(\text{Ni}_2\text{Mo}_3\text{N}\) and Ni material has been incorrectly reported as the \(\text{Ni}_3\text{Mo}_3\text{N}\) phase in the literature in a number of instances [49] [60]. The presence of impurities caused by this difference in ratio suggests that a different method is essential in order to obtain a single
phase nitride. The Ni$_3$Mo$_3$N phase has not been synthesised to date and instead there is a preference for the formation of the β-manganese structured Ni$_2$Mo$_3$N.

One way to overcome this problem of impure phase formation is to use freeze-dried polymetallic precursors [61]. Aqueous solutions containing the suitable metal salts were prepared so as to give the ratio of 2:3 for Ni:Mo. Heating the mixed oxide precursor with ammonia gas at 950°C resulted in single phase Ni$_2$Mo$_3$N. However, impurities were formed depending on the rate of the cooling process. The single phase nitride can also be prepared via a sol-gel precursor by using a modified Pechini method [36]. An oxide precursor with a 2/3 Ni/Mo ratio is formed and this yields the desired nitride when nitrided under a N$_2$/3H$_2$ mixture. The ammonia synthesis activity of this nitride prepared via the sol-gel route was compared to the one prepared from NiMoO$_4$ precursor [36]. It was found that the activity was significantly enhanced when the modified Pechini method was used. Therefore, the preparation route has an important impact on the catalytic activity of the nitride.

### 3.1.2 Synthesis of Nickel Molybdenum Carbides

When the TPR method was used to prepare nickel molybdenum carbides with CH$_4$/H$_2$, some issues arose as reported in the literature. When trying to prepare the carbide from the oxide precursor, β-Mo$_2$C and nickel metal are formed instead [62] [63]. Nagai et al. investigated the carburisation of nickel molybdenum oxides with different Ni:Mo ratios [62]. The Ni$_{0.25}$Mo$_{0.75}$ catalyst was carburised at 600°C and was shown to contain β-Mo$_2$C and NiMoC$_{3.6}$O$_{1.4}$. This could be transformed to the Ni$_6$Mo$_6$C phase when heated to 900°C under helium. The Ni$_6$Mo$_6$C structure has been studied by Newsam et al [64], who prepared the material by carburising the precursor with CO/CO$_2$ gas at 1000°C. It was observed that all the carbon atoms are located at the (0,0,0) sites in Ni$_6$Mo$_6$C, leaving the 1/8 sites empty.

A similar study by Hirose et al. focused on varying the carburisation temperature to prepare nickel molybdenum carbide from the oxide [65]. X-ray diffraction (XRD) data and temperature programmed carburisation (TPC) showed the transformation of the starting oxides as the carburisation temperature increased. MoO$_3$ was transformed to MoO$_2$ and NiMoO$_4$ to NiMoO$_{y}$C$_x$, which was further converted to β-Mo$_2$C and Ni metal. Therefore, reduction of Ni$^{2+}$ to Ni results in the decomposition of the oxide. These results suggest that the Ni$_2$Mo$_3$C cannot be produced from the oxide precursor.
Puello-Polo and Brito have compared the carburisation of different starting precursors and their resulting products [66]. An activated carbon support was co-impregnated with ammonium heptamolybdate and a nickel salt. The XRD patterns showed that the carburisation of Ni-Mo sulfate precursor caused the formation of a Ni$_6$Mo$_6$C$_2$ phase along with nickel metal. However, when the Ni-Mo nitrate precursor was used, β-Mo$_2$C and nickel metal was produced, comparable to when the oxide precursor was used. Thus, different precursors may go through different intermediates and so can affect the final product that is formed.

Instead of using an oxide precursor, Alconchel et al. looked at using Ni$_2$Mo$_3$N as the starting precursor in the carburisation process [67]. The idea was that the structure would remain unaltered and the nitrogen atoms would be exchanged for carbon in a topotactic manner. From this method, a new carbonitride was produced, Ni$_2$Mo$_3$C$_x$N$_y$, which had the filled β-Mn structure.

Other sources of carbon have also been used to synthesise carbides. Smirnov et al. claim to have made Ni$_2$Mo$_3$C and Ni$_6$Mo$_6$C$_{1.06}$ from a Pechini based method by using citric acid as a complexing agent and by adding ethylsilicate-32 [68]. They prepared Ni$_3$MoC-SiO$_2$ materials with different Ni to Mo ratios. Their XRD patterns show that a mixture of phases were formed with impurities of β-Mo$_2$C and an alloy Ni$_x$Mo$_{1-x}$. For all the prepared samples, XRD indicated that only a small amount of Ni$_2$Mo$_3$C was produced, with β-Mo$_2$C being the majority phase for the Ni$_{10.5}$MoC-SiO$_2$ material. Zhao et al. have also prepared a mixed phase Ni$_6$Mo$_6$C by using citric acid and ethylene glycol as the sources of carbon [69]. These results suggest that this method is not ideal for producing a single phase nickel molybdenum carbide.

Ni$_6$Mo$_6$C and Ni$_3$Mo$_3$C have been prepared by using decolourising carbon as the carburisation source [48]. The lower carbon content Ni$_6$Mo$_6$C was prepared at a lower temperature of 975°C and the Ni$_3$Mo$_3$C was formed at 1030°C. Therefore, the different phases can be formed depending on the carbothermic reduction temperature. The authors were able to show through XRD patterns that the transformation from Ni$_6$Mo$_6$C to Ni$_3$Mo$_3$C resulted in the material decomposing, before recombining to form the high carbon content phase. Therefore, this transition did not occur by the insertion of carbon into Ni$_6$Mo$_6$C.
3.1.3 Structures of Nickel Molybdenum Nitrides and Carbides

Bimetallic nitrides and carbides often form crystal structures where the non-metal atom is located in the interstitial sites between the metal atoms. In face-centered cubic (fcc) and hexagonal closed packed (hcp) structures this position is often in the octahedral sites as these are the largest available interstitial sites. It has been stated that the crystal structure is determined by two important factors [70]. The first is Hägg’s rule, which states that if the number generated by dividing the atomic radii of the metal by the non-metal lies between 0.41 and 0.59, then an interstitial compound will be formed [71]. The second factor relates to Engel-Brewer theory for metals and alloys, which connects the structure to the number of valence electrons in certain orbitals [72]. Thus, the number of valence electrons in carbon and nitrogen can affect the structure. For example, molybdenum carbide forms an hcp based structure whereas the nitride forms an fcc based structure. However, despite the explanations offered by these theories, it is still unclear why certain compositions are formed and not others. For example, Ni$_3$Mo$_3$C, Co$_3$Mo$_3$N and Fe$_3$Mo$_3$N are known phases whereas Ni$_3$Mo$_3$N has not been successfully synthesised to date.

The two crystal structures of interest in this thesis are the η-carbide and filled β-manganese structures.

3.1.4 Filled β-Manganese Structure

The filled β-manganese structure has a cubic unit cell corresponding to the P4$_1$32 space group. Ni$_2$Mo$_3$N is one example of a nitride that has the filled β-Mn structure [59]. There are two types of metal atom sites in this structure, the Wyckoff 8c site and 12d site. For Ni$_2$Mo$_3$N, the nickel atoms occupy the 8c sites and are arranged in a (10,3)-a network. Molybdenum atoms occupy the 12d sites and form corner sharing Mo$_6$ octahedra, with the non-metal atom occupying the interstitial site by binding to the six molybdenum atoms. Therefore, the filled β-manganese structure can be considered as two separate subunits. The Mo$_6$N octahedra and the nickel framework in Ni$_2$Mo$_3$N are shown in Figure 9.
Figure 9: The crystal structure of Ni$_2$Mo$_3$N, showing the Mo$_6$N octahedra and the Ni-Ni bonding framework. Data plotted from Ni$_2$Mo$_3$N structure reported by Prior and Battle [73]. Elements: Nickel (green), molybdenum (light blue) and nitrogen (dark blue).

3.1.5 η-Carbide Structure

The η-carbide structure has a primitive cubic unit cell corresponding to the space group Fd3m. A range of carbides and nitrides with the formula M$_3$M’$_3$X (M, M’ = metals and X = non-metal) are known to have this structure, including Co$_3$Mo$_3$C and Fe$_3$Mo$_3$N [64] [74]. The structure consists of a distorted face centred cubic (fcc) arrangement of the M metal atoms. As in the filled β-manganese structure, the non-metal atom is situated in the interstitial site and is surrounded by six M’ atoms to form an M’$_6$X octahedron. These octahedra are corner sharing and have mainly ionic bonding. The M’ atoms are located on the 48f Wyckoff sites and the non-metals on the 16c Wyckoff sites. The M atoms occupy the 16d and 32e Wyckoff sites. The atoms on the 32e sites form a tetrahedron and are capped at each end by M on the 16d sites. Thus, forming pseudo-icosahedron, which share corners to produce a network of metal atoms [60]. These pseudo-icosahedra have metallic character. The Mo$_6$N and nickel network in Ni$_3$Mo$_3$C is displayed in Figure 10.
Figure 10: The crystal structure of Ni$_3$Mo$_3$C, showing the Mo$_6$N octahedra and the Ni-Ni bonding framework. Data plotted from Ni$_3$Mo$_3$C structure reported by Ettmayer and Suchentrunk [75]. Elements: Nickel (green), molybdenum (blue) and carbon (grey).

The η-carbide structure also has a low non-metal content variant phase, with stoichiometry of M$_6$M’$_6$X and is denoted as η-12 structure. In this case, the non-metal is located in the 8a octahedral Wyckoff site and the rest of the structure remains the same. Examples of materials that adopt this structure are Co$_6$Mo$_6$C and Ni$_6$Mo$_6$C [64]. The crystal structure of Ni$_6$Mo$_6$C is presented in Figure 11. It has been observed that topotactic cycling can occur between the low and high nitrogen content cobalt molybdenum nitrides analogous phases [50].

Contrasting with the η-carbide structure, the filled β-Mn structure does not possess a low non-metal content analogue with partly occupied interstitial sites. However, Ni$_2$Mo$_3$N can exchange some nitrogen under certain pre-treatment conditions [36]. The local nitrogen environment between the η-carbide and the filled β-Mn structured nitrides is very similar. This is of interest as Co$_3$Mo$_3$N possibly operates via a Mars-van Krevelen mechanism for ammonia synthesis [54], where lattice N mobility is important and therefore, other nitrides may also operate via this mechanism.
Both the \( \eta \)-carbide and the filled \( \beta \)-Mn structures exhibit interesting behaviour, with influences from covalent, ionic and metallic bonding. They are known to have high hardness and incompressibility [76], suggesting that they are covalently bonded. However, they also have conductivities that are associated with metallic properties. This is due to the bond distances between the metals and metal and non-metal. The bonds for Mo-Ni are shown to have distances similar to covalent bonding, although they possess a degree of ionic character. The Ni-Ni bond distances are shorter and are more similar to metallic bonding [59].

3.1.6 \( \text{Co}_3\text{Mo}_3\text{C}/\text{Co}_3\text{Mo}_3\text{N} \) System for Ammonia Synthesis

\( \text{Co}_3\text{Mo}_3\text{N} \) has the comparatively high rate of 652 \( \mu \text{mol h}^{-1} \text{ g}^{-1} \) for ammonia synthesis at 400°C and ambient pressure. This is higher than the commercial Haber Bosch catalyst under the same conditions (330 \( \mu \text{mol h}^{-1} \text{ g}^{-1} \)) [39]. Through nitrogen isotopic exchange studies, it was seen that lattice N exchanged with \( ^{15}\text{N}_2 \), suggesting that the nitride may operate under a Mars-van Krevelen mechanism as stated earlier [77]. Furthermore, half of the lattice nitrogen can be removed from \( \text{Co}_3\text{Mo}_3\text{N} \) to form \( \text{Co}_6\text{Mo}_6\text{N} \), the high and low N variants of the \( \eta \)-carbide structure, when reacted under 1:3 \( \text{Ar}/\text{H}_2 \) [50], showing the high lattice nitrogen reactivity and mobility of this material.

Supported Co-Mo nanoparticles reportedly have 20 times the ammonia synthesis activity of bulk \( \text{Co}_3\text{Mo}_3\text{N} \) [78]. The nanoparticles are observed to transform to \( \text{Co}_3\text{Mo}_3\text{N} \) during the reaction. The formation of nitrogen vacancies on the nanoparticles is easier compared
to the bulk material and this has been stated to indicate that the creation of these vacancy sites is important for nitrogen activation [79].

One possible explanation for the high activity of Co$_3$Mo$_3$N is advanced by Norskov’s volcano plot as shown in Figure 12. As can be seen, the combination of cobalt and molybdenum has almost optimal binding energy for nitrogen to give a high turnover frequency (TOF) for ammonia synthesis. Therefore, in relation to this explanation, it is proposed that CoMo is the active phase and the lattice nitrogen has no active role. Instead, the nitrogen is stated to be only required in order to give the correct structural ordering such that the (111) face comprising both Co and Mo is expressed. An alternative suggestion for the high activity of Co$_3$Mo$_3$N is that, as mentioned above, it operates via a Mars-van Krevelen mechanism and therefore, the lattice nitrogen is the active component. In this explanation, the lattice nitrogen is hydrogenated to yield ammonia, creating a transient lattice vacancy, which is then replenished by nitrogen from the reactant gas.

![Figure 12: Calculated turnover frequencies (TOF) for ammonia synthesis against the adsorption energy for nitrogen for different elements [24].](image)

In order to examine the effect of composition on activity, the corresponding carbide phase has been synthesised [54]. The carbide was prepared by carburisation of the Co$_3$Mo$_3$N with 20% CH$_4$/H$_2$ at 700°C for 2 hours. The formation of Co$_3$Mo$_3$C from Co$_3$Mo$_3$N is stated to be topotactic and pseudomorphic [80] and therefore, any difference in activity between these materials would not be due to a difference in morphology. The ammonia synthesis activities of Co$_3$Mo$_3$N and Co$_3$Mo$_3$C are shown in Figure 13. A reaction temperature of 500°C was required for activity to be exhibited by Co$_3$Mo$_3$C. However, the corresponding
nitride was active at 400°C. An induction period was required for the carbide at 500°C before it became active.

![Graph showing ammonia yield](image)

**Figure 13:** Ammonia yield under 60 ml/min of H₂/N₂ at 500°C (▲) Co₃Mo₃N, (■) Co₃Mo₃C and (●) Co₆Mo₆C [54].

During this period, nitridation of the Co₃Mo₃C lattice occurred, which eventually lead to the formation of Co₃Mo₃N upon prolonged reaction time. This substitution of carbon with nitrogen, going through an intermediate carbonitride phase, is displayed in Figure 14. Through computational modelling studies, it has also been proposed that nitrogen vacancies in Co₃Mo₃N occur and that the vacancy concentrations are significant at the temperatures necessary for ammonia synthesis [81]. These results suggest that ammonia synthesis activity in the cobalt molybdenum systems could be associated with its lattice nitrogen via a Mars-van Krevelen mechanism.
In comparison, the production of ammonia from Ni$_2$Mo$_3$N under an Ar/H$_2$ treatment is minimal, suggesting that bulk lattice nitrogen appears to be relatively unreactive. As both Ni$_2$Mo$_3$N and Co$_3$Mo$_3$N have different lattice nitrogen reactivities, it suggests that this is not a direct indicator of ammonia synthesis activity. It is interesting to note that the lattice nitrogen in these two nitrides have similar environments by being coordinated to six molybdenum species. However, nitrogen isotopic exchange studies of Ni$_2$Mo$_3$N indicate a degree of lattice nitrogen is exchangeable depending on the pre-treatment conditions [11] and the observation of lattice nitrogen exchange for Ni$_2$Mo$_3$N suggests the possibility of a surface limited Mars-van Krevelen mechanism for ammonia synthesis for this material. Thus, it would be of interest to prepare and test the activity of the corresponding carbide as has been performed for the cobalt molybdenum system. This would therefore give a greater understanding on the part the lattice nitrogen plays in the activity for this nitride.

3.2 Results and Discussion

Part I: Filled β-Mn Structured Materials

3.2.1 Nickel Molybdenum Carbonitride (Ni$_2$Mo$_3$C$_x$N$_y$)

3.2.1.1 Nickel Molybdenum Oxide (Ni$_2$Mo$_3$O$_x$)

At atmospheric pressure, there are four phases of NiMoO$_4$: the low temperature $\alpha$-phase ($\alpha$-NiMoO$_4$) [82], the $\alpha'$-phase (a distorted form of the $\alpha$-phase) [67], the high temperature $\beta$-phase ($\beta$-NiMoO$_4$) [83] and the hydrate (NiMoO$_4$·nH$_2$O) [84]. The phase can be identified from the XRD pattern by matching the peak positions between 20–36° 20 with

Figure 14: Co$_3$Mo$_3$C composition against reaction time during ammonia synthesis reaction at 500°C (▲) fractional carbon content and (●) fractional nitrogen content [54].
the corresponding JCPDS files. For the material prepared in this work, it appears that the α-NiMoO₄ phase had been formed as seen in Figure 15 (JCPDS file number 00-033-0948). Al Sobhi et al. [85], who used the same preparation method, also obtained the α-NiMoO₄ phase. However, the presence of the peak at 26.7° 20, which is characteristic for β-NiMoO₄ [86], suggests that the material was a mixture of α-NiMoO₄ and β-NiMoO₄. A previous study has shown that β-NiMoO₄ can be synthesised at low temperature by using a sol-gel route [87]. Furthermore, there have been reports of mixed phase α, β-NiMoO₄ in the literature [88] [86].

From Figure 15, it can be seen that the oxide precursor also contained a MoO₃ phase fraction. This observation is consistent with the previously published work that used the sol-gel method to prepare Ni₂Mo₃N [85] [36]. This mixture of oxides is preferential as the difference in metal ratios of the Ni and Mo between the NiMoO₄ (1:1) and the nitride (2:3) can lead to impurities of nickel metal when the nitride is synthesised [36]. Therefore, this mixture of oxide phases was targeted to form stoichiometric Ni₂Mo₃N.

Figure 15: XRD pattern of nickel molybdenum oxide (Ni₂Mo₃Oₓ). Reflections marked: ▼ NiMoO₄ (JCPDS file number 00-033-0948) and X MoO₃ (JCPDS file number 00-035-0609).

The elemental analysis shows that there were only trace amounts of carbon and nitrogen present in the material after calcination (C: 0.70 wt. %, H: 0.00 wt. % and N: 0.01 wt. %).
This suggests that the citric acid and any other nitrogen from the starting precursors had largely been removed from the oxide during calcination.

Raman spectroscopy is a very good technique for characterising oxide materials and distinguishing between different oxide phases. The Raman spectrum of this material was analysed by comparing Figure 16 with the spectra of NiMoO₄ published in the literature. The Raman bands at positions of approximately 961, 913 and 706 cm⁻¹ were attributed to α-NiMoO₄ [89]. These Raman shifts are in very good agreement with NiMoO₄ spectra reported in the literature [67]. The bands at 961 and 913 cm⁻¹ have been assigned in the literature as the symmetric and asymmetric stretching modes of the terminal Mo=O bond [90]. The band at 706 cm⁻¹ was assigned to the Ni-O-Mo symmetric stretch [67] [89]. However, another report in the literature suggests that the band at 818 cm⁻¹ is due to either the symmetric or asymmetric stretching mode of Mo-O and the band at 706 cm⁻¹ is due to the asymmetric mode of Ni-O-Mo bonds [91]. The weak bands at approximately 420, 390, 370 cm⁻¹ are attributed to α-NiMoO₄ in the literature [89] and have been assigned to the bending mode of Mo–O. The weak band at 265 cm⁻¹ has also been assigned to α-NiMoO₄ and is associated with the deformation mode of Mo–O–Mo [89].

The bands at 995, 818 and 665 cm⁻¹ are related to MoO₃ [90] and are attributed to the Mo=O stretching mode, Mo-O-Mo asymmetric stretching mode and the Mo-O-Mo symmetric stretching mode respectively [67]. The Raman bands at 336 and 283 cm⁻¹ have also been assigned to MoO₃ and are most likely due to the Mo-O bending and Mo-O-Mo deformation mode [90].

The presence of bands for both NiMoO₄ and MoO₃ agrees with the XRD results, which showed that both these oxides were present. Alconchel et al. [67] also observed the occurrence of bands for both these oxides in their starting precursor.
Figure 16: Raman spectrum of nickel molybdenum oxide (Ni$_2$Mo$_3$O$_x$)

Representative SEM images for the oxide precursor are displayed in Figure 17. The material appears to be porous with pores ranging in diameter from approximately 1 – 10 \( \mu \text{m} \). The material had a surface area of 46 m$^2$/g, a pore volume of 0.26 cc/g and an average pore radius of 26.44 Å. To the author’s knowledge, previous studies by groups that used the same sol-gel method, did not publish SEM images for the oxide and therefore, a comparison cannot be made [85] [36] [92]. Umapathy et al. published SEM images for NiMoO$_4$, which was prepared by a sol-gel method that used ethyl cellulose [93]. Their images showed that the material contained agglomerated particle-like nanostructures.

The elemental map in Figure 18 shows that the nickel, molybdenum and oxygen were evenly dispersed across the sample, as expected. The EDX analysis showed that nickel, molybdenum and oxygen were the only elements present in the sample.
Figure 17: SEM images of nickel molybdenum oxide (Ni$_2$Mo$_3$O$_x$). a) 1000x magnification, b) 2000x magnification, c) 4000x magnification and d) 6000x magnification.

Figure 18: Element Map for Ni$_2$Mo$_3$O$_x$. Elements: Ni (red), Mo (green) and O (blue).

The EDX data in Table 1 details the weight percentages for each element. The stoichiometric percentage of nickel, molybdenum and oxygen in NiMoO$_4$ is 26.85 wt. %, 43.88 wt. % and 29.27 wt. % respectively. From the table, it can be seen that the oxygen weight percentage was higher than predicted and the nickel percentage was lower. From the XRD pattern, it was shown that the material consisted of both NiMoO$_4$ and MoO$_3$. Therefore, the stoichiometric percentage of nickel, molybdenum and oxygen in the theoretical NiMo$_2$O$_7$ (Ni$_2$Mo$_3$O$_{11}$) would be 16.19% (20.20%), 52.92% (49.52%) and 30.89% (30.28%) respectively. The theoretical composition NiMo$_2$O$_7$ assumes that there
was a 1:1 ratio of NiMoO₄ and MoO₃. Ni₂Mo₃O₁₁ was stated as the product when the oxide is formed by the modified Pechini method [36].

<table>
<thead>
<tr>
<th>Area</th>
<th>Ni weight (%)</th>
<th>Mo weight (%)</th>
<th>O weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>16</td>
<td>44</td>
<td>40</td>
</tr>
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<tr>
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<td>40</td>
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</tbody>
</table>

Table 1: EDX values for nickel molybdenum oxide (Ni₂Mo₃Oₓ)

### 3.2.1.2 Nickel Molybdenum Nitride (Ni₂Mo₃N)

The filled β-Mn structured Ni₂Mo₃N is a known ammonia synthesis catalyst [39] [94]. Ni₂Mo₃N was prepared via temperature programmed nitridation of the bimetallic oxide, which was obtained via a sol-gel route. The preparation of this material was inspired by prior literature that reported the formation of Ni₂Mo₃N without nickel impurity [36]. An advantage of the Ni₂Mo₃N phase is that it can be prepared directly by nitridation of the oxide with N₂/H₂ at 700°C. Therefore, ammonolysis is not required in its preparation and this overcomes problems with using ammonia at a large scale [95].

As can be seen in Figure 19, the desired ternary nitride phase had been formed without any nickel impurities. However, a minor impurity phase of β-Mo₂N can be observed at 37.6° 20. The XRD pattern confirms that the material was free from reflections relating to molybdenum metal or any metal oxide phases. This result is consistent with previously published literature [36] [85].

The elemental analysis shows that there was no carbon or hydrogen present in the material after nitridation with N₂/H₂ (C: 0.00 wt. %, H: 0.00 wt. % and N: 4.58 wt. %). The percentage of nitrogen present in the material was higher than the expected stoichiometric value of 3.34 wt. %. Any residual NH₃ species formed on the surface of the nitride would contribute towards this value. The β-Mo₂N phase content which could contribute to excess N content looks to be minimal as inferred from the XRD pattern and therefore, the contribution from this phase would be small. Therefore, it is unclear where the extra nitrogen originated from.
Figure 19: XRD pattern of nickel molybdenum nitride (Ni$_2$Mo$_3$N). Reflections marked: ■ Ni$_2$Mo$_3$N (JCPDS file number 01-089-4564) and ● β-Mo$_2$N (JCPDS file number 01-075-1150).

Raman spectroscopy is a valuable technique to characterise surface oxide species. These oxide species may affect the ammonia synthesis activity and therefore, it is important to observe if they are present on the surface of the material. The Raman spectra of Ni$_2$Mo$_3$N was taken at two different areas with 10% and 25% filters. The spectra are presented in Figure 20. The Raman spectra are very different between the two different areas. However, both show the formation of a surface oxide layer on the nitride, consisting of either α-NiMoO$_4$ or β-NiMoO$_4$. The formation of an oxide surface layer was observed in previous work investigating cobalt molybdenum nitrides [55].

For the area taken with a 10% filter, the Raman bands at positions of approximately 962, 914 and 709 cm$^{-1}$ were attributed to α-NiMoO$_4$. These Raman shifts are in very good agreement with α-NiMoO$_4$ spectra reported in the literature [67] and match with the spectrum in Figure 16 for the oxide precursor. The weak bands at approximately 420, 390, 370, and 265 cm$^{-1}$ are also attributed to α-NiMoO$_4$ in the literature [89]. The bands at 962 and 914 cm$^{-1}$ have been assigned in the literature as the symmetric and asymmetric stretching modes of the terminal Mo=O bond. The band at 709 cm$^{-1}$ was assigned to the Ni-O-Mo symmetric stretch [67]. The weak bands at 420, 390, and 370 cm$^{-1}$ have been
assigned to the bending mode of Mo–O. The other weak band at 265 cm\(^{-1}\) is associated with the deformation mode of Mo–O–Mo [89].

At the second area with a 25% filter, Raman bands were detected at 344, 370, 820, 894 and 941 cm\(^{-1}\). These bands match well with the literature values for β-NiMoO\(_4\), which has bands at 370, 818, 890 and 936 cm\(^{-1}\) [96]. The bands at 894 and 941 cm\(^{-1}\) are due to the asymmetric and symmetric Mo-O vibration of Mo in a tetrahedral environment [96] [97]. The band at 820 cm\(^{-1}\) has been reported to be due to either the asymmetric stretching mode of the Ni-O-Mo bond [96] or the Mo-O vibration of Mo in tetrahedral coordination [97]. Furthermore, the band at 370 cm\(^{-1}\) has been assigned to the bending mode of Mo-O [96]. The presence of β-NiMoO\(_4\) in the Raman spectra of Ni\(_2\)Mo\(_3\)N has been reported previously in the literature [67].

![Raman spectra of nickel molybdenum nitride (Ni\(_2\)Mo\(_3\)N). The two spectra were taken at different points of the material and either at 10% or 25% filter.](image)

It is important to investigate the morphology of a material as this can affect the ammonia synthesis activity. Figure 21 displays representative SEM images for Ni\(_2\)Mo\(_3\)N. The SEM images show a similar morphology to that of the oxide precursor. The sample consisted of rounded porous particles with an uneven surface. The nitride had a BET surface area of 5 m\(^2\)/g, a pore volume of 0.04 cc/g and an average pore radius of 15.92 Å. These values are lower than those for the oxide precursor. However, as observed from the Raman spectra for Ni\(_2\)Mo\(_3\)N, when the sample was in contact with air for a short time, a surface oxide...
phase formed. Therefore, the BET surface area value for the nitride might not be a representative measurement in terms of the material under reaction conditions.

To the author’s knowledge, only SEM images for Ni$_2$Mo$_3$N prepared by ammonolysis are published in the literature [85] [36] [59]. The morphology of the ammonolysis prepared samples are very different, comprising of well-formed rounded particles.

Figure 21: SEM images of nickel molybdenum nitride (Ni$_2$Mo$_3$N). a) 1000x magnification, b) 2000x magnification, c) 6000x magnification and d) 6000x magnification.

The element maps in Figure 22 show that there was an even distribution of nickel, molybdenum and nitrogen over the sample and that there was more molybdenum present than nickel.
The EDX analysis for the sample is shown in Table 2. The stoichiometric percentage of nickel, molybdenum and nitrogen for Ni$_2$Mo$_3$N is 28.00 wt. %, 68.66 wt. % and 3.34 wt. % respectively. The nitrogen weight percentage from EDX was greater than the stoichiometric nitrogen predicted for Ni$_2$Mo$_3$N. This could possibly be due to the limitations of EDX for light element analysis. The percentage of molybdenum and nickel was approximately as expected, suggesting that the weight ratio of Ni to Mo was close to that expected for Ni$_2$Mo$_3$N.

<table>
<thead>
<tr>
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<th>Mo weight (%)</th>
<th>N weight (%)</th>
</tr>
</thead>
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</tr>
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<td><strong>Average</strong></td>
<td><strong>28</strong></td>
<td><strong>65</strong></td>
<td><strong>7</strong></td>
</tr>
</tbody>
</table>

Table 2: EDX values for nickel molybdenum nitride (Ni$_2$Mo$_3$N)

### 3.2.1.2.1 Lattice Nitrogen Reactivity of Ni$_2$Mo$_3$N

Ni$_2$Mo$_3$N has been explored for its ammonia synthesis activity [36] [39] and lattice nitrogen reactivity [36] [92] [98]. Most of the ammonia synthesis reactions were performed at 400°C and atmospheric pressure. The highest ammonia synthesis rates for Ni$_2$Mo$_3$N reported under these conditions are 383 ± 22 µmol h$^{-1}$ g$^{-1}$ [36] and 275 µmol h$^{-1}$ g$^{-1}$ [39]. For the nitride prepared with N$_2$/H$_2$, the rate was stated to be 395 ± 6 µmol h$^{-1}$ g$^{-1}$ at 400°C [36] and 466 µmol h$^{-1}$ g$^{-1}$ at 500°C [85] when there was no nickel impurity. The presence of nickel metal in the material drastically reduces the ammonia synthesis rate [36] [98]. Therefore, it is of importance to form the pure phase bimetallic nitride.

In order to determine the reactivity of lattice nitrogen in Ni$_2$Mo$_3$N, the material has been reacted under 1:3 Ar/H$_2$ from 400°C to 700°C [98] and isotopic exchange studies with $^{15}$N$_2$ have been performed [36] [92]. If the lattice nitrogen was active for ammonia synthesis via
a Mars-van Krevelen mechanism, there would be a reduction in the nitrogen content of Ni$_2$Mo$_3$N when reduced under Ar/H$_2$. Furthermore, there may be a transformation of the structure. The studies showed that the lattice N was only slightly reactive under Ar/H$_2$ up to 700°C and that there was no phase transition for the nitride. However, it was seen through nitrogen isotopic exchange studies that some lattice nitrogen exchanges with $^{15}$N$_2$ depending on the pre-treatment conditions [36].

In order to understand the role of lattice nitrogen reactivity in Ni$_2$Mo$_3$N, the material was reduced at 900°C under 1:3 ratio of Ar/H$_2$ at atmospheric pressure for 7 hours. The vent gas was passed through a dilute solution of H$_2$SO$_4$ and the conductivity was recorded over the reaction. A linear decrease in conductivity over time would represent a steady state reaction. As observed from the conductivity data in Figure 23, the rate was non-steady state. The $R^2$ value of the straight-line fit was 0.9751 and the data deviates from this at the start and the end. The conductivity decreased by only 49 µS/cm over the 7 hours. This result suggests that the lattice nitrogen in Ni$_2$Mo$_3$N is fairly unreactive with respect to ammonia production even at elevated temperatures. It must be noted that ammonia formation at this temperature is greatly unfavoured [99] and that the lattice nitrogen may be lost as N$_2$ instead, which would not result in a change in conductivity of the H$_2$SO$_4$ solution through which the reactor effluent gas is flowed.

![Figure 23: Conductivity profile for Ni$_2$Mo$_3$C$_x$N$_y$ reacted with 3:1 H$_2$/Ar at 900°C for 7 hours.](image-url)
The XRD pattern in Figure 24 shows that the filled \( \beta \)-Mn structure was maintained after the reaction. There does not appear to be any major change in phase compared to pre-reaction suggesting that the material was not reduced under these conditions. The very minor Mo\( _2\)N phase present in the material was reduced to Mo metal during the reaction as evidenced by the XRD pattern post-reaction. The XRD pattern confirms that the bulk lattice nitrogen in Ni\( _2\)Mo\( _3\)N was fairly unreactive under these conditions.

![XRD pattern comparison](image)

Figure 24: Comparison of XRD patterns for Ni\( _2\)Mo\( _3\)N pre- and post-reaction with 3:1 H\(_2\)/Ar at 900\(^\circ\)C for 7 hours. Reflections marked: ■ Ni\( _2\)Mo\( _3\)N (JCPDS file number 01-089-4564) and ◇ Mo (JCPDS file number 01-089-5023).

Figure 25 illustrates that there was no lattice shift between the pre- and post-reaction samples. This is consistent with the results published in the literature for Ni\( _2\)Mo\( _3\)N tested under Ar/H\(_2\) up to 700\(^\circ\)C [36] [92].

The elemental analysis shows that the percentage of nitrogen present in the material after reduction with 1:3 Ar/H\(_2\) had slightly decreased (C: 0.00 wt. %, H: 0.00 wt. % and N: 3.94 wt. %) compared to pre-reaction (4.58 wt. %). The percentage of nitrogen present in the material was still higher than the expected stoichiometric value of 3.34 wt. %. The decrease in nitrogen could be due to the reduction of the \( \beta \)-Mo\( _2\)N to molybdenum or the loss of some surface nitrogen from nickel molybdenum nitride. Assuming the loss of
nitrogen was solely due to the Ni$_2$Mo$_3$N, the percentage of lattice nitrogen lost that was converted to ammonia was 34.22%.

Ni$_2$Mo$_3$N and Co$_3$Mo$_3$N display very different behaviour with respect to one another under Ar/H$_2$ treatment. This may be explained by the difference in structure type or composition between these two nitrides and the origin of this difference will be explored further in this thesis.

Figure 25: Comparison of XRD patterns between Ni$_2$Mo$_3$N pre- (black) and post-reaction (red) with 3:1 H$_2$/Ar at 900°C for 7 hours.

SEM analysis was conducted in order to investigate if there was any change in morphology of Ni$_2$Mo$_3$N during the reaction. Figure 26 displays characteristic SEM images at different magnifications of the post-reaction Ni$_2$Mo$_3$N. The sample consisted of porous particles with pores ranging in diameter from 0.5 µm to 10 µm. The crystallite shape and size had been retained compared to pre-reaction. However, there appeared to be smaller pores in the particles.
Figure 26: SEM images of nickel molybdenum nitride (Ni$_2$Mo$_3$N) post-reaction with 3:1 H$_2$/Ar at 900°C. a) 1000x magnification, b) 2000x magnification, c) 5000x magnification and d) 6000x magnification.

The nickel, molybdenum and nitrogen appear to have been evenly distributed across the material as evidenced by the element maps in Figure 27. This confirms that there had been no phase separation under the reducing conditions.

Figure 27: Element Maps for Ni$_2$Mo$_3$N post-reaction with 3:1 H$_2$/Ar at 900°C. Elements: Ni (red), Mo (green) and N (blue).

The EDX analysis for the post-reaction sample is presented in Table 3. The stoichiometric percentage of nickel, molybdenum and nitrogen for Ni$_2$Mo$_3$N is 28.00 wt. %, 68.66 wt. % and 3.34 wt. % respectively, as stated previously. The nitrogen weight percentage from
EDX was much lower than the predicted stoichiometric value and the result obtained from CHN analysis. However, there are limitations to EDX for measuring light elements. The percentage of nickel was higher than expected and therefore the mass ratio of Ni to Mo was higher than predicted for Ni$_2$Mo$_3$N. This is in contrast to the XRD pattern, which showed that the Ni$_2$Mo$_3$N phase had been retained post-reaction.

![Table 3: EDX values for nickel molybdenum nitride (Ni$_2$Mo$_3$N) post-reaction with 3:1 H$_2$/Ar at 900°C.](image)

### 3.2.1.3 Nickel Molybdenum Carbide (Ni$_2$Mo$_3$C)

#### 3.2.1.3.1 Preparation with 20% CH$_4$/H$_2$

In order to have a greater understanding on the role lattice nitrogen plays in the ammonia synthesis activity of Ni$_2$Mo$_3$N, determination of the reactivity of the corresponding isostructural carbide would be of interest. From this it may prove possible to determine the influence phase composition has upon ammonia synthesis performance. Similar studies have been undertaken for the Co$_3$Mo$_3$N/Co$_3$Mo$_3$C system [54]. Although, the reactivity of lattice nitrogen in Ni$_2$Mo$_3$N has been shown to be very low, it has been observed and the topotactic replacement of the nitrogen with carbon to form a nickel molybdenum carbonitride has been reported in the literature [67].

The activity of Ni$_2$Mo$_3$N could be explained by Norskov’s volcano plot [24], which states that the combination of Mo, which binds N$_2$ strongly and Ni, which binds N$_2$ weakly,
results in a suitable binding energy for N\textsubscript{2} to give high ammonia synthesis activity. The lattice nitrogen is assumed to be non-reactive in this explanation and therefore, Ni\textsubscript{2}Mo\textsubscript{3}C would be expected to display similar performance to its nitride counterpart.

Preparation of Ni\textsubscript{2}Mo\textsubscript{3}C was attempted initially via carburisation of Ni\textsubscript{2}Mo\textsubscript{3}N with 20\% CH\textsubscript{4}/H\textsubscript{2}. The pure phase carbide was not produced under these conditions, with instead the material decomposing at high temperatures. The optimum preparation temperature was found to be 560 °C, which produced a carbonitride phase containing 1.42 wt. % carbon and 1.93 wt. % nitrogen as shown in Table 4. When the temperature was increased above 560°C, with the intention of substituting more of the lattice nitrogen with carbon, the material began to decompose. At temperatures above 600°C, the material fully decomposed to give mixed phases of Ni and α-Mo\textsubscript{2}C as demonstrated in Figure 28. The decomposition of the material observed agrees with what has been reported in the literature [62] [65]. The formation of a nickel molybdenum carbonitride phase has been reported by Alconchel et al. [67], who formed the phase by carburisation of Ni\textsubscript{2}Mo\textsubscript{3}N with CH\textsubscript{4}/H\textsubscript{2}/Ar gas mixture at 650°C.

Figure 28: XRD patterns of nickel molybdenum materials prepared at different carburisation temperatures with 20\% CH\textsubscript{4}/H\textsubscript{2}: (1) 560°C, (2) 600°C, (3) 650°C, (4) 700°C and (5) 725°C. Reflections marked: α-Mo\textsubscript{2}C (JCPDS file number 00-035-0787) and Ni (JCPDS file number 00-001-1258).
Table 4: Elemental Analysis for the nickel molybdenum materials prepared at different carburisation temperatures with 20% CH\textsubscript{4}/H\textsubscript{2}.

SEM was conducted to investigate the effect carburisation had on the morphology. The SEM results of the nickel molybdenum materials prepared at different carburisation temperatures are shown in Figure 29. As can be seen, the morphology of the materials was similar, even though the higher temperature materials decomposed. The BET surface area was observed to decrease as the carburisation temperature increased as shown in Table 5.

Table 5: BET surface area, pore volume and average pore radius for the nickel molybdenum materials prepared at different carburisation temperatures with 20% CH\textsubscript{4}/H\textsubscript{2}.
Figure 29: SEM images of nickel molybdenum materials prepared at different carburisation temperatures with 20% CH₄/H₂: a) 560°C, b) 600°C, c) 650°C, d) 700°C and e) 725°C. All of the images were taken at 4000x magnification.

The element maps in Figure 30 show the phase separation as the carburisation temperature increases. In Figure 30 (a), the nickel and molybdenum appear to be fairly evenly distributed over the material. As the carburisation temperature was increased to 600°C, phase separation was apparent (Figure 30 (b)) with areas of molybdenum and nickel. This is the same at the higher carburisation temperatures. In Figure 30 (d), it can be seen that carbon is only located in areas where there was molybdenum present. This is consistent with the XRD patterns that show only the molybdenum has formed a carbide phase whereas Ni was present as Ni metal.
Figure 30: Element Maps for nickel molybdenum materials prepared at different carburisation temperatures with 20% CH₄/H₂. Elements: Ni (green), Mo (red) and C (blue). a) 560°C, b) 600°C, c) 650°C, d) 700°C and e) 725°C.

The EDX results show that the molybdenum weight percentage decreased as the carbon content increased as observed in Table 6. However, care needs to be taken as the samples were not homogeneous and EDX is semi-quantitative. The stoichiometric percentage of nickel, molybdenum and nitrogen for Ni + Mo₂C (assuming a Ni:Mo ratio of 2:3) is 27.74 wt. %, 68.01 wt. % and 4.26 wt. %, respectively. There is no nitrogen present in the material after carburisation temperature at 650°C, which agrees with the CHN analysis. Areas with more nickel content have a lower percentage of carbon (EDX tables provided in Appendix II). This is consistent with the XRD and element maps that show the nickel has not formed a carbide phase. The percentages of carbon were higher than expected and there did not appear to be any evidence for carbon in the XRD patterns. However, the EDX measurements are semi-quantitative and restrictive for light elements.
<table>
<thead>
<tr>
<th>Area</th>
<th>Ni weight (%)</th>
<th>Mo weight (%)</th>
<th>C weight (%)</th>
<th>N weight (%)</th>
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<td>54</td>
<td>17</td>
<td>5</td>
</tr>
<tr>
<td>600°C Average</td>
<td>28</td>
<td>51</td>
<td>19</td>
<td>1</td>
</tr>
<tr>
<td>650°C Average</td>
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<tr>
<td>725°C Average</td>
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<td>43</td>
<td>38</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 6: EDX values for nickel molybdenum materials prepared at different carburisation temperatures with 20% CH₄/H₂

3.2.1.3.2 Preparation with 30% CH₄/H₂

In order to prepare a pure phase bimetallic carbide, the methane content of the gas feed was increased to 30% CH₄/H₂. From section 3.2.1.3.1, it can be seen that higher temperatures may be required in order to replace all of the lattice nitrogen of Ni₂Mo₅N with carbon. The reaction was carried out the same way as for the materials prepared with the 20% CH₄/H₂. The carbide was prepared by carburisation of the nitride in 30% CH₄/H₂ at a flow rate of 12 mL/min. The material was heated to 350°C at a ramp rate of 6°C/min and then, the ramp rate was changed to 1°C/min to reach a final temperature of 650°C. The sample was kept at this temperature for two hours, then cooled down to room temperature under the CH₄/H₂.

The elemental analysis shows that carbon and nitrogen were present in the material after carburisation (C: 3.50 wt. %, H: 0.00 wt. % and N: 0.32 wt. %). The XRD pattern for the material post-carburisation is provided in Figure 31. It can be seen that there are still peaks relating to a nickel molybdenum phase in this material, suggesting that the material has not completely decomposed under these conditions. When the nitride was carburised with 20% CH₄/H₂ at the same temperature, the material had completely decomposed as observed in its XRD pattern (Figure 28). Therefore, the material did not decompose as much when there was a higher methane percentage in the gas feed. However, the ternary carbide phase was not formed under 30% CH₄/H₂ and the material had started to decompose at 650°C carburisation temperature. The carburisation temperature could be lowered in order to try and form the carbide and prevent the observed decomposition. However, as nitrogen was still present in the material at 650°C, this would suggest that at lower carburisation temperature, the carbonitride would be formed. Thus, the pure carbide phase cannot be formed under 30% CH₄/H₂ in the procedure adopted.
Figure 31: XRD pattern of the nickel molybdenum material prepared at 650°C carburisation temperature with 30% CH₄/H₂. Reflections marked: • α-Mo₂C (JCPDS file number 00-035-0787) and ▲ Ni (JCPDS file number 00-001-1258).

SEM images of the material post-carburisation are displayed in Figure 32. The morphology of the sample was similar to the morphology of the materials prepared under 20% CH₄/H₂ (Figure 29).

Figure 32: SEM images of nickel molybdenum material prepared at 650°C carburisation temperature with 30% CH₄/H₂. Both images were taken at 4000x magnification.

The element map also shows the phase segregation between the nickel and molybdenum as displayed in Figure 33. The average EDX values for this material were 25 wt. %, 50 wt. % and 25 wt. % for nickel, molybdenum and carbon respectively. There was no nitrogen
detected in the areas that were examined. This is in disagreement with the CHN analysis, which showed that 0.32 wt. % of nitrogen was present. However, it needs to be borne in mind that detecting light elements by EDX can be problematic.

Figure 33: Element Map for nickel molybdenum material prepared at 650°C carburisation temperature with 30% CH₄/H₂. Elements: Ni (red) and Mo (green).

3.2.1.3.3 Preparation with Pure C₂H₆

Methane was substituted with ethane to investigate the effect a more reactive source of carbon had on obtaining pure phase Ni₂Mo₃C from Ni₂Mo₃N. The material was prepared by carburisation of the nitride in C₂H₆ at 500°C, 550°C and 575°C. The XRD patterns for these materials are displayed in Figure 34. However, this proved unsuccessful with a carbonitride phase being formed instead as seen from the elemental analysis presented in Table 7. Only 30% of the lattice nitrogen was removed from the materials at all three temperatures tested and the stoichiometries of the carbonitrides formed are shown in Table 8.

<table>
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<tr>
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<th>Hydrogen Content from Elemental Analysis (wt. %)</th>
<th>Nitrogen Content from Elemental Analysis (wt. %)</th>
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<td>575°C</td>
<td>1.32</td>
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<td>2.32</td>
</tr>
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</table>

Table 7: Elemental Analysis for the nickel molybdenum materials prepared at different carburisation temperatures with C₂H₆.

<table>
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<tr>
<th>Material</th>
<th>Proposed Stoichiometry</th>
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<tbody>
<tr>
<td>500°C</td>
<td>Ni₂Mo₃C₀.₃₅N₀.₇₂</td>
</tr>
<tr>
<td>550°C</td>
<td>Ni₂Mo₃C₀.₄₁N₀.₇₀</td>
</tr>
<tr>
<td>575°C</td>
<td>Ni₂Mo₃C₀.₄₆N₀.₆₉</td>
</tr>
</tbody>
</table>

Table 8: Stoichiometry proposed for the bulk sample for nickel molybdenum materials prepared at different carburisation temperatures with C₂H₆.
Figure 34: XRD patterns of nickel molybdenum materials prepared at different carburisation temperatures with C₂H₆: (1) 500°C, (2) 550°C and (3) 575°C.

As can be seen in Figure 35, there was almost no shift in peak positions between the three samples. This suggests that lattice nitrogen was not being substituted by more carbon at the higher temperature.
3.2.1.3.4 Preparation with 10% C\textsubscript{2}H\textsubscript{6}/H\textsubscript{2}

Due to the inability to form the nickel molybdenum carbide under pure ethane, hydrogen was added to the feed stream to assist with the carbide formation. The material was prepared by carburisation of Ni\textsubscript{2}Mo\textsubscript{3}N in 10% C\textsubscript{2}H\textsubscript{6}/H\textsubscript{2} at a flow rate of 12 mL/min at 520°C, 560°C and 610°C. From the XRD patterns in Figure 36, it can be seen that the resulting material at 560°C was similar to the material carburised under 20% CH\textsubscript{4}/H\textsubscript{2} at the same temperature. However, at the carburisation temperature of 610°C, it can be seen that the material possessed a higher relative intensity of molybdenum carbide and nickel reflections compared to the material carburised at 600°C under 20% CH\textsubscript{4}/H\textsubscript{2}. This suggests that more of the material had decomposed under the ethane atmosphere. This is consistent with what would be expected. According to literature, ethane lowers the temperature at which the carbide is formed [100] [101] [102]. The formation of a pure phase Ni\textsubscript{2}Mo\textsubscript{3}C was unsuccessful when an ethane and hydrogen gas mixture was applied to the nitride. Instead, the nickel molybdenum carbonitride was formed as was the case when methane was used as the carbon source.
Figure 36: XRD patterns of nickel molybdenum materials prepared at different carburisation temperatures with 10% C₂H₆/H₂: 520°C (black), 560°C (red) and 610°C (blue). Reflections marked: ● α-Mo₂C (JCPDS file number 00-035-0787) and ▲ Ni (JCPDS file number 00-001-1258).

The stoichiometries proposed for the bulk samples prepared at 520°C and 560°C were Ni₂Mo₃C₀.2₀N₀.₆₆ and Ni₂Mo₃C₀.₄₃N₀.₆₆ respectively, as predicated from the elemental analysis shown in Table 9. The sample carburised at 610°C contains Mo₂C and therefore, this contributes to the carbon content and a stoichiometry relating to a ternary phase cannot be proposed. The material prepared at 560°C under 20% CH₄/H₂ had a stoichiometry of Ni₂Mo₃C₆.₄₉N₀.₅₈. The sample prepared with 10% C₂H₆/H₂ would be expected to contain more carbon due to the ethane lowering the temperature for carburisation. From elemental analysis and the proposed stoichiometry, it is seen that this is not the case. However, when comparing the 600°C carburised materials it can be observed that more carbon is present for the material carburised with 10% C₂H₆/H₂.
### Table 9: Elemental Analysis for the nickel molybdenum materials prepared at different carburisation temperatures with 10% C2H6/H2.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Carbon Content from Elemental Analysis (wt. %)</th>
<th>Hydrogen Content from Elemental Analysis (wt. %)</th>
<th>Nitrogen Content from Elemental Analysis (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>520°C</td>
<td>0.59</td>
<td>0.07</td>
<td>2.19</td>
</tr>
<tr>
<td>560°C</td>
<td>1.23</td>
<td>0.13</td>
<td>2.20</td>
</tr>
<tr>
<td>610°C</td>
<td>2.26</td>
<td>0.05</td>
<td>0.92</td>
</tr>
</tbody>
</table>

A comparison of the XRD patterns of the materials carburised at 560°C with 20% CH4/H2, pure C2H6 and 10% C2H6/H2 are presented in Figures 37 and 38. It must be noted that the nitride carburised with pure ethane was reacted at a lower temperature of 550°C. When comparing the shift in peak positions, it can be seen that the material carburised with 10% C2H6/H2 had the smallest shift to lower 2θ values. When consideration is given to the relative atomic radii of N and C with C being larger, this is in contrast with the elemental analysis that showed the material carburised with pure ethane had the lowest amount of carbon present and therefore, would be expected to have the smallest shift in peak positions. However, the carbon values from elemental analysis for the materials prepared under C2H6 and 10% C2H6/H2 are within experimental error, as observed in Table 10. This lower shift in peak position for the material carburised with 10% C2H6/H2 suggests that not all the carbon may be incorporated into the lattice. Instead, some of the carbon may be laid down on the surface of the material. Although, there is no peak associated with graphitic carbon in the XRD pattern for this material, the carbon may be in a different form or in trace amounts that the XRD can’t detect.

### Table 10: Elemental Analysis for the nickel molybdenum materials prepared with 20% CH4/H2, C2H6 and 10% C2H6/H2.

<table>
<thead>
<tr>
<th>Material</th>
<th>Carbon Content from Elemental Analysis (wt. %)</th>
<th>Hydrogen Content from Elemental Analysis (wt. %)</th>
<th>Nitrogen Content from Elemental Analysis (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20% CH4/H2</td>
<td>1.42</td>
<td>0.00</td>
<td>1.93</td>
</tr>
<tr>
<td>C2H6</td>
<td>1.17</td>
<td>0.00</td>
<td>2.33</td>
</tr>
<tr>
<td>10% C2H6/H2</td>
<td>1.23</td>
<td>0.13</td>
<td>2.20</td>
</tr>
</tbody>
</table>
3.2.1.4 Nickel Molybdenum Carbonitride (Ni$_2$Mo$_3$C$_x$N$_y$)

As discussed in the introduction, the production of ammonia from Ni$_2$Mo$_3$N could be due to either a Mars van Krevelen mechanism, where lattice nitrogen is an active component, or the combination of nickel and molybdenum having a good binding energy for N$_2$. 

Figure 37: XRD patterns of nickel molybdenum materials prepared at 560°C with different carburisation sources: (1) 20% CH$_4$/H$_2$, (2) C$_2$H$_6$ (550°C) and (3) 10% C$_2$H$_6$/H$_2$.

Figure 38: Comparison of XRD patterns for nickel molybdenum materials prepared at 560°C with different carburisation sources: 20% CH$_4$/H$_2$ (black), C$_2$H$_6$ (550°C, red) and 10% C$_2$H$_6$/H$_2$ (blue).
Therefore, it is of interest to examine the behaviour of the carbonitride for ammonia synthesis and relate it to its nitride counterpart.

The carbonitride that was prepared with 20% CH\textsubscript{4}/H\textsubscript{2} at 560\textdegree C was analysed further as it was the material that gave the highest apparent substitution of lattice nitrogen with carbon. It has been previously reported that the ratio of 20% CH\textsubscript{4}/H\textsubscript{2} is the most efficient way of forming β-Mo\textsubscript{2}C from MoO\textsubscript{3} [103]. From Figure 39, it can be seen that the material corresponds to the filled β-Mn structure. The identity of the impurity phase marked with a star in Figure 39 is currently unknown. Pattern matches with the JCPDS database were performed for β-Mo\textsubscript{2}N, Mo\textsubscript{3}N\textsubscript{2}, Mo\textsubscript{5}N\textsubscript{6}, α-Mo\textsubscript{2}C, β-Mo\textsubscript{2}C and β-Mo\textsubscript{1.93}C\textsubscript{0.96}. However, none of these materials aligned with the peak at 37\textdegree 20. One possible suggestion for this impurity is that it was a molybdenum carbonitride phase due to the shift of the peak to lower 20 values by 0.6016\textdegree 20 from the position for β-Mo\textsubscript{2}N.

The elemental analysis shows that carbon and nitrogen were present in the material after carburisation (C: 1.42 wt. %, H: 0.00 wt. % and N: 1.93 wt. %). The expected stoichiometric value for carbon in Ni\textsubscript{2}Mo\textsubscript{3}C is 2.88 wt. %. The carbon content of the material was approximately half of the calculated stoichiometric value. The shift in peak
position compared to the nitride (Figure 40) and elemental analysis suggests that a carbonitride phase may have been formed. The stoichiometry proposed for the bulk sample is $\text{Ni}_2\text{Mo}_3\text{C}_{0.49}\text{N}_{0.58}$. From the stoichiometry, it is observed that the nitrogen content was higher than expected. This could be due to the possible molybdenum nitride phase contributing to the nitrogen percentage.

The absence of a peak at $25^\circ 2\theta$ suggests that the carbon was not present as graphitic carbon and had instead been incorporated into the bimetallic lattice.

![Figure 40: Comparison of XRD patterns for $\text{Ni}_2\text{Mo}_3\text{N}$ and $\text{Ni}_2\text{Mo}_3\text{C}_x\text{N}_y$ showing the shift in reflections.](image)

Raman spectroscopy was performed to investigate if there were any surface oxide species on the material. The Raman spectra were collected to 3000 cm$^{-1}$ and there were no bands observed above 1000 cm$^{-1}$. The absence of D and G bands suggests that the carbon present in the material was not due to carbon laydown on the nitride but that it was instead incorporated into the lattice, which, as mentioned above, is consistent with the XRD results. The spectra are presented in Figure 41. As seen with $\text{Ni}_2\text{Mo}_3\text{N}$, the Raman spectra were different between the two different areas measured. Both areas show either the presence of $\alpha$-$\text{NiMoO}_4$ or $\beta$-$\text{NiMoO}_4$, which is consistent with the formation of a surface oxide layer on the carbonitride. The bands at 368, 815, 888 and 936 cm$^{-1}$ match well with the literature values for $\beta$-$\text{NiMoO}_4$ [96]. Raman bands at positions of approximately 953,
905 and 700 cm\(^{-1}\) were attributed to \(\alpha'\)-NiMoO\(_4\) [104]. Alconchel et al. [67] did not detect any bands in the Raman spectrum for their nickel molybdenum carbonitride. However, this group used a lower laser power (80 mW) compared to this study and also they did not state the filter percentage they used for taking Raman spectra.

The ammonia synthesis activity of a material can be affected by its morphology and therefore, SEM analysis was performed for Ni\(_2\)Mo\(_3\)C\(_x\)N\(_y\). Typical SEM images of Ni\(_2\)Mo\(_3\)C\(_x\)N\(_y\) at different magnifications are presented in Figure 42. It can be seen that the carbonitride consisted of a porous structure and that the morphology had been retained from the nitride precursor. It has been previously reported that the conversion of Ni\(_2\)Mo\(_3\)N to the carbonitride is topotactic and pseudomorphic [67]. The topotactic production of carbides from their corresponding nitride has been reported for Co\(_3\)Mo\(_3\)C [54] [105], Fe\(_3\)Mo\(_3\)C [105], Mo\(_2\)Ta\(_2\)C\(_x\), Mo\(_3\)Nb\(_2\)C\(_x\) and W\(_9\)Nb\(_8\)C\(_x\) [102]. Therefore, any difference in activity between Ni\(_2\)Mo\(_3\)N and the carbonitride is not due to a difference in morphology between the two materials.

The nickel molybdenum carbonitride had a surface area of 9 m\(^2\)/g, a pore volume of 0.10 cc/g and an average pore radius of 22.94 Å. The BET surface area had increased compared to the nitride, which had a value of 5 m\(^2\)/g. However, it must be noted that the measure of

![Figure 41: Raman spectra of nickel molybdenum carbonitride (Ni\(_2\)Mo\(_3\)C\(_x\)N\(_y\)). The two spectra were taken at different points of the material and either at 25% or 50% filter.](image-url)
very low surface areas using nitrogen as the adsorbate can give large inaccuracies. Therefore, it would be better to use krypton rather than nitrogen for BET surfaces areas that are small. Furthermore, as with the nitride, the formation of the oxide layer on the surface of the material may mean that the BET surface area value is inaccurate in the sense that it does not strictly conform to the material under operation.

Figure 42: SEM images of nickel molybdenum carbonitride (Ni$_2$Mo$_3$C$_x$N$_y$). a) 1000x magnification, b) 2000x magnification, c) 6000x magnification and d) 6000x magnification.

The element map in Figure 43 illustrates that there was an even distribution of nickel and molybdenum over the sample and that there was more molybdenum present.

Figure 43: Element Map for Ni$_2$Mo$_3$C$_x$N$_y$. Elements: Ni (red) and Mo (green).
The weight percentages obtained from EDX for Ni$_2$Mo$_3$C$_x$N$_y$ are provided in Table 11.

From CHN analysis, the stoichiometry calculated for the bulk sample is Ni$_2$Mo$_3$C$_{0.49}$N$_{0.58}$. Therefore, the stoichiometric percentage of nickel, molybdenum, carbon and nitrogen in the sample is 28.00 wt. %, 68.66 wt. %, 1.40 wt. % and 1.94 wt. % respectively. The carbon and nitrogen weight percentages were greater than the stoichiometric values expected for Ni$_2$Mo$_3$C$_{0.49}$N$_{0.58}$. However, EDX can be problematic in analysing light elements and also carbon stubs are used to mount the samples. The molybdenum percentage was lower than the expected stoichiometric value. However, EDX is semi-quantitative and therefore, these values may not be representative.

<table>
<thead>
<tr>
<th>Area</th>
<th>Ni weight (%)</th>
<th>Mo weight (%)</th>
<th>C weight (%)</th>
<th>N weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25</td>
<td>50</td>
<td>23</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>22</td>
<td>53</td>
<td>16</td>
<td>9</td>
</tr>
<tr>
<td>3</td>
<td>25</td>
<td>57</td>
<td>15</td>
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<td>4</td>
<td>30</td>
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<td>40</td>
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<tr>
<td>6</td>
<td>27</td>
<td>49</td>
<td>20</td>
<td>4</td>
</tr>
<tr>
<td>Average</td>
<td>25</td>
<td>49</td>
<td>21</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 11: EDX values for nickel molybdenum carbonitride (Ni$_2$Mo$_3$C$_x$N$_y$)

### 3.2.1.4.1 Ammonia Synthesis at 400°C for Ni$_2$Mo$_3$C$_x$N$_y$

The Ni$_2$Mo$_3$C$_x$N$_y$ was tested for ammonia synthesis activity at 400°C and atmospheric pressure under 3:1 H$_2$/N$_2$ atmosphere for 36 hours. This was performed to establish the influence the phase composition had upon ammonia synthesis activity. Performing the reaction at atmospheric pressure is not thermodynamically desirable. However, it is easier to follow the influence the transformation of phase has on the development of activity since it will be expected to occur on a longer timescale than when running under higher pressure, since compositional changes are expected to be more gradual.

The activity of this carbonitride was very different compared to Co$_3$Mo$_3$C at 400°C [54]. The carbonitride material had steady state activity and there was no induction period, as shown in Figure 44. Therefore, the surface oxide layer did not impede the ammonia synthesis activity. Two different rates have been calculated and are shown in Table 12 as the system was accidentally interrupted during the reaction run. The Ni$_2$Mo$_3$N nitride material prepared by the modified Pechini method has been tested previously and gave an activity of 395 ± 6 μmol h$^{-1}$ g$^{-1}$ [36].

To determine the reproducibility of the Ni$_2$Mo$_3$C$_x$N$_y$ activity for ammonia synthesis, the material was tested for a second time by reacting it with 3:1 H$_2$/N$_2$ at 400°C for ten hours. The rate exhibited by the material was 211 μmol h$^{-1}$ g$^{-1}$. The stoichiometry proposed for
this bulk sample is \( \text{Ni}_2\text{Mo}_3\text{C}_{0.50}\text{N}_{0.49} \), meaning that the initial amount of carbon in each sample is comparable. However, there was approximately 16% more nitrogen present pre-reaction in the sample that was tested for 36 hours.

Figure 44: Conductivity profile for \( \text{Ni}_2\text{Mo}_3\text{C}_x\text{N}_y \) reacted with 3:1 \( \text{H}_2/\text{N}_2 \) at 400°C for 36 hours.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Rate (µmol h(^{-1}) g(^{-1})) at 400°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Ni}_2\text{Mo}_3\text{C}_x\text{N}_y ) Before MFC was switched off</td>
<td>174</td>
</tr>
<tr>
<td>( \text{Ni}_2\text{Mo}_3\text{C}_x\text{N}_y ) After the MFC was switched back on</td>
<td>206</td>
</tr>
</tbody>
</table>

Table 12: Ammonia synthesis rates for \( \text{Ni}_2\text{Mo}_3\text{C}_x\text{N}_y \) at 400°C and reacted with 3:1 \( \text{H}_2/\text{N}_2 \) for 36 hours.

The XRD pattern of the material post-reaction is displayed in Figure 45. If the material underwent nitridation during the reaction as observed for \( \text{Co}_3\text{Mo}_3\text{C} \) [54], the XRD pattern would be expected to show a change in lattice parameter. As nitrogen is smaller than carbon, it would be expected that the unit cell would decrease in size and the XRD peaks would shift to larger angles with progressive incorporation of N. After reaction, as seen in Figure 46, the shifts in peak positions were not consistent with the expected change in lattice parameter due to replacement of carbon with nitrogen. This observation requires further investigation as the reason for it is currently unknown. If oxygen was incorporated into the lattice the peaks would be expected to shift to higher 2θ values.
Figure 45: Comparison of XRD patterns for Ni$_2$Mo$_3$C$_x$N$_y$ pre and post reaction with 3:1 H$_2$/N$_2$ at 400°C for 36 hours. Reflections marked: ▲ Mo$_{0.09}$Ni$_{0.91}$ (JCPDS file number 01-071-9766) and the peak marked with ★ is an unknown phase.

Figure 46: Comparison of XRD patterns for Ni$_2$Mo$_3$C$_x$N$_y$ pre- (black) and post-reaction (red) with 3:1 H$_2$/N$_2$ at 400°C for 36 hours.
The elemental analysis for the post reaction material is provided in Table 13. Post-reaction, it is observed that the nitrogen content of the nickel molybdenum carbonitride had slightly increased and the carbon content of the material had decreased. The stoichiometry proposed for the bulk sample is now Ni$_2$Mo$_3$C$_{0.43}$N$_{0.61}$. However, this increase in nitrogen content has not resulted in a discernible shift of the peak positions in the XRD to higher 2θ values, possibly due to the increase being small.

<table>
<thead>
<tr>
<th>Material</th>
<th>Calculated Stoichiometric Nitrogen Content (wt. %)</th>
<th>Calculated Stoichiometric Carbon Content (wt. %)</th>
<th>Nitrogen Content from Elemental Analysis (wt. %)</th>
<th>Carbon Content from Elemental Analysis (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$_2$Mo$_3$C$_x$N$_y$ Pre-Reaction</td>
<td>-</td>
<td>2.88</td>
<td>1.93</td>
<td>1.42</td>
</tr>
<tr>
<td>Ni$_2$Mo$_3$C$_x$N$_y$ Post-Reaction</td>
<td>-</td>
<td>2.88</td>
<td>2.04</td>
<td>1.24</td>
</tr>
</tbody>
</table>

Table 13: Elemental Analysis for Ni$_2$Mo$_3$C$_x$N$_y$ comparing pre- and post-reaction with 3:1 H$_2$/N$_2$ at 400°C for 36 hours.

SEM analysis was performed in order to examine any changes in the morphology and structure of Ni$_2$Mo$_3$C$_x$N$_y$ during the ammonia synthesis reaction. Representative SEM images of the post-reaction material are presented in Figure 47. The material had a porous structure and the morphology was similar to the pre-reaction material. Therefore, the lower ammonia synthesis activity of the carbonitride compared to the nitride was not due to a change in morphology upon carburisation.
Figure 47: SEM images of nickel molybdenum carbonitride (Ni$_2$Mo$_3$C$_{x}$N$_y$) post-reaction with 3:1 H$_2$/N$_2$ at 400°C for 36 hours. a) 1000x magnification, b) 2000x magnification, c) 6000x magnification and d) 6000x magnification.

The element map in Figure 48 shows that the even nickel and molybdenum distribution had been retained.

Figure 48: Element Map for Ni$_2$Mo$_3$C$_{x}$N$_y$ post-reaction with 3:1 H$_2$/N$_2$ at 400°C. Elements: Ni (red) and Mo (green).

Table 14 gives the weight percentage for each element from the EDX for the post-reaction Ni$_2$Mo$_3$C$_{x}$N$_y$. The CHN analysis shows that the stoichiometry for the bulk sample post 36 hour reaction at 400°C was Ni$_2$Mo$_3$C$_{0.43}$N$_{0.61}$. Thus, the stoichiometric content of nickel, molybdenum, carbon and nitrogen in the sample should be 28.02 wt. %, 68.71 wt. %, 1.23 wt. % and 2.04 wt. % respectively. As with the pre-reaction sample, the carbon and
nitrogen percentages were higher than expected. However, the amount of carbon decreased by 5.59 wt. % and the weight percentage of nitrogen increased by 1.05 wt. % compared to pre-reaction. These values compare very well with the stoichiometric differences between the pre- (Ni₂Mo₃C₀.₄⁹N₀.₅₈) and post-reaction sample. The molybdenum percentage increased by 5.10 wt. % compared to the pre-reaction Ni₂Mo₃CxNy.

<table>
<thead>
<tr>
<th>Area</th>
<th>Ni weight (%)</th>
<th>Mo weight (%)</th>
<th>C weight (%)</th>
<th>N weight (%)</th>
</tr>
</thead>
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<tr>
<td>1</td>
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<tr>
<td>Average</td>
<td>25</td>
<td>54</td>
<td>16</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 14: EDX values for nickel molybdenum carbonitride (Ni₂Mo₃CxNy) post reaction with 3:1 H₂/N₂ at 400°C for 36 hours.

The formation of the oxide layer on the surface of the carbonitride and its potential effect on the ammonia synthesis activity of the material where examined by ToF-SIMS. It is important to understand if the development of activity requires removal of the oxide layer and/or restructuring of the near surface region of the material. ToF-SIMS is a surface sensitive technique and therefore, can give information on the elements present at the surface of a material. This technique can also be used for depth profiling and in this work, could be used to determine the depth of the oxide surface layer.

The ToF-SIMS instrument used a pulsed Cs⁺ ion beam to remove species from the top layer of the carbonitride surface. Bi³⁺ was used as the primary ion for depth profiling. The removed molecules from the surface are the secondary ions and their mass are determined by the time they take to reach the detector.

The mass spectrum for molybdenum can be complex due to the element having seven naturally occurring isotopes of 92, 94, 95, 96, 97, 98 and 100. In Ni₂Mo₃CₓNy, the nitrogen and carbon are bonded to six molybdenum species as explained in the introduction. Therefore, the mass fragments for this material would contain MoC and MoN. The mass spectrum of MoC, MoN and MoO fragments overlap. Therefore, there was no peak that was attributable solely to a MoN fragment. The peak at 106 m/z can result from both ⁹⁴MoC and ⁹²MoN. In this study, to show the depth profiling of a MoN fragment, the contribution of ⁹⁴MoC was subtracted from the total intensity for 106 m/z to give the intensity for ⁹²MoN. The ⁹⁴MoC contribution was calculated by comparing the expected ratio of the isotopes with ⁹²MoC at 104 m/z (⁹²Mo is 14.8% and ⁹⁴Mo is 9.2%).
The pre- and post-36 hour reaction materials were examined by ToF-SIMS and the data is provided in Appendix III. For both the pre- and post-reaction samples, nitrogen and carbon were present at a depth of 10 nm, suggesting that although there was an oxide layer, these elements were present near the surface. Oxygen was also present in the materials and the intensity appeared to decrease as the depth increased, which is consistent with this being a surface layer. From this analysis, it can be determined that although there was an oxygen passivation layer, due to the presence of nitrogen and carbon near the surface, this would not need to be removed significantly in order for the material to be active.

As the pre- and post-reaction mass spectra appeared to be very similar, this suggests that the material has not undergone restructuring (i.e. segregation) during the reaction. However, the intensity of the $^{92}$MoN peak had increased post-reaction compared to pre-reaction and the intensities of the $^{92}$MoC and MoO$_3^-$ peaks had decreased. This suggests that more nitrogen was present near the surface of the material after the reaction, as expected.

The mass peak due to oxygen (m/z = 16) was observed to reach saturation during the depth profiling of the material. It was suggested that the vacuum may have been insufficient to remove the oxygen from the chamber and therefore, there may have been a problem with the sample reabsorbing the oxygen.

3.2.1.4.2 Ammonia Synthesis at 500°C for Ni$_2$Mo$_3$C$_x$N$_y$
Ni$_2$Mo$_3$C$_x$N$_y$ was tested for ammonia synthesis activity at 500°C and atmospheric pressure under 3:1 H$_2$/N$_2$ to investigate if the increase in temperature would have a more notable effect on the phase composition. At this temperature, there is an induction period of approximately 50 minutes before the material develops steady state ammonia synthesis activity, as seen in Figure 49. The steady state activity of the material after the induction period is shown in Figure 50. This is in contrast to the material tested at 400°C, which had no induction period and therefore, an instantaneous decrease in conductivity. The reason as to why this was observed was unclear. However, the induction period may be due to removal of an oxide surface layer and/or restructuring of the material. The ammonia synthesis rate of the material at 500°C was determined to be $619 \pm 14 \mu$mol h$^{-1}$ g$^{-1}$. In comparison, the rate at 400°C was calculated to be approximately $197 \pm 23 \mu$mol h$^{-1}$ g$^{-1}$. Hence, beyond the induction period, the material is much more active at the higher temperature as might be expected. Co$_3$Mo$_3$C was stated to have a rate of $461 \pm 17 \mu$mol h$^{-1}$ g$^{-1}$ at 500°C under the same conditions [54], suggesting that Ni$_2$Mo$_3$C$_x$N$_y$ is yet more
reactive, although the comparative surface areas of the materials would need to be considered in drawing further inferences. The cobalt molybdenum material also had an induction period that lasted for 40 minutes before it became active during which the material underwent nitridation to form a carbonitride. $\text{Co}_3\text{Mo}_3\text{C}_x\text{N}_y$ was active for ammonia synthesis at 500°C and had similar activity to the corresponding nitride [54].

**Figure 49**: Conductivity profile for $\text{Ni}_2\text{Mo}_3\text{C}_x\text{N}_y$ reacted with 3:1 $\text{H}_2/\text{N}_2$ at 500°C for 7.5 hours.

**Figure 50**: Conductivity profile for $\text{Ni}_2\text{Mo}_3\text{C}_x\text{N}_y$ reacted with 3:1 $\text{H}_2/\text{N}_2$ at 500°C for 7.5 hours, highlighting the linear part of the graph used for calculating the rate.
The XRD patterns in Figures 51 and 52 show a small shift in the position of the peaks to higher 20 values between pre- and post-reaction. All the XRD reflections of Ni$_2$Mo$_3$C$_x$N$_y$ are shifted to higher 20 angles after the reaction. This implies that the lattice carbon is being replaced with nitrogen to give a material with a composition containing more nitrogen. The XRD patterns illustrate a more notable effect on the phase transformation at the higher reaction temperature.

![XRD patterns comparison](image)

**Figure 51:** Comparison of XRD patterns for Ni$_2$Mo$_3$C$_x$N$_y$ pre- and post-reaction with 3:1 H$_2$/N$_2$ at 500°C for 7.5 hours. Reflections marked: ▲ Mo$_{0.09}$Ni$_{0.91}$ (JCPDS file number 01-071-9766) and the peak marked with ★ is an unknown phase.
Figure 52: Comparison of XRD patterns for Ni$_2$Mo$_3$C$_x$N$_y$ pre- (black) and post-reaction (red) with 3:1 H$_2$/N$_2$ at 500°C for 7.5 hours.

From the elemental analysis, it appears that some of the carbon had been removed from the sample and had been replaced with nitrogen, as observed in Table 15. The stoichiometry proposed for the bulk sample is now Ni$_2$Mo$_3$C$_{0.15}$N$_{0.83}$. This is a significant change in composition compared to pre-reaction (Ni$_2$Mo$_3$C$_{0.43}$N$_{0.61}$). The post-reaction elemental analysis confirms that the carbon was not completely removed from the carbonitride to form the corresponding nitride. However, at 500°C reaction temperature, the replacement of lattice carbon with nitrogen is much more noticeable. A similar transformation was seen for Co$_3$Mo$_3$C, which formed Co$_3$Mo$_3$C$_x$N$_y$ when reacted with 3:1 H$_2$/N$_2$ at 500°C [54].

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<th>Calculated Stoichiometric Carbon Content (wt. %)</th>
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<th>Carbon Content from Elemental Analysis (wt. %)</th>
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<tr>
<td>Ni$_2$Mo$_3$C$_x$N$_y$ Post 500°C Reaction</td>
<td>-</td>
<td>2.88</td>
<td>2.78</td>
<td>0.42</td>
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</table>

Table 15: Elemental Analysis for Ni$_2$Mo$_3$C$_x$N$_y$ comparing pre- and post-reaction with 3:1 H$_2$/N$_2$ at 500°C for 7.5 hours.
A representative Raman spectrum of the post 500°C reaction carbonitride is displayed in Figure 53. Alconchel et al. [67] observed no Raman bands for Ni$_2$Mo$_3$C$_x$N$_y$ and they suggested that the carbonitride was less oxygen sensitive compared to the corresponding nitride. In the pre-reaction material, Raman bands were observed corresponding to a passivation layer (Figure 41). These bands were not observed in the Raman spectra post-reaction. This would suggest that the induction phase observed for this material could be due to the removal of the oxide layer, although surface segregation effects also need to be considered. However, the induction phase could also be due to restructuring of the material.

Figure 53: Raman spectrum of nickel molybdenum carbonitride (Ni$_2$Mo$_3$C$_x$N$_y$) post-reaction with 3:1 H$_2$/N$_2$ at 500°C for 7.5 hours.

ToF-SIMS was utilised to determine the reason for the induction period for Ni$_2$Mo$_3$C$_x$N$_y$ before it obtained steady state activity. The mass spectrum for the post-reaction material is displayed in Appendix III. Oxygen was observed at the surface and therefore, the material had an oxide surface layer. This is in contrast to the Raman spectrum that showed no bands for an oxide. However, ToF-SIMS is a very sensitive technique with amounts in the ppm/ppb range being detected. Carbon and nitrogen were also detected at the surface of the material. This suggests that the removal of an oxide layer might not straightforwardly be the reason for the induction period.
3.2.2 Nickel Molybdenum Carbide (Ni₆Mo₆C)

Although there have been reports of Ni₃Mo₃N formation in the literature, this phase is not currently established [60] [35]. Instead, nitridation of the NiMoO₄ precursor results in a mixture of Ni and Ni₂Mo₃N. In contrast, the carbide, Ni₃Mo₃C, is an established phase and therefore, its preparation and possible topotactic nitridation during ammonia synthesis might be a route to preparing Ni₃Mo₃N. The nitridation of carbides and carbonitrides has been reported for Ni₂Mo₃CxNy in this thesis and for Co₃Mo₃C [54]. Comparison of the catalytic performance of Ni₃Mo₃C and Ni₂Mo₃C would also give information on the effect structure (η-carbide versus filled β-Mn) has on the ammonia synthesis activity.

Attempts have been made to prepare nickel molybdenum carbide directly from the bimetallic oxide by using methane as the carburising source. However, this has proved to be difficult, with reports in the literature showing the formation of β-Mo₂C and Ni instead [62]. Therefore, in this work, a different approach was undertaken in order to prepare Ni₃Mo₃C. The citric acid used in the preparation of the oxide precursor via the modified Pechini method, was used as the carburising source. Other studies have shown that a precursor can be used as the carbon source to form carbides, for example hexamethylenetetramine (HMTA) [106] and glucose [107]. Ni₆Mo₆C has been previously synthesised by reduction of citric acid under Ar or H₂ [69] [108] [68]. However, the materials were not pure phase, with impurities of β-Mo₂C, a nickel molybdenum alloy and Ni₃C being formed. A pure phase Ni₆Mo₆C had been formed by Newsam et al. [64] under CO/CO₂ at 1000°C.

3.2.2.1 Nickel Molybdenum Oxide (Ni₃Mo₃Oₓ)

To prepare the nickel molybdenum carbide, first the oxide precursor was synthesised via the modified Pechini method. The oxide was not calcined in order for the citric acid to be used as the source of carbon. The XRD pattern of the material is shown in Figure 54 and a broad peak was observed at approximately 24° 20. This peak may be due to carbon or graphite, which shows a peak at 26° 20. The 2° 20 difference in d-spacing may be due to the poorly defined nature of the peak due to the disordered nature of the material. Elemental analysis of the oxide material showed that there was a large percentage of carbon present (C: 23.31%, H: 2.95% and N: 1.32%). Nitrogen was also detected in this material and possibly originated from the Ni(NO₃)₂·6H₂O and ((NH₄)₆Mo₇O₂₄·4H₂O starting materials.
As the XRD pattern showed that the material was amorphous, Raman analysis was conducted for this material to examine the oxide species present. In addition, information on the type of carbon can be obtained from Raman analysis. The Raman spectrum of uncalcined Ni$_3$Mo$_3$O$_x$ has a strong band at 943 cm$^{-1}$ along with bands at 895, 822 and 376 cm$^{-1}$, as shown in Figure 55. These bands match well with those reported in the literature for β-NiMoO$_4$ [109] [110]. The bands at 943, 895 and 822 cm$^{-1}$ are attributed in the literature to symmetric and asymmetric stretching modes of the Mo-O bond [88] [91]. The band at 376 cm$^{-1}$ has been assigned to the bending mode of Mo-O [96]. The weak band at 290 cm$^{-1}$ has been assigned to the deformation mode of Mo–O–Mo [91].

There are also two broad bands at 1368 and 1572 cm$^{-1}$, which are associated with the D and G bands of graphitic carbon. Carbon is present in the material from the starting citric acid precursor and is used as the source of carbon when the material is reduced. The D band at 1368 cm$^{-1}$ is attributed to defects characteristic of disorder in the graphite, whereas the G band is due to the vibration of sp$^2$ bonded carbon atoms and relates to the E$_{2g}$ mode of graphite [111]. In the literature, heating from the laser has been shown to shift the position of the G band down as far as 1567 cm$^{-1}$ [112]. For the spectrum taken with a 50% filter, the G band shifts down to 1572 cm$^{-1}$, which suggests that laser-induced heating has
shifted this band. However, other research states that the shift in band position is due to the number of layers of graphene present [113] [114]. As the number of layers increases, the G band shifts to lower wavenumber. It has been suggested that this is due to a slight weakening of the bonds as each additional layer is added [114].

![Raman spectrum of uncalcined nickel molybdenum oxide (Ni$_3$Mo$_3$O$_x$).](image)

**Figure 55:** Raman spectrum of uncalcined nickel molybdenum oxide (Ni$_3$Mo$_3$O$_x$).

### 3.2.2.2 Nickel Molybdenum Carbide (Ni$_6$Mo$_6$C)

Nickel molybdenum carbide was prepared by reducing the uncalcined oxide precursor under a 3:1 ratio of H$_2$/Ar gas mixture at 700°C. The XRD pattern in Figure 56 shows that the low carbon content Ni$_6$Mo$_6$C was formed. There were also impurities of Mo$_2$C and Ni$_2$Mo$_3$N present in the material. Nitrogen was observed in the oxide precursor and possibly resulted from the Ni(NO$_3$)$_2$·6H$_2$O and (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O used in the Pechini method. The Ni$_2$Mo$_3$N and Ni$_6$Mo$_6$C have many XRD reflections that overlap. However, unique reflections for Ni$_6$Mo$_6$C are observed at 35.9°, 50.2° and 60.7° 20 and for Ni$_2$Mo$_3$N at 30.1° and 45.3° 20. This result demonstrates that the nickel molybdenum carbide can be prepared by using citric acid as the carbon source. Both Ni$_6$Mo$_6$C and Ni$_3$Mo$_3$C have a similar η-carbide structure. The material was also prepared at a temperature of 750°C. However, the intensity of the Ni$_2$Mo$_3$N peaks increased suggesting that the nitride formation is favoured at higher temperatures. It is currently unclear why this is the case.

![Graph showing Raman shift](image)
The stoichiometric weight percentage of carbon expected in Ni₆Mo₆C is 1.28%. Elemental analysis of the ‘Ni₆Mo₆C’ material prepared at 700°C showed that the amount of carbon present was almost the same as the stoichiometric percentage (C: 1.18 wt. %, H: 0.15 wt. % and N: 0.65 wt. %). However, the Mo₂C impurity will contribute towards this value. The nitrogen present is likely due to the apparent occurrence of the Ni₂Mo₃N phase. The material that was prepared at 750°C had a higher nitrogen percentage according to CHN analysis.

The formation of Ni₆Mo₆C suggests that there may be a preference for the carbon to reside in the 8a Wyckoff site compared to the 16c site that would be required to form Ni₃Mo₃C. The 8a Wyckoff site is a more perfect octahedral site, which could explain this apparent preference.

![XRD pattern of nickel molybdenum carbide (Ni₆Mo₆C). Reflections marked: Ni₆Mo₆C (JCPDS file number 03-065-4436), Ni₂Mo₃N (JCPDS file number 01-072-6569) and Mo₂C (JCPDS file number 00-001-1188).](image)

Raman analysis was performed to investigate if there was oxide species on the surface of the material. The Raman spectrum of ‘Ni₆Mo₆C’ has bands at 937, 885, 813 and 704 cm⁻¹, as seen in Figure 57, that match well with those reported in the literature for β-NiMoO₄ [109][110]. This result suggests that an oxide layer was present on the surface of the
carbide. The bands at 937, 885 and 813 cm\(^{-1}\) are attributed in the literature to symmetric and asymmetric stretching modes of the Mo-O bond [88] [91]. The band at 704 cm\(^{-1}\) was assigned to the symmetric stretch of Ni–O–Mo [67]. The bands at 477 cm\(^{-1}\) and 126 cm\(^{-1}\) could be due to \(\alpha\)-MoO\(_3\) [115], which would result from the passivation layer on Mo\(_2\)C. To the author’s knowledge, there are no Raman spectra for Ni\(_6\)Mo\(_6\)C reported in the literature. There were no bands associated with graphitic and other forms of extra-lattice carbon seen in the Raman spectrum, suggesting that the carbon is incorporated into the lattice of the carbide.

![Raman spectrum of nickel molybdenum carbide (Ni\(_6\)Mo\(_6\)C).](image)

**Figure 57**: Raman spectrum of nickel molybdenum carbide (Ni\(_6\)Mo\(_6\)C).

SEM images of the mixed phase ‘Ni\(_6\)Mo\(_6\)C’ are presented in Figure 58 illustrate that the material was porous with pores ranging in diameter from approximately 1 – 10 µm. The EDX data in Table 16 gives the element weight percentages for ‘Ni\(_6\)Mo\(_6\)C’. The stoichiometric percentage of nickel, molybdenum and carbon in Ni\(_6\)Mo\(_6\)C is 37.47 wt. %, 61.25 wt. % and 1.28 wt. %, respectively. From the table, it can be seen that the carbon weight percentage was much higher than predicted. Correspondingly, the nickel and molybdenum percentages were lower. This could suggest that there is a large amount of carbon laydown on the material. However, the Raman spectrum showed no evidence of carbon laydown and the XRD pattern did not contain any peaks associated with carbon. It must be noted that the samples are placed on carbon stubs for SEM and EDX analysis and...
therefore, this may have contributed to the carbon percentage. From the XRD pattern, it was shown that the material consisted of Ni₆Mo₆C, Mo₂C and Ni₂Mo₃N. However, nitrogen was not detected for the material by EDX suggesting that the amount was low. The EDX data appears to support the assignment of the composition as Ni₆Mo₆C.

Figure 58: SEM images of nickel molybdenum carbide (Ni₆Mo₆C). a) 1000x magnification, b) 2000x magnification, c) 4000x magnification and d) 5000x magnification.

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Table 16: EDX values for nickel molybdenum carbide (Ni₆Mo₆C) prepared under 3:1 H₂/Ar at 700°C.
3.2.2.2.1 Ammonia Synthesis at 400°C for Ni₆Mo₆C

‘Ni₆Mo₆C’ was tested for ammonia synthesis activity at 400°C and atmospheric pressure under 3:1 H₂/N₂ atmosphere for 8.5 hours. This was performed to establish the influence the phase composition had upon ammonia synthesis activity. The conductivity only decreased by a small amount over the time the material was tested as observed in Figure 59. For the first 150 minutes, there is a small decrease in conductivity. However, after this time, the conductivity began to level off and therefore, ammonia was no longer being produced. Whilst there seems to be Ni₂Mo₃N contained within this material, which would be expected to be active, the XRD pattern suggests it to be at only a very low level.

The behaviour of ‘Ni₆Mo₆C’ was similar to the performance of Co₆Mo₆C tested at 500°C for ammonia synthesis [54]. Co₆Mo₆C was found to be inactive at 500°C, even upon extended reaction times of 48 hours. It is interesting to note that Ni₂Mo₃N and Ni₂Mo₃CₓNᵧ are active for ammonia synthesis at 400°C, which implies that the relatively small phase fraction of Ni₂Mo₃N present in the current material does not significantly contribute activity under these conditions. This suggests that the carbide is relatively stable in comparison to the carbonitride and nitride. There may be a relationship between the ammonia synthesis activity and structure of these materials. Both Ni₂Mo₃N and Ni₂Mo₃CₓNᵧ have the filled β-Mn structure whereas Ni₆Mo₆C has the η-carbide structure, although the difference in interstitial element may also affect the ammonia synthesis activity.

![Conductivity profile for ‘Ni₆Mo₆C’ reacted with 3:1 H₂/N₂ at 400°C for 8.5 hours.](image)

Figure 59: Conductivity profile for ‘Ni₆Mo₆C’ reacted with 3:1 H₂/N₂ at 400°C for 8.5 hours.
The XRD patterns presented in Figure 60 show that the η-carbide structure of Ni₆Mo₆C was maintained after the reaction. There does not appear to be any change in phase compared to pre-reaction suggesting that the material does not undergo nitridation during the reaction.

![XRD pattern comparison](image)

**Figure 60:** Comparison of XRD patterns for ‘Ni₆Mo₆C’ pre- and post-reaction with 3:1 H₂/N₂ at 400°C for 8.5 hours. Reflections marked: ◻ Ni₆Mo₆C (JCPDS file number 03-065-4436), □ Ni₂Mo₃N (JCPDS file number 01-072-6569) and ▲ Mo₂C (JCPDS file number 00-001-1188).

Figure 61 confirms that the peaks due to Ni₆Mo₆C do not shift in position compared to the pre-reaction material. These results may suggest that the inactivity of ‘Ni₆Mo₆C’ is due to the material not undergoing nitridation. It has been suggested that Co₃Mo₃C does not become active for ammonia synthesis until nitrogen is incorporated into the lattice [54]. It was observed that Co₃Mo₃C was inactive at 400°C and became active when the temperature was increased to 500°C. The higher reaction temperature may be required in order to incorporate nitrogen into the material.

The elemental analysis demonstrates that the percentage of carbon present in the material post-reaction has slightly increased (C: 1.23 wt. %, H: 0.00 wt. % and N: 0.48 wt. %) compared to pre-reaction (1.18 wt. %). This increase may be due to the nitrogen...
percentage slightly decreasing or the error within the CHN analysis, which is ± 5%. The expected stoichiometric percentage of carbon in Ni₆Mo₆C is 1.28 wt. % and therefore, the elemental analysis for carbon agrees very well with this value. However, the Mo₂C impurity will contribute towards this value.

![Figure 61](image.png)

Figure 61: Comparison of XRD patterns for ‘Ni₆Mo₆C’ pre- (black) and post-reaction (red) with 3:1 H₂/N₂ at 400°C for 8.5 hours, highlighting the 2θ values for peaks due only to Ni₆Mo₆C.

For the post-reaction material, there was one very weak band at 2332 cm⁻¹ relating to the 2D band for carbon, as shown in Figure 62. The 2D band is the second order of the D band and involves a two phonon process [111]. The 2D band can be used to determine the graphene thickness from its intensity and shape. When successive layers of graphene are added, the 2D band separates into overlapping modes due to the decrease in symmetry. The unique shape differences of this band can give information on the number of layers of graphene. Therefore, the low intensity of this band suggests that there were few layers of carbon present in this material.

There is also a broad band between 550 and 1050 cm⁻¹ that could be assigned to NiMoO₄. However, there were no well-defined peaks, which suggests that there was only a very
small passivation layer on the material post reaction. This result suggests that the oxide layer is removed during the reaction.

![Graph showing Raman spectrum with peak at 2332 cm⁻¹](image)

Figure 62: Raman spectrum of ‘Ni₆Mo₆C’ post-reaction with 3:1 H₂/N₂ at 400°C for 8.5 hours.

SEM analysis was performed to see if there was any change in the morphology of the material during the ammonia synthesis reaction. Representative SEM images of post 400°C reaction ‘Ni₆Mo₆C’ are displayed in Figure 63. The material is porous and retains the morphology of the pre-reaction material. The stoichiometric percentage of nickel, molybdenum and carbon in Ni₆Mo₆C is 37.47 wt. %, 61.25 wt. % and 1.28 wt. %, respectively. The EDX data displayed in Table 17 shows that the carbon and nickel weight percentages were higher compared to pre-reaction and that the molybdenum percentage was lower. However, it must be noted that EDX is a semi-quantitative technique and therefore, care needs to be taken when considering statistical relevance etc. The Raman spectrum showed a small amount of carbon laydown. However, the amount of carbon detected by EDX was much greater and therefore, the carbon stub on which the material was placed must have contributed to this value. Nitrogen was not detected by EDX suggesting that the contribution of nitrogen from Ni₂Mo₃N must be small.
Figure 63: SEM images of ‘Ni$_6$Mo$_6$C’ post-reaction with 3:1 H$_2$/N$_2$ at 400°C for 8.5 hours. a) 2000x magnification and b) 5000x magnification.

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Table 17: EDX values for ‘Ni$_6$Mo$_6$C’ post-reaction with 3:1 H$_2$/N$_2$ at 400°C for 8.5 hours.

3.2.2.2 Ammonia Synthesis at 700°C for Ni$_6$Mo$_6$C
As the material was inactive for ammonia synthesis at 400°C, the temperature was increased to 700°C, despite ammonia synthesis being thermodynamically unfavourable at this temperature. The conductivity profile for the material at 700°C is provided in Figure 64.

The ammonia synthesis rate for the material at 700°C was calculated to be 152 ± 89 µmol h$^{-1}$ g$^{-1}$. For the first 20 minutes, there was a lag period before the material became active. The lag period could possibly be explained by the incorporation of nitrogen into the lattice and therefore, the transition of the material from the carbide to the nitride or due to surface segregation/restructuring.
Figure 64: Conductivity profile for ‘Ni$_6$Mo$_6$C’ reacted with 3:1 H$_2$/N$_2$ at 700°C for 8 hours.

The XRD pattern of the material post 700°C reaction shows that Ni$_2$Mo$_3$N and Mo$_{0.99}$Ni$_{0.01}$ are the only phases present, as observed in Figure 65. This suggests that Ni$_6$Mo$_6$C has undergone nitridation during the reaction and could explain the reason for the material becoming active. The formation of either nickel or a nickel molybdenum alloy, alongside Ni$_2$Mo$_3$N, have been reported in the literature [36] [98]. Rietveld refinement by Conway and Prior [60] confirms that the structure is Ni$_2$Mo$_3$N and not Ni$_3$Mo$_3$N. The nitride has previously been reported to be active for ammonia synthesis [39] [94] [36]. Therefore, it is of interest to know whether the material was active due to the incorporation of nitrogen into the lattice to form the nitride or if nitrogen was present because the carbide was active thereby producing NH$_3$, which further nitrided the sample.

Co$_6$Mo$_6$C has been shown to form Co$_3$Mo$_3$N when reacted under 3:1 H$_2$/N$_2$ at 600°C [55]. Co$_6$Mo$_6$N was not formed as an intermediate phase but instead only Co$_6$Mo$_6$C$_x$ and Co$_3$Mo$_3$N$_x$ phases were observed during the transformation.

Almost all of the carbon had been removed from the material during the reaction as seen from the elemental analysis (C: 0.08 wt. %, H: 0.02 wt. % and N: 2.16 wt. %). The nitrogen content has also significantly increased. This further confirms that a nitride phase has been formed during the reaction. The expected stoichiometric percentage of nitrogen in Ni$_2$Mo$_3$N, taking into account the presence of additional nickel, is 2.93 wt. %. The obtained value of 2.16 wt. % for the material agrees quite well with this expected value.
This replacement of carbon with nitrogen contrasts with the observation for Co₆Mo₆C, which showed no incorporation of nitrogen [54]. However, the material was not tested at a temperature of 700°C and therefore, the higher temperature may be required for the replacement to occur in that case.

![XRD pattern of 'Ni₆Mo₆C' post-reaction with 3:1 H₂/N₂ at 700°C for 8 hours. Reflections marked: □ Ni₂Mo₃N (JCPDS file number 01-072-6569) and ▼ Mo₀.₀₉Ni₀.₉₁ (JCPDS file number 01-071-9766).](image)

The Raman spectrum of the post-reaction material appears to be similar to the one for the pre-reaction sample, as shown in Figure 66. This suggests that there is a passivating oxide layer on the surface of the material. The Raman bands at 936, 887, 816 and 704 cm⁻¹ can be attributed to β-NiMoO₄. Bands due to α-MoO₃ are also observed at 478 and 126 cm⁻¹. Another area of the sample was examined and there appeared to be no well-defined bands as was seen for the sample post 400°C reaction.
As there was a change in phase, as evidenced by the XRD pattern, SEM analysis was performed on the material to see if there was also a change in the morphology. The SEM images of ‘Ni₆Mo₆C’ post 700°C reaction in Figure 67 show that the morphology has been retained compared to the pre-reaction material. This suggests that the nitridation process is pseudomorphic. The stoichiometric percentage of nickel, molybdenum and nitrogen in Ni₂Mo₃N is 28.00 wt. %, 68.66 wt. % and 3.34 wt. %, respectively. The EDX data presented in Table 18 shows that nitrogen was detected, which was not observed in the pre-reaction material. This further indicates that the carbide had transformed to Ni₂Mo₃N during the reaction. A large percentage of carbon was detected for this material but this may be due to the carbon stub the sample was placed on for EDX analysis.
Figure 67: SEM images of ‘Ni$_6$Mo$_6$C’ post-reaction with 3:1 H$_2$/N$_2$ at 700°C for 8 hours. a) 1000x magnification, b) 2000x magnification, c) 4000x magnification and d) 6000x magnification.

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Table 18: EDX values for ‘Ni$_6$Mo$_6$C’ post-reaction with 3:1 H$_2$/N$_2$ at 700°C for 8 hours.
The formation of the nitride from Ni$_6$Mo$_6$C was investigated by thermogravimetric analysis of the pre-reaction material under 5% H$_2$/N$_2$. Mass spectrometry was employed to determine the product formed when Ni$_6$Mo$_6$C was nitrided to Ni$_2$Mo$_3$N and Mo$_{0.09}$Ni$_{0.91}$. The TGA curve and first derivative weight change of ‘Ni$_6$Mo$_6$C’ is presented in Figure 68. The material was heated from room temperature to 1000°C at a ramp rate of 10°C/min under 5% H$_2$/N$_2$. The first feature of the TGA curve is a weight loss of approximately 0.4% at 358°C. Whilst methane may be the expected product, the mass spectral ion curves of 2 and 44 m/z show peaks at this temperature, as seen in Figure 69 and Figure 70, suggesting the loss of H$_2$ and either CO$_2$ or C$_3$H$_8$. The oxygen present in any CO$_2$ produced could arise from the oxygen surface layer on the material and therefore, this weight loss would correspond to the removal of the passivation layer. The weight loss could also be due to the reaction of lattice carbon to form propane. The loss of carbon from Ni$_6$Mo$_6$C would result in a weight loss of 1.28%. However, only a weight loss of 0.4% was observed, suggesting that only a small amount of carbon was being removed from the material. Therefore, this needs to be investigated further.

The second feature of the TGA curve is a weight gain of approximately 0.6% at 777°C. It is observed that after TGA, the final material has gained a small amount of weight. It is not certain what the weight gain is due to but the ion curve of H$_2$ (m/z = 2) shows a peak at this temperature. The mass spectra of 14, 15, 16, 17, 18, 28, 30, 32 and 46 m/z were investigated but they did not show any features. Assuming the following equation to be true, the formation of Ni$_2$Mo$_3$N and Ni from Ni$_6$Mo$_6$C would result in a weight gain of 1.70%. This does not take into account the presence of Ni$_2$Mo$_3$N and Mo$_2$C in the starting material. The total weight gain at 906°C was observed to be only 0.1%.

\[
\text{Ni}_6\text{Mo}_6\text{C} + \text{N}_2 \rightarrow 2 \text{Ni}_2\text{Mo}_3\text{N} + 2 \text{Ni} + \text{C}
\]

**Equation 3: Equation for the formation of Ni$_2$Mo$_3$N from Ni$_6$Mo$_6$C**

The mass began to decrease again after 906°C and resulted in a 0.2% weight loss. This reduction in mass could be due to the loss of nitrogen from the material and therefore, the reduction of the material to nickel and molybdenum metal. The total loss of nitrogen from the material would equate to a weight loss of 2.93%. This would suggest that only a small percentage of nitrogen had been removed from the material.
Figure 68: TGA and derivative weight profile of 'Ni$_6$Mo$_6$C' under 5%H$_2$/N$_2$ in the range from room temperature to 1000°C.

Figure 69: The mass spectrum ion curve for 2 m/z and the derivative weight profile.
Figure 70: The mass spectrum ion curve for 44 m/z and the derivative weight profile.

Attempting to prepare the Ni₃Mo₃C phase has proved to be difficult. The oxide is seen to decompose to Mo₂C and nickel metal at temperatures above 600°C when carburised with 20% CH₄/H₂ as seen in section 3.2.1.3. However, Ni₆Mo₆C has been easier to synthesise by using citric acid as the source of carbon. ‘Ni₆Mo₆C’ was active for ammonia synthesis at 700°C and was seen to undergo nitridation to form Ni₂Mo₃N and Mo₉Ni₀.₀₉ during the reaction. It is therefore proposed that this transformation of the carbide is required for the material to be active. However, further work needs to be performed to understand if the carbide or the nitrided material is the active phase for the ammonia synthesis activity. Testing the Ni₃Mo₃C phase for ammonia synthesis may provide an explanation and also the preference of the carbide to form Ni₂Mo₃N instead of Ni₃Mo₃N when it is nitrided.

### 3.2.3 Nickel Molybdenum Carbide (Ni₃Mo₃C)

#### 3.2.3.1 Preparation with Activated Charcoal

Regmi and Leonard have prepared Ni₃Mo₃C by mixing nickel molybdenum oxide with decolourising carbon and reacting the material at high temperature [48]. Therefore, this method was replicated in order to form Ni₃Mo₃C. Part of the work outlined in this section was undertaken in collaboration with Shane Mckenna, who was a final year project student that helped with the preparation of the material. To try and reduce the amount of carbon lost as methane during the preparation, hydrogen was removed from the gas mixture. Excess activated charcoal was mixed with the oxide precursor (Ni₃Mo₃Oₓ) and then, this was heated to 1000°C under argon. Contrary to the literature, Ni₃Mo₃C has not formed
under these conditions in the present study as shown by the XRD pattern in Figure 71. The material has instead decomposed to Mo$_2$C and Mo$_{0.09}$Ni$_{0.91}$, with small amounts of Ni$_6$Mo$_6$C present. Regmi and Leonard suggest that the Ni$_3$Mo$_3$C is formed at a temperature of 1030°C using this method [48]. From XRD patterns, the authors were able to show that Ni$_6$Mo$_6$C forms at a lower temperature of 975°C. During the transformation of the carbide from Ni$_6$Mo$_6$C to Ni$_3$Mo$_3$C, the material apparently decomposed into a mixture of MoNi$_4$ and a Mo-Ni phase with the W type structure at 990°C. The alloys then react with carbon to form Ni$_3$Mo$_3$C at 1030 °C. However, these phases are different to the ones reported here and therefore, it is concluded that this material has not followed this transformation pathway.

![XRD pattern of Ni$_3$Mo$_3$O$_x$ + C post-preparation at 1000°C under argon. Reflections marked: • Ni$_6$Mo$_6$C (JCPDS file number 03-065-4436), ▲ Mo$_2$C (JCPDS file number 00-001-1188) and ▼ Mo$_{0.09}$Ni$_{0.91}$ (JCPDS file number 01-071-9766).](image)

The elemental analysis showed that the starting oxide precursor had 23.74 wt. % carbon in the material after activated carbon had been added (C: 23.74 wt. %, H: 3.06 wt. %, N: 5.11 wt. %). A high percentage of nitrogen was also present, which could result from the starting nickel and molybdenum materials used in the Pechini method. The amount of carbon in the material was higher than the expected amount from using a stoichiometric
ratio of oxide precursor to carbon. However, this excess carbon can be accounted for, as it originates from the citric acid used in the preparation method. Both the carbon and nitrogen percentage decreased after treatment at 1000°C under Ar (C: 14.57 wt. %, H: 0.07 wt. %, N: 1.71 wt. %). The carbon percentage was greater than the expected stoichiometric percentage for Mo$_2$C (5.89 wt. %) and Ni$_6$Mo$_6$C (1.28 wt. %), which are phases present in the material according to the XRD pattern. Therefore, this suggests that there may be carbon laydown on the material. A peak is observed at approximately 26° 20, which is expected to relate to carbon and thus confirms the presence of deposited carbon.

As the Ni$_3$Mo$_3$C phase was not formed by this method, even with a large percentage of carbon remaining after the preparation, it suggests that hydrogen was required in the gas feed to form the targeted phase.

Raman analysis was conducted for this material to investigate if there was carbon laydown due to the activated carbon and if there was any surface oxide species. The Raman spectra taken at two different areas of the material exhibit different spectra, as observed in Figure 72. In the first area, the Raman spectrum shows the presence of carbon with the D band at 1338 cm$^{-1}$, the G band at 1570 cm$^{-1}$ and the 2D band observed at 2681 cm$^{-1}$. There are also bands present at approximately 2450 cm$^{-1}$ and 2950 cm$^{-1}$ attributed to D+D$''$ and D+G respectively [116]. The intensity of the G band is related to the number of layers of graphene present. As the number of layers of graphene increases, the intensity of the band increases, and therefore this can be used to determine the thickness of graphene. The 2D band can also be used to determine the graphene thickness from its intensity and shape. The unique shape differences of this band can give information on the number of layers of graphene. Furthermore, the intensity ratio of the 2D and G bands, I$_{2D}$/I$_G$, for graphene without defects is two. As the intensity of the 2D band in this sample is less than half of the G band this suggests that graphene is not present in the material and instead consists of graphite. Although, the symmetrical shape of the 2D band suggests that the material is composed of graphene, it must be noted that turbostratic graphite has a similar shaped band [117]. Turbostratic carbon has multiple graphene layers that are rotated and thus reduced orbital hybridisation.

Additional Raman bands associated with an oxide phase were detected at 934 and 887 cm$^{-1}$ and could be due to NiMoO$_4$. When the filter size was increased, the bands due to carbon significantly decreased and the bands due to the oxide became more prominent. This suggests that the laser had removed the graphite from the material.
In the second area examined, the bands due to carbon were not detected. Instead, bands due to $\beta$-NiMoO$_4$ were observed at 940, 884, 811 cm$^{-1}$. Bands due to $\alpha$-MoO$_3$ are also observed at 481, 287, 218, 192 and 148 cm$^{-1}$ [118].

The XRD pattern demonstrated that the material had decomposed to Mo$_2$C and Mo$_{0.09}$Ni$_{0.91}$ and only a small intensity was observed for Ni$_6$Mo$_6$C. However, the Raman spectra showed that there were bands due to $\beta$-NiMoO$_4$. These bands could be related to the nickel molybdenum alloy or the Ni$_6$Mo$_6$C phase. The large amount of carbon laydown observed from the Raman bands suggests that the carbon from the citric acid is relatively unreactive under the argon atmosphere. Therefore, hydrogen is required in the feed stream in order to carburise the material.

![Raman spectra of Mo$_2$C + Mo$_{0.09}$Ni$_{0.91}$ prepared at 1000°C under Ar. The spectra were taken at two different areas with a 25% filter.](image)

Figure 72: Raman spectra of Mo$_2$C + Mo$_{0.09}$Ni$_{0.91}$ prepared at 1000°C under Ar. The spectra were taken at two different areas with a 25% filter.

The SEM images displayed in Figure 73 show that the morphology of this material is similar to the morphology observed for the Mo$_2$C + Ni materials described in section 3.2.1.3.1 (Figure 29). The EDX results in Table 19 show that there was a large percentage of carbon present in this material, which agrees with the carbon laydown observed in the Raman spectrum. The stoichiometric percentage of nickel, molybdenum and nitrogen for Ni + Mo$_2$C (assuming a Ni:Mo ratio of 1:1) is 36.54 wt. %, 59.72 wt. % and 3.74 wt. %,
respectively. However, the stoichiometric ratio of Ni to Mo from the EDX analysis does not appear to be as expected. Instead, there appears to be more molybdenum present in the material.

Figure 73: SEM images of Ni$_3$Mo$_3$O$_x$ + C post-preparation at 1000°C under argon. a) 1000x magnification, b) 2000x magnification, c) 4000x magnification and d) 5000x magnification.

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Table 19: EDX values for Ni$_3$Mo$_3$O$_x$ + C post-preparation at 1000°C under argon.
3.2.3.1.1 Ammonia Synthesis at 700°C for Mo₂C and Mo₀.₀⁹Ni₀.₉₁

The conductivity profile of the material at 700°C is presented in Figure 74. The ammonia synthesis rate for the material at 700°C was 252 µmol h⁻¹ g⁻¹. This value is very similar to Ni₆Mo₀C. There was a lag period of 10 minutes at the start before the material became active. This may be due to the transition of the material to form the nitride as was observed for Ni₆Mo₀C. The activity of this material can be explained by the XRD pattern and elemental analysis.

![Conductivity profile for Mo₂C + Mo₀.₀⁹Ni₀.₉₁ reacted with 3:1 H₂/N₂ at 700°C for 8 hours.](image)

**Figure 74:** Conductivity profile for Mo₂C + Mo₀.₀⁹Ni₀.₉₁ reacted with 3:1 H₂/N₂ at 700°C for 8 hours.

The XRD pattern of the material in Figure 75 shows that Ni₂Mo₃N had indeed been formed during the reaction. This suggests that the Mo₂C and nickel phases combined at this temperature to form the nitride. Nickel metal and Mo₂C were also still present in the sample, however, the intensity of the reflections associated with them had decreased compared to pre-reaction.

A large percentage of the carbon has been removed from the material during the reaction as can be seen from the elemental analysis (C: 0.95 wt. %, H: 0.00 wt. %, N: 1.97 wt. %). This result confirms that the material underwent nitridation as observed by the XRD pattern. The remaining carbon was most likely due to the Mo₂C phase present in the material. The nitrogen content had increased a small amount compared to pre-reaction (1.71 wt. %). The expected stoichiometric percentage of nitrogen in Ni₂Mo₃N, taking into
account the presence of Ni and Mo₂C, is 2.05 wt. %. The obtained value of 1.97 wt. % for the material agrees quite well with this expected value.

The conversion of the material to form the nitride may explain the similar activities of the Ni₆Mo₆C and the mixed Mo₂C and Mo₀.₀₉Ni₀.₉₁. Therefore, the nitride may be responsible for the activity of these materials and not the carbide. As mentioned previously, the induction period may be due to the materials undergoing nitridation and once a sufficient amount of nitrogen is incorporated into the lattice, the material becomes active.

![XRD Pattern](image)

**Figure 75**: XRD pattern of Mo₂C + Mo₀.₀₉Ni₀.₉₁ post-reaction with 3:1 H₂/N₂ at 700°C for 8 hours. Reflections marked: □ Ni₂Mo₃N (JCPDS file number 01-072-6569), ▼ Mo₀.₀₉Ni₀.₉₁ (JCPDS file number 01-071-9766) and ▲ Mo₂C (JCPDS file number 00-001-1188).

The Raman spectrum is very similar to that for β-NiMoO₄, as seen in Figure 76, which most likely relates to a passivation layer on the surface of the sample. The Raman bands at 937, 888, 811, 345 and 284 cm⁻¹ can be accredited to β-NiMoO₄ [96] [97]. There were no bands observed for carbon in the areas that were investigated. This agrees with the elemental analysis that showed almost all the of the carbon had been removed from the material.
As the material changed phase during the reaction, SEM analysis was performed to see if this resulted in a change in the morphology. Representative SEM images for the material post-reaction are displayed in Figure 77. The morphology of this material was different to the Ni$_2$Mo$_3$N discussed in section 3.2.1.2 and the pre-reaction material. The material consists of fine needles and possesses porous surfaces. The difference in morphology from the pre-reaction material may be due to the formation of Ni$_2$Mo$_3$N. The stoichiometric percentage of nickel, molybdenum and nitrogen for Ni$_2$Mo$_3$N is 28.00 wt. %, 68.66 wt. % and 3.34 wt. % respectively. However, the EDX results in Table 20 show that the stoichiometric ratio of Ni to Mo from the EDX analysis is not the expected mass ratio as the amount of molybdenum is lower than expected. However, it must be noted that the EDX measurement is semi-quantitative and therefore, care must be taken when comparing results. Furthermore, a large percentage of carbon was detected in this material, which was difficult to determine due to the samples being placed on carbon stubs.
Figure 77: SEM images of Mo$_2$C + Mo$_{0.09}$Ni$_{0.91}$ post-reaction with 3:1 H$_2$/N$_2$ at 700°C for 8 hours. a) 1000x magnification, b) 2000x magnification, c) 4000x magnification and d) 6000x magnification.

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Table 20: EDX values for Mo$_2$C + Mo$_{0.09}$Ni$_{0.91}$ post-reaction with 3:1 H$_2$/N$_2$ at 700°C for 8 hours.

3.2.3.2 Preparation of Ni$_6$Mo$_6$C by Carburisation

The apparent difficulty in forming Ni$_3$Mo$_3$C is interesting considering the relative ease in forming Co$_3$Mo$_3$C. Co$_3$Mo$_3$C can be prepared from its nitride analogue at 700°C under 20% CH$_4$/H$_2$ [54]. Interestingly, Co$_6$Mo$_6$C can be prepared via reduction of the Co$_3$Mo$_3$C under Ar/H$_2$ at a higher temperature of 900°C for 5 hours. It has also proved possible to form Co$_3$Mo$_3$C from Co$_6$Mo$_6$C by reacting it with 75% CH$_4$/N$_2$ at 800°C for 8 hours [119].
However, the material contained impurities of $\beta$-Mo$_2$C and graphite. The authors noted that the carbon located in the 0 0 0 (8a) site moved to the 1/8 1/8 1/8 (16c) sites and thus formed the Co$_3$Mo$_3$C phase. It has also been shown that transitioning from low to high nitrogen content Co$_6$Mo$_6$N and Co$_3$Mo$_3$N was possible by using a N$_2$/H$_2$ gas mixture at 400°C and N$_2$ alone at 700°C [50] [120]. From this work, it appears that the Ni$_6$Mo$_6$C can be formed under Ar or Ar/H$_2$. The material is more phase pure when prepared with Ar/H$_2$, however, it must be noted that the temperature was lower under these conditions. The higher temperature of 1000°C used when applying Ar may have resulted in the decomposition of Ni$_6$Mo$_6$C to Mo$_2$C and Mo$_{0.09}$Ni$_{0.91}$. However, from the characterisation results, it appears that the carbon was not incorporated into the lattice but instead resulted in carbon laydown. Following on from these reports in the literature, attempts were made to prepare Ni$_3$Mo$_3$C from Ni$_6$Mo$_6$C. The Ni$_6$Mo$_6$C prepared with Ar/H$_2$ at 700°C was used as the precursor. ‘Ni$_6$Mo$_6$C’ was carburised in 20% CH$_4$/H$_2$ at 800°C for 6 hours to replicate the conditions used to form Co$_3$Mo$_3$C from Co$_6$Mo$_6$C.

The XRD pattern in Figure 78 shows that the Ni$_6$Mo$_6$C decomposed to give a mixture of molybdenum carbides and nickel metal. There was also graphitic carbon present in the material. Therefore, it appears that the carburisation temperature needs to be lowered to form the Ni$_3$Mo$_3$C phase. Elemental analysis of the material post carburisation shows that there was a large percentage of carbon present, which was most likely due to the graphitic carbon (C: 23.90 wt. %, H: 0.00 wt. %, N: 0.15 wt. %).
As the material decomposed at the high temperature, the carburisation temperature was lowered to 560°C. ‘Ni₆Mo₆C’ was carburised in 20% CH₄/H₂ for 6 hours. The XRD pattern of the material shows that Ni₃Mo₃C has been formed at this temperature along with impurities of Mo₂C and Ni₂Mo₃N. Ni₂Mo₃N was observed in the starting Ni₆Mo₆C precursor and the nitrogen most likely resulted from the Ni(NO₃)₂·6H₂O and (NH₄)₆Mo₇O₂₄·4H₂O used to prepare the oxide. However, the peaks associated with Ni₂Mo₃N appear to have shifted to lower 2θ values as seen in Figure 79, which suggests that the nitride has undergone carburisation to form Ni₂Mo₃CₓN_y.

The expected stoichiometric percentage of carbon in Ni₃Mo₃C is 2.52% and in Ni₆Mo₆C is 1.28%. The elemental analysis of the material post carburisation was as follows, C: 1.84 wt. %, H: 0.00 wt. % and N: 0.42 wt. %. The carbon percentage had increased compared to pre-reaction (1.18 wt. %). This could be due to both Ni₆Mo₆C undergoing carburisation to Ni₃Mo₃C and the nitride forming the carbonitride. The nitrogen percentage had decreased post-reaction, which suggests that some nitrogen had been lost in the formation of the carbonitride.
Figure 79: XRD pattern of ‘Ni$_3$Mo$_3$C’ prepared at 560°C under 20% CH$_4$/H$_2$. Reflections marked: ♦ Ni$_3$Mo$_3$C (JCPDS file number 01-089-4883), ▲ Mo$_2$C (JCPDS file number 00-001-1188), ▼ Mo$_{0.09}$Ni$_{0.91}$ (JCPDS file number 01-071-9766) and ■ Ni$_2$Mo$_3$N (JCPDS file number 01-072-6569).

The Raman spectra were taken at two areas of the material and display different spectra, as observed in Figure 80. In the first area, the Raman spectrum shows the presence of carbon with weak bands at 1557 cm$^{-1}$ and 2332 cm$^{-1}$ corresponding to the G band and the 2D band, respectively. As the intensities of the G band and 2D band were low, this suggests that there was not much carbon laydown on this material.

In the second area inspected, the bands due to carbon were more prominent with bands at 1350, 1577 and 2332 cm$^{-1}$ relating to the D band, G band and 2D band, respectively. Bands due to β-NiMoO$_4$ were also observed at 941, 891, 820 cm$^{-1}$. Bands due to α-MoO$_3$ were also detected at 486, 291, 222, 197 and 143 cm$^{-1}$ [118]. This result is consistent with the formation of a passivation layer on the material.

The XRD pattern showed that the material consisted of Ni$_3$Mo$_3$C, Ni$_2$Mo$_3$N, Mo$_2$C and Mo$_{0.09}$Ni$_{0.91}$. The Raman bands due to β-NiMoO$_4$ might result from the passivation layer on the Ni$_3$Mo$_3$C and Ni$_2$Mo$_3$N and the bands due to α-MoO$_3$ might result from the surface
oxygen layer on Mo2C. The carbon laydown observed from the Raman spectra contrasts somewhat with the elemental analysis that showed only 1.84 wt. % of carbon was present in the material.

**Figure 80:** Raman spectra of ‘Ni3Mo3C’ prepared at 560°C with 20% CH4/H2. The spectra were taken at two areas with a 50% filter.

SEM was used to investigate the effect the carburisation process had on the morphology of the material. Figure 81 exhibits representative SEM images for ‘Ni3Mo3C’. The material has a similar morphology to the ‘Ni6Mo6C’ precursor and suggests that the carburisation process was pseudomorphic. The sample was porous with pores ranging in diameter from approximately 1 – 10 µm.

The EDX analysis in Table 21 gives the element weight percentages for ‘Ni3Mo3C’. The stoichiometric percentage of nickel, molybdenum and carbon in Ni3Mo3C is 37.00 wt. %, 60.48 wt. % and 2.52 wt. %, respectively. From the table, it can be seen that the carbon weight percentage was higher than predicted and nitrogen was present in the material. Furthermore, the molybdenum percentage was lower. This result suggests that there was a large amount of carbon laydown on the material, although obtaining accurate carbon percentages was difficult due to the use of carbon stubs. In addition, EDX measurements
are limiting for light elements such as carbon and nitrogen. The Raman spectra showed only weak bands associated with carbon laydown. From the XRD pattern, it was shown that the material consisted of $\text{Ni}_2\text{Mo}_3\text{N}$ and this therefore, accounts for the presence of nitrogen observed by EDX. The EDX data shows that the mass ratio of Ni to Mo was not as predicted as the percentage of molybdenum was lower than expected. However, some areas contained a lot less molybdenum than others as observed in Table 21.

![SEM images of 'Ni$_3$Mo$_3$C' prepared at 560°C with 20% CH$_4$/H$_2$. a) 1000x magnification, b) 2000x magnification, c) 4000x magnification and d) 6000x magnification.](image)

The element map in Figure 82 shows that molybdenum was evenly distributed across the sample. However, there were areas that contained more nickel and carbon, suggesting that there was phase separation over the sample.
Figure 82: Element Map for ‘Ni₃Mo₃C’. Elements: Ni (red), Mo (green) and C (blue).

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Table 21: EDX values for ‘Ni₃Mo₃C’ prepared at 560°C with 20% CH₄/H₂.

3.2.3.2.1 Ammonia Synthesis at 500°C for Ni₃Mo₃C

‘Ni₃Mo₃C’ was tested for ammonia synthesis at 500°C under a 3:1 H₂/N₂ atmosphere. The activity testing of ‘Ni₃Mo₃C’ may give an understanding on the role structure and composition play in ammonia synthesis activity. Furthermore, if Ni₃Mo₃C undergoes nitridation during the reaction, as observed in the case of Co₃Mo₃C, it might prove possible to form Ni₃Mo₃N. The steady state ammonia synthesis rate of ‘Ni₃Mo₃C’ at 500°C was calculated to be 41 μmol h⁻¹ g⁻¹. The ammonia synthesis rate of Ni₂Mo₃CₓNₙ at 500°C was 619 ± 14 μmol h⁻¹ g⁻¹ and for Co₃Mo₃C was 461 ± 17 μmol h⁻¹ g⁻¹ [54]. Therefore, ‘Ni₃Mo₃C’ had a much lower activity. The conductivity of the sulfuric acid solution through which the reactor effluent was flowed appeared to decrease at a greater rate for the first 60 minutes before it reached steady state, as observed in Figure 83. This is the opposite of the behaviour observed for Ni₂Mo₃CₓNₙ and Co₃Mo₃C, which initially had an induction period before the materials became active.
Figure 83: Conductivity profile for Ni$_3$Mo$_3$C + Ni$_2$Mo$_3$C$_x$N$_y$ reacted with 3:1 H$_2$/N$_2$ at 500°C for 8 hours. The steady state activity of the material after the initial 60 minutes is shown in Figure 84.

Figure 84: Conductivity profile for Ni$_3$Mo$_3$C + Ni$_2$Mo$_3$C$_x$N$_y$ reacted with 3:1 H$_2$/N$_2$ at 500°C for 8 hours, highlighting the linear part of the graph used for calculating the rate.
The XRD pattern of the material post-reaction shows that the Ni$_3$Mo$_3$C phase had apparently been maintained during the reaction, as shown in Figure 85.

Figure 85: XRD pattern of Ni$_3$Mo$_3$C + Ni$_2$Mo$_3$C$_x$N$_y$ post-reaction with 3:1 H$_2$/N$_2$ at 500°C for 8 hours. Reflections marked: ◦ Ni$_3$Mo$_3$C (JCPDS file number 01-089-4883), ▲ Mo$_2$C (JCPDS file number 00-001-1188), ● Ni$_6$Mo$_6$C (JCPDS file number 03-065-4436), □ Ni$_2$Mo$_3$N (JCPDS file number 01-072-6569) and ▼ Mo$_{0.09}$Ni$_{0.91}$ (JCPDS file number 01-071-9766).

However, as can be seen in Figure 86, the positions of the peaks due to Ni$_2$Mo$_3$C$_x$N$_y$ have shifted to higher 2θ values compared to pre-reaction and therefore, the material had undergone a degree of nitridation during the reaction. The peak positions for Ni$_3$Mo$_3$C have not shifted position suggesting that this phase had not been nitrided. However, peaks due to Ni$_6$Mo$_6$C are observed in the XRD pattern, which were not present in the pre-reaction material. This suggests that Ni$_3$Mo$_3$C lost carbon to form the Ni$_6$Mo$_6$C phase. Co$_3$Mo$_3$C was shown to undergo nitridation during the ammonia synthesis reaction and the peak positions were shifted to higher 2θ values [54]. This suggests that Ni$_3$Mo$_3$C is more stable than the cobalt molybdenum material and is less susceptible to nitridation. As can be seen in Figure 86, the intensity of the peaks due to Ni$_2$Mo$_3$C$_x$N$_y$ have increased compared...
to pre-reaction. However, Ni₆Mo₆C has similar peak positions and therefore, this phase is contributing to the intensity.

It is unclear whether Ni₃Mo₃C or the Ni₂Mo₃N impurity is the active component for ammonia synthesis. Therefore, it would be beneficial to produce a pure phase Ni₃Mo₃C and test this material.

The elemental analysis of the material post-reaction at 500°C was C: 1.43 wt. %, H: 0.00 wt. % and N: 0.50 wt. %. The pre-reaction material contained 1.84 wt. % carbon and therefore this suggests that some carbon had been lost during the reaction as would be expected for the transformation of Ni₃Mo₃C to Ni₆Mo₆C. The nitrogen percentage had increased slightly compared to pre-reaction (0.42 wt. %). These results could be due to Ni₃Mo₃C or the Ni₂Mo₃CₓNᵧ phase undergoing nitridation during the reaction.

![Graph](image_url)

**Figure 86:** Comparison of XRD patterns for Ni₃Mo₃C + Ni₂Mo₃CₓNᵧ pre- (black) and post-reaction (red) with 3:1 H₂/N₂ at 500°C for 8 hours, highlighting the peaks due to Ni₃Mo₃C, Ni₆Mo₆C or Ni₂Mo₃N.

The Raman spectrum showed that there was carbon laydown on the material with bands for carbon observed at 1559 and 2332 cm⁻¹, corresponding to the G band and the 2D band, respectively, as shown in Figure 87. The intensities of these bands were low and therefore,
there was not much carbon on the surface of the material. A wide band was observed between 500 – 1000 cm$^{-1}$.

![Raman spectrum](image)

**Figure 87:** Raman spectrum of Ni$_3$Mo$_3$C + Ni$_2$Mo$_3$C$_x$N$_y$ post-reaction with 3:1 H$_2$/N$_2$ at 500°C for 8 hours.

Typical SEM images of mixed phase ‘Ni$_3$Mo$_3$C’ post 500°C reaction are displayed in Figure 88. It can be seen that the material consists of a porous structure and that the morphology had been retained from the pre-reaction material. The weight percentages obtained from EDX for ‘Ni$_3$Mo$_3$C’ are provided in Table 22. The stoichiometric percentage of nickel, molybdenum and carbon for Ni$_3$Mo$_3$C is 37.00 wt. %, 60.48 wt. % and 2.52 wt. %, respectively. The carbon weight percentage was greater than the stoichiometric value expected but the measurement of light elements by EDX can be restrictive. The molybdenum and nickel percentages were lower than the expected stoichiometric values and from these values the mass ratio of nickel and molybdenum can be observed to not be as predicted. However, EDX is semi-quantitative and therefore, these values may not be representative. The nickel and carbon percentages had decreased compared to the pre-reaction material and the molybdenum and nitrogen values had increased. This may suggest that the material was transforming from Ni$_3$Mo$_3$C to Ni$_2$Mo$_3$N and Ni.
Figure 88: SEM images of $\text{Ni}_3\text{Mo}_3\text{C} + \text{Ni}_2\text{Mo}_3\text{C}_x\text{N}_y$ post-reaction with 3:1 $\text{H}_2/\text{N}_2$ at 500°C for 8 hours. a) 1000x magnification, b) 2000x magnification, c) 4000x magnification and d) 6000x magnification.

The element maps in Figure 89 demonstrate that the nickel was more evenly distributed compared to the pre-reaction sample.

Figure 89: Element Maps for $\text{Ni}_3\text{Mo}_3\text{C} + \text{Ni}_2\text{Mo}_3\text{C}_x\text{N}_y$ post-reaction with 3:1 $\text{H}_2/\text{N}_2$ at 500°C for 8 hours. Elements: Ni (red) and Mo (green).
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Table 22: EDX values for Ni₃Mo₃C + Ni₂Mo₃CₓNᵧ post-reaction with 3:1 H₂/N₂ at 500°C for 8 hours.

### 3.2.3.2.2 Ammonia Synthesis at 700°C for Ni₃Mo₃C

As the Ni₃Mo₃C did not undergo nitridation to form a carbonitride phase at 500°C, the reaction temperature was increased to 700°C. The ammonia synthesis rate for the material at 700°C was calculated to be 80 µmol h⁻¹ g⁻¹ when at steady state. This is possibly lower than the rate obtained for Ni₆Mo₆C at 700°C (152 ± 89 µmol h⁻¹ g⁻¹). There is a small induction period of 10 minutes at the start of the reaction before the material became active. This may be due to the transformation of the material from the carbide to the nitride as observed for the Ni₆Mo₆C phase. The conductivity decreased at a faster rate for the first 180 minutes before it became steady state, as observed in Figure 90. This behaviour was similar when the material was tested at 500°C. The steady state activity of the material after the initial 180 minutes is shown in Figure 91.
Figure 90: Conductivity profile for Ni$_3$Mo$_3$C + Ni$_2$Mo$_3$C$_x$N$_y$ reacted with 3:1 H$_2$/N$_2$ at 700$^\circ$C for 9 hours.

Figure 91: Conductivity profile for Ni$_3$Mo$_3$C + Ni$_2$Mo$_3$C$_x$N$_y$ reacted with 3:1 H$_2$/N$_2$ at 700$^\circ$C for 9 hours. Highlighting the linear part of the graph used for calculating the rate.

The XRD of the material post-reaction shows that Ni$_3$Mo$_3$C has undergone nitridation to form Ni$_2$Mo$_3$N and nickel metal, as shown in Figure 92. Ni$_6$Mo$_6$C was also present in the material, which suggests that Ni$_3$Mo$_3$C is reduced and loses carbon to form Ni$_6$Mo$_6$C. This suggests that the Ni$_3$Mo$_3$C does not form a carbonitride of composition Ni$_3$Mo$_3$C$_x$N$_y$ and
therefore, Ni$_3$Mo$_3$N cannot be easily formed from the corresponding carbide. The XRD pattern appears to show that the Ni$_3$Mo$_3$C phase may first lose half of the lattice carbon to form Ni$_6$Mo$_6$C and then this is nitrided to form Ni$_2$Mo$_3$N.

Elemental analysis shows that the sample had been nitrided during the reaction with a large percentage of the carbon having been removed (C: 0.28 wt. %, H: 0.03 wt. %, N: 2.00 wt. %). The percentage of nitrogen was lower than the expected stoichiometric value (3.34 wt. %). However, the contribution due to Ni$_6$Mo$_6$C must be taken into consideration.

Figure 92: XRD pattern of Ni$_3$Mo$_3$C + Ni$_2$Mo$_3$C$_x$N$_y$ post-reaction with 3:1 H$_2$/N$_2$ at 700°C for 9 hours. Reflections marked: Ni$_6$Mo$_6$C (JCPDS file number 03-065-4436), Ni$_2$Mo$_3$N (JCPDS file number 01-072-6569) and Mo$_{0.09}$Ni$_{0.91}$ (JCPDS file number 01-071-9766).

The Raman spectra in Figure 93 were taken from two areas of the material and show different spectral bands. Both areas show G and 2D bands relating to carbon suggesting that the material has carbon laydown even after reaction at 700°C. In one of the areas, bands due to an oxide surface layer were observed. The Raman bands at 944, 897 and 820 cm$^{-1}$ are due to $\beta$-NiMoO$_4$ and are assigned to asymmetric and symmetric Mo-O vibration of Mo in a tetrahedral environment [96] [97] or for the band at 820 cm$^{-1}$ to the asymmetric stretching mode of the Ni-O-Mo bond [96]. The band at 820 cm$^{-1}$ is also observed in the Raman spectra for MoO$_3$ [90]. A weak band due to $\alpha$-MoO$_3$ was also detected at 995 cm$^{-1}$.
Bands due to $\alpha$-MoO$_3$ were observed in the pre-reaction material and were likely due to a surface oxide layer. The elemental analysis showed that only 0.28 wt. % of carbon was present in the material and therefore, this contrasts with the carbon laydown observed from the Raman bands.

Figure 93: Raman spectra of Ni$_3$Mo$_3$C + Ni$_2$Mo$_3$C$_x$N$_y$ post-reaction with 3:1 H$_2$/N$_2$ at 700°C for 9 hours. The spectra were taken at two areas with a 50% filter.

SEM analysis was performed in order to examine any changes in the morphology and structure of ‘Ni$_3$Mo$_3$C’ during the ammonia synthesis reaction. Representative SEM images of the post-reaction material are displayed in Figure 94. The material had a porous structure and the morphology was similar to the pre-reaction material. Therefore, although the sample underwent nitridation, the morphology did not change. The EDX analysis for the material post 700°C reaction is shown in Table 23. The stoichiometric percentage of nickel, molybdenum and nitrogen for Ni$_2$Mo$_3$N is 28.00 wt. %, 68.66 wt. % and 3.34 wt. % respectively. The EDX weight percentage for nitrogen was greater than the stoichiometric nitrogen predicted for Ni$_2$Mo$_3$N. The amount of nitrogen was higher than the pre-reaction material and was detected in every area inspected. This suggests that the material had transformed to the nitride. The percentage of molybdenum was higher compared to the
pre-reaction material and nickel value was lower suggesting that the material was transforming from Ni₃Mo₃C to Ni₂Mo₃N and nickel metal.

Figure 94: SEM images of Ni₃Mo₃C + Ni₂Mo₃CₙNₙ post-reaction with 3:1 H₂/N₂ at 700°C for 9 hours. a) 1000x magnification, b) 2000x magnification, c) 4000x magnification and d) 6000x magnification.

The nickel and molybdenum were evenly distributed across the sample as evidenced from the element maps in Figure 95.

Figure 95: Element Maps for Ni₃Mo₃C + Ni₂Mo₃CₙNₙ post-reaction with 3:1 H₂/N₂ at 700°C for 9 hours. Elements: Ni (red), Mo (green) and N (blue).
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Table 23: EDX values for Ni$_3$Mo$_3$C + Ni$_2$Mo$_3$C, N$_x$ post-reaction with 3:1 H$_2$/N$_2$ at 700°C for 9 hours.

The formation of the nitride and reduction of the material to Ni$_6$Mo$_6$C was investigated by thermogravimetric analysis of ‘Ni$_3$Mo$_3$C’ under 5% H$_2$/N$_2$. The TGA curve and first derivative weight change of ‘Ni$_3$Mo$_3$C’ is provided in Figure 96. The material was heated from room temperature to 1000°C at a ramp rate of 10°C/min. The material only lost 0.43% of its weight from room temperature to 600°C. This can possibly explain why Ni$_3$Mo$_3$C did not show nitridation when tested at 500°C, although the TGA procedure was not performed under the same ratio of N$_2$:H$_2$.

A major weight loss is observed from 600°C and corresponds to a loss of 5.65%. There appears to be two weight losses from 600°C to 1000°C, a main peak at 860°C and a shoulder peak at 790°C. The formation of Ni$_6$Mo$_6$C from Ni$_3$Mo$_3$C would result in a weight loss of 1.26%. Therefore, this does not account for the 5.65% decrease observed. However, between 600°C and 700°C, there is a weight loss of 0.74%. From the XRD pattern of the material post 700°C reaction, it was observed that Ni$_3$Mo$_3$C had been reduced to Ni$_6$Mo$_6$C and Ni$_2$Mo$_3$N had been formed.

$$3\text{Ni}_3\text{Mo}_3\text{C} + \frac{1}{2} \text{N}_2 \rightarrow \text{Ni}_6\text{Mo}_6\text{C} + \text{Ni}_2\text{Mo}_3\text{N} + \text{Ni} + 2\text{C}$$

Equation 4: Equation for the formation of Ni$_6$Mo$_6$C and Ni$_2$Mo$_3$N from Ni$_3$Mo$_3$C

The formation of Ni$_2$Mo$_3$N and Ni from Ni$_3$Mo$_3$C would result in a weight gain of 0.42%. Taking this into consideration, the transformation of Ni$_3$Mo$_3$C into Ni$_6$Mo$_6$C, Ni$_2$Mo$_3$N and Ni would result in a 0.84% total loss in mass. Ni$_2$Mo$_3$N was shown in section 3.2.1.2.1 to maintain its structure when reduced with 25% Ar/H$_2$ at 900°C. Therefore, this would suggest that the weight loss observed above 700°C is not due to Ni$_2$Mo$_3$N decomposing. If Ni$_2$Mo$_3$N decomposed to molybdenum and nickel metal, the weight loss for the material would be 3.34%. The mass spectrum for 28 m/z showed an increased ion current during this temperature range as seen in Figure 97. Therefore, this suggests that the material is losing nitrogen and may be decomposing. The mass spectra of 2, 15, 16, 17, 18, 30, 32, 44 and 46 m/z were followed but they did not show any features.
Figure 96: TGA and derivative weight profile of ‘Ni$_3$Mo$_3$C’ under 5%H$_2$/N$_2$ in the range from room temperature to 1000°C.

Figure 97: The mass spectrum ion curve for 28 m/z and the derivative weight profile.

The results in this thesis suggest that there may be a possible limitation to the idea that combining metals based on their N$_2$ binding energy will give a highly active ammonia synthesis catalyst. ‘Ni$_6$Mo$_6$C’ was not active at 400°C and ‘Ni$_3$Mo$_3$C’ was not active at 500°C. The materials became active when the temperature was increased to 700°C and this
activity may be associated with the substitution of lattice carbon with nitrogen. This behaviour is similar to Co$_2$Mo$_3$C and suggests that lattice nitrogen is required for these materials to be active. Although, conversely, lattice nitrogen may be present in these materials as a direct result of them being active. It has proved difficult to form phase-pure Ni$_2$Mo$_3$C with a carbonitride phase being formed instead. Ni$_2$Mo$_3$C$_x$N$_y$ was active at 400°C for ammonia synthesis and may suggest that lattice nitrogen is required for the materials to be active at lower temperatures. NiCoMo$_3$N has been tested for ammonia synthesis activity and lattice nitrogen reactivity and was found to behave similar to Ni$_2$Mo$_3$N [92]. Cobalt was introduced into Ni$_2$Mo$_3$N to give it a closer electronic structure to Co$_3$Mo$_3$N and this result would therefore suggest that the structure may be more important than electronic considerations.

### 3.2.4 Nickel Gallium Molybdenum Nitride (Ni$_2$GaMo$_3$N)

A nickel and molybdenum containing nitride that has an η-carbide structure has been prepared to give a further understanding on the relationship between structure and ammonia synthesis activity. Prior and Battle [121] have previously published work on Ni$_2$GaMo$_3$N and have shown that the nickel and gallium are completely ordered with nickel residing in the 32e sites and gallium in the 16d sites. The authors suggest that this ordering may be due to the sizes of these metal atoms, electronic factors or a result that is outwith the first coordination shell as the mean bond lengths of the 32e and 16d sites were similar. Ordering of such mixed metal atoms in η-carbide structured compounds is uncommon, with one other example being Al$_2$NiTi$_3$N [122]. The structure of Ni$_2$GaMo$_3$N is presented in Figure 98.

![Figure 98: The crystal structure of Ni$_2$GaMo$_3$N, showing the Mo$_6$N octahedra. Data plotted on VESTA from Ni$_2$GaMo$_3$N structure from Springer Materials [123].](image)
It is of interest that both \( \eta \)-carbide \( \text{Ni}_2\text{GaMo}_3\text{N} \) and \( \text{Ni}_2\text{GeMo}_3\text{N} \) [124] can be synthesised but \( \text{Ni}_3\text{Mo}_3\text{N} \) has proved much harder to form. As with \( \text{Ni}_2\text{GaMo}_3\text{N} \), the nickel atoms in \( \text{Ni}_2\text{GeMo}_3\text{N} \), reside in the 32e sites and the germanium or gallium atoms are located in the 16d sites, suggesting that the nickel atoms, which are larger than gallium and germanium atoms, are not favoured in the smaller 16d sites. Therefore, it could be proposed that \( \text{Ni}_3\text{Mo}_3\text{N} \) cannot be synthesised, as the nickel atoms are too large to fit in these sites. The empirical atomic radii of nickel, gallium and germanium are 135 pm, 130 pm and 125 pm respectively [125]. However, there is a deviation from these values depending on the method used to measure the radius. The empirical method calculates the radii by assuming that the atomic distance of two atoms forming a bond in a crystal is the sum of their radii. It must be noted, however, that Co has been stated to have the same empirical atomic radius (135 pm) as nickel [125] and can form \( \text{Co}_3\text{Mo}_3\text{N} \).

### 3.2.4.1 Nickel Gallium Molybdenum Oxide (\( \text{Ni}_2\text{GaMo}_3\text{O}_x \))

\( \text{Ni}_2\text{GaMo}_3\text{N} \) was prepared by ammonolysis of a nickel gallium molybdenum oxide. The oxide was synthesised by using a similar modified Pechini method as was used to prepare \( \text{Ni}_2\text{Mo}_3\text{N} \) [36]. From TPO analysis of the uncalcined starting material, it was found that a higher calcination temperature was needed than for \( \text{Ni}_2\text{Mo}_3\text{N} \). As can be seen from Figure 99, carbon was removed from the material at 610°C, resulting in a weight loss of 10.40%. This value agrees with the 6 – 8% of carbon observed from the elemental analysis for the oxide that was calcined at 500°C. When the material was calcined at 500°C, there were two major weight losses at 560°C and 725°C as seen in Figure 100. The weight loss at 560°C was proposed to be due to carbon. All the carbon and water observed below 500°C had been removed from the calcined sample. The weight loss at 560°C was 5.96%, which corresponds to the expected percentage of carbon from elemental analysis. A weight loss of 17.88% was observed at 725°C. The results from the TPO suggest that the material should be calcined at a temperature of 650°C.
Figure 99: TGA curve and derivative weight profile for uncalcined Ni$_2$GaMo$_3$ under air in the range from room temperature to 900°C.

From the XRD pattern of the oxide as seen in Figure 101, it can be observed that the material consists of $\alpha$-NiMo$_4$ and MoO$_3$. Gallium oxide phases are also observed in the XRD pattern. Other peaks are observed in the XRD pattern and may relate to a mixed metal gallium phase but
these could not be identified with any files on the database (marked as red peaks). The XRD pattern is similar to the pattern obtained for Ni$_2$Mo$_3$O$_x$ that was prepared by the same sol-gel route. The mixture of oxides is desired due to the difference in the elemental ratios between the oxide and the nitride.

The elemental analysis showed that there was a trace amount of carbon present in the material after calcination and no nitrogen (C: 0.10 wt. %, H: 0.00 wt. % and N: 0.00 wt. %), suggesting that the higher calcination temperature was mostly sufficient to remove the nitrates and citric acid from the material.

![Figure 101: XRD pattern of nickel gallium molybdenum oxide calcined at 650°C (Ni$_2$GaMo$_3$O$_x$). Reflections marked: ▼ NiMoO$_4$ (JCPDS file number 00-033-0948), X MoO$_3$ (JCPDS file number 00-035-0609), □ α-Ga$_2$O$_3$ (JCPDS file number 01-074-1610) and □ Ga$_{2.667}$O$_4$ (JCPDS file number 01-074-7709).](image)

The Raman spectrum of the oxide was analysed by comparing Figure 102 with the published spectra of NiMoO$_4$ and MoO$_3$. The Raman bands at positions of 960, 911 and 700, 381, 366 and 265 cm$^{-1}$ were attributed to α-NiMoO$_4$ [89]. The bands at 960 and 911 cm$^{-1}$ have been assigned in the literature as the symmetric and asymmetric stretching modes of the terminal Mo=O bond [90] and the band at 700 cm$^{-1}$ was assigned to the Ni-O-
Mo symmetric stretch [67] [89]. The weak bands at 381 and 366 cm\(^{-1}\) are due to the bending mode of Mo–O [89] and the band at 265 cm\(^{-1}\) is attributed to the deformation mode of Mo–O–Mo [89]. Interestingly, there are no bands at approximately 994, 665 or 338 cm\(^{-1}\) that would be associated with MoO\(_3\) [90]. Although, the band at 821 cm\(^{-1}\) could be attributed to the Mo-O-Mo asymmetric stretching mode of MoO\(_3\) [90]. The presence of bands associated with NiMoO\(_4\) agrees with the XRD result, which showed that the material contained this oxide.

Figure 102: Raman spectrum of nickel gallium molybdenum oxide (Ni\(_2\)GaMo\(_3\)O\(_x\)).

Figure 103 gives the representative SEM images for the oxide. The sample consisted of porous particles with an uneven surface and also thin small needles. The stoichiometric percentage of nickel, gallium, molybdenum and oxygen in the theoretical Ni\(_2\)GaMo\(_3\)O\(_{11}\) is 18.03 wt. %, 10.71 wt. %, 44.22 wt. % and 27.04 wt. %, respectively. From the EDX analysis in Table 24, it can be seen that the oxygen weight percentage was higher than predicted and the molybdenum percentage was lower. Therefore, the ratio of nickel, gallium and molybdenum was not 2:1:3 as expected. However, the XRD pattern shows that the material consisted of a separate molybdenum oxide phase and from the EDX data it can be seen that some areas contained more molybdenum than others.
Figure 103: SEM images of nickel gallium molybdenum oxide (Ni$_2$GaMo$_3$O$_x$). a) 1000x magnification, b) 2000x magnification, c) 4000x magnification and d) 6000x magnification.

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Table 24: EDX values for nickel gallium molybdenum oxide (Ni$_2$GaMo$_3$O$_x$).

3.2.4.2 Nickel Gallium Molybdenum Nitride (Ni$_2$GaMo$_3$N)

The η-carbide structured Ni$_2$GaMo$_3$N is a known phase that has previously been prepared by the reaction of MoO$_3$, hydrated gallium nitrate and nickel oxide under 10% H$_2$/N$_2$ with a heating regime up to 975°C [121]. In order to prepare the nitride at a lower temperature,
in this work the oxide was treated with ammonia gas at 785°C via a temperature programmed regime. Pure phase η-carbide materials have previously been formed by the ammonolysis of their oxides [54] [35].

As can be seen in Figure 104, the desired quaternary nitride phase was formed. Ni$_2$GaMo$_3$N is not listed on the database; however, a CIF file from Springer materials [123] was plotted on VESTA to give the expected XRD reflections for the nitride. Impurities of GaNi and Mo$_3$N$_2$ were observed, suggesting that the material had not been completely nitrided. Prior and Battle observed a filled β-Mn structured impurity when they formed the nitride [121].

The elemental analysis shows that there was trace amounts of carbon and no hydrogen present in the material after ammonolysis (C: 0.14%, H: 0.00% and N: 3.73%). The percentage of nitrogen present in the material was higher than the expected stoichiometric value of 2.86 wt. %. This may be due to NH$_x$ species on the surface of the nitride after ammonolysis, which is a common occurrence.

![XRD pattern of nickel gallium molybdenum nitride (Ni$_2$GaMo$_3$N). Reflections marked: ■ Ni$_2$GaMo$_3$N (CIF file from Springer Materials [123]), □ GaNi (JCPDS file number 01-071-8617) and ▼ Mo$_3$N$_2$ (JCPDS file number 03-065-4278).](image-url)
Raman analysis was conducted for this material to investigate if there was any surface oxide species present. The Raman spectrum is presented in Figure 105 and shows that the material had formed a surface oxide layer. The positions of the Raman bands at 934, 886 and 812 cm\(^{-1}\) are observed in \(\beta\)-NiMoO\(_4\) [96] [97] and CoMoO\(_4\) [126]. These Raman bands are assigned to the Mo-O stretching vibrations or for the band at 820 cm\(^{-1}\) the asymmetric stretching mode of the Ni-O-Mo bond. To the author’s knowledge, there is no published Raman spectrum of Ni\(_2\)GaMo\(_3\)N in the literature.

Figure 105: Raman spectrum of nickel gallium molybdenum nitride (Ni\(_2\)GaMo\(_3\)N).

As the morphology of a material can affect the ammonia synthesis activity, this was investigated by SEM analysis. The SEM images of the quaternary nitride are provided in Figure 106. The morphology of the material is similar to the pre-reaction material. However, there are more of the thin, small needles in the post-reaction material. The formation of needles has been observed for \(\eta\)-carbide structured Co\(_3\)Mo\(_3\)N that was prepared by ammonolysis [54]. The stoichiometric percentage of nickel, gallium, molybdenum and nitrogen in Ni\(_2\)GaMo\(_3\)N is 24.01 wt. %, 14.26 wt. %, 58.87 wt. % and 2.86 wt. %, respectively. The EDX data in Table 25 shows that the molybdenum percentage was slightly lower than expected and therefore, the ratio of the metals was not 2:1:3. Some areas contained more molybdenum and were observed as flat platelets as seen in Figure 106 (a) and may correspond to the Mo\(_3\)N\(_2\) impurity. The nitrogen percentage was
higher than the expected stoichiometric amount and the 3.73 wt. % value obtained from CHN analysis. However, light elements are difficult to measure by EDX.

Figure 106: SEM images of nickel gallium molybdenum nitride (Ni$_2$GaMo$_3$N). a) 1000x magnification, b) 2000x magnification, c) 4000x magnification and d) 6000x magnification.
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Table 25: EDX values for nickel gallium molybdenum nitride (Ni$_2$GaMo$_3$N).

3.2.4.2.1 Ammonia Synthesis for Ni$_2$GaMo$_3$N

In order to establish the relationship between structure and ammonia synthesis activity for ternary nitrides, Ni$_2$GaMo$_3$N was tested for its activity. The material was first pre-treated at 700°C for 2 hours under 3:1 H$_2$/N$_2$. Then, the material was tested under the same gas mixture at 400°C and 500°C. Figure 107 presents the plot of conductivity versus time for Ni$_2$GaMo$_3$N at the three temperatures tested. The rate of ammonia production at 700°C was $96 \pm 12$ µmol h$^{-1}$ g$^{-1}$ and at 500°C was $7$ µmol h$^{-1}$ g$^{-1}$. At 400°C, the activity was not steady state and therefore, a rate could not be calculated. The value was comparable to the rate for ‘Ni$_3$Mo$_3$C’ at 700°C ($80$ µmol h$^{-1}$ g$^{-1}$) and lower than for ‘Ni$_6$Mo$_6$C’ ($152 \pm 89$ µmol h$^{-1}$ g$^{-1}$). However, the rate calculated for 500°C reaction temperature, was lower than for ‘Ni$_3$Mo$_3$C’ ($41$ µmol h$^{-1}$ g$^{-1}$) and Ni$_2$Mo$_3$C$_x$N$_y$ ($619 \pm 14$ µmol h$^{-1}$ g$^{-1}$). These differences in activity suggest that the composition and structure have an effect, although morphology and surface area can also affect the rate. Although, Ni$_3$Mo$_3$C and Ni$_2$GaMo$_3$N both have a η-carbide structure and have a similar rate at 700°C, the carbide transforms to the filled β-Mn structured Ni$_2$Mo$_3$N during the reaction.
Figure 107: Conductivity profile for Ni$_2$GaMo$_3$N reacted with 3:1 H$_2$/N$_2$ at 700°C for 2 hours, 400°C for 3 hours and 500°C for 4 hours.

The XRD pattern in Figure 108 shows that the Ni$_2$GaMo$_3$N η-carbide structure was maintained after the reaction. The impurities of GaNi and Mo$_3$N$_2$ were also present in the material post-reaction.

The elemental analysis shows that the percentage of nitrogen present in the material after reaction with 3:1 H$_2$/N$_2$ had decreased (C: 0.12 wt. %, H: 0.00 wt. % and N: 2.77 wt. %) compared to pre-reaction (3.73 wt. %). The percentage of nitrogen present in the material agreed well with the expected stoichiometric value of 2.86 wt. % and may correspond to the loss of NH$_x$ species form the surface. The Mo$_3$N$_2$ impurity had shifted to higher 2θ values as seen for the peak at 37.37° 20 and suggests that it is losing nitrogen as the lattice parameter is getting smaller. Therefore, the decrease in nitrogen may also be due to the reduction of the Mo$_3$N$_2$. 

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Figure 108: XRD pattern of Ni$_2$GaMo$_3$N post-reaction with 3:1 H$_2$/N$_2$. Reflections marked: ■ Ni$_2$GaMo$_3$N (CIF file from Springer Materials [123]), □ GaNi (JCPDS file number 01-071-8617) and ▼ Mo$_3$N$_2$ (JCPDS file number 03-065-4278).

SEM analysis was performed on the material to observe any possible changes in morphology or structure during the reaction. Representative SEM images are provided in Figure 109. The material appears to have retained the morphology of the pre-reaction material and consists of porous surfaces, platelets and small needles. The platelets range in size and can be as large as 40 µm x 60 µm as observed in Figure 109 (b). The EDX data showed that these platelets consisted of a large percentage of molybdenum as seen in Table 26. The stoichiometric percentage of nickel, gallium, molybdenum and nitrogen in Ni$_2$GaMo$_3$N is 24.01 wt. %, 14.26 wt. %, 58.87 wt. % and 2.86 wt. %, respectively. As with the pre-reaction material, the molybdenum percentage was lower than expected and therefore, the ratio of metals was not as predicted. The EDX values of the pre- and post-reaction material were very similar suggesting that the phase does not change during the reaction.
Figure 109: SEM images of Ni$_2$GaMo$_3$N post-reaction with 3:1 H$_2$/N$_2$. a) 1000x magnification, b) 2000x magnification, c) 4000x magnification and d) 6000x magnification.

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Table 26: EDX values for Ni$_2$GaMo$_3$N post-reaction with 3:1 H$_2$/N$_2$. 
3.2.4.2.2 Lattice Nitrogen Reactivity of Ni$_2$GaMo$_3$N at 700°C

In order to determine the reactivity of lattice nitrogen in Ni$_2$GaMo$_3$N, the material has been reacted under 3:1 H$_2$/Ar at 700°C. If the lattice nitrogen is reactive and the material operates via a Mars-van Krevelen mechanism, there would most likely be a reduction in the nitrogen percentage and occupancy of Ni$_2$GaMo$_3$N under these conditions. Figure 110 shows that the lattice nitrogen was only slightly reactive under Ar/H$_2$ at 700°C with only a small amount of ammonia being produced. There was a decrease in conductivity of 34 µS/cm over the 7 hours. This result is similar to Ni$_2$Mo$_3$N that has previously been tested under Ar/H$_2$ at 700°C [98] and was found that the lattice nitrogen was fairly unreactive. Ni$_2$Mo$_3$N has the filled β-Mn structure, suggesting that structure does not play a role in lattice nitrogen reactivity. Instead it appears that composition is more important. This result suggests that Ni$_2$GaMo$_3$N may not operate via a Mars-van Krevelen mechanism and could explain its low ammonia synthesis activity.

![Figure 110: Conductivity profile for Ni$_2$GaMo$_3$N reacted with 3:1 H$_2$/Ar at 700°C for 7 hours.](image)

The XRD pattern presented in Figure 111 demonstrates that there was no phase transition for the nitride during the reaction. The Mo$_3$N$_2$ impurity was reduced to β-Mo$_2$N during the reaction as evidenced from the XRD pattern. The XRD pattern confirms that the bulk lattice nitrogen in the material was unreactive as there was no shift of the XRD reflections to higher 2θ values as expected for a loss of nitrogen. Ni$_2$Mo$_3$N has also been shown to have no shift in the XRD reflections when tested under Ar/H$_2$ at 700°C [36] [92], whereas
Co$_3$Mo$_3$N has been shown to lose half of its lattice nitrogen to form Co$_6$Mo$_6$N when reacted under these conditions. Both Co$_3$Mo$_3$N and Ni$_2$GaMo$_3$N have a $\eta$-carbide structure but show different behaviour when reduced under Ar/H$_2$. This further suggests that the structure does not have an effect on the lattice nitrogen reactivity, but the composition may have a greater importance. However, in contrast to this inference, filled $\beta$-Mn structured NiCoMo$_3$N has been previously prepared and tested for ammonia synthesis activity and lattice nitrogen reactivity and it was found to behave similar to Ni$_2$Mo$_3$N [92]. NiCoMo$_3$N was prepared to explore the relationship between structure and lattice nitrogen activity and to move the electronic structure of Ni$_2$Mo$_3$N closer to Co$_3$Mo$_3$N. This could be used to probe how specific the material was to pure nickel. Therefore, as the quaternary nitride had a similar activity to Ni$_2$Mo$_3$N, it was proposed that electronic factors were not responsible for the material’s activity.

The elemental analysis shows that the percentage of nitrogen was similar after reduction with 3:1 H$_2$/Ar (C: 0.50 wt. %, H: 0.00 wt. % and N: 2.41 wt. %) to pre-reaction (2.40 wt. %). The percentage of nitrogen present in the material was lower than the expected stoichiometric value of 2.86 wt. %. This result confirms that the bulk lattice nitrogen in the material was unreactive.

Figure 111: XRD pattern of Ni$_2$GaMo$_3$N post-reaction with 3:1 H$_2$/Ar at 700°C. Reflections marked: ■ Ni$_2$GaMo$_3$N (CIF file from Springer Materials [123]), ○ GaNi (JCPDS file number 01-071-8617) and ● $\beta$-Mo$_2$N (JCPDS file number 01-075-1150).
In order to see if there was any change in morphology during the reaction, SEM analysis was performed. The representative SEM images of the post-reaction material are displayed in Figure 112. The sample consisted of porous particles with pores ranging in diameter from 1 µm to 20 µm and thin needles. The morphology had been retained compared to the pre-reaction material. The nickel, gallium, molybdenum and nitrogen appear to be fairly evenly distributed across the material as seen in the element map in Figure 113. This confirms that there had been no phase segregation under the reducing conditions.

The stoichiometric percentage of nickel, gallium, molybdenum and nitrogen for Ni$_2$GaMo$_3$N is 24.01 wt. %, 14.26 wt. %, 58.87 wt. % and 2.86 wt. %, respectively. The EDX analysis for the post-reaction sample is presented in Table 27 and shows that the nitrogen percentage had decreased compared to pre-reaction suggesting that some nitrogen may have been lost during the reaction. However, there are limitations to measuring light elements by EDX. The percentage of nickel and gallium had increased compared to pre-reaction and the molybdenum had decreased. Therefore, the ratio of Ni to Ga to Mo was not 2:1:3. This is in contrast to the XRD pattern, which showed that the Ni$_2$GaMo$_3$N phase had been retained.

![SEM images of Ni$_2$GaMo$_3$N post-reaction with 3:1 H$_2$/Ar at 700°C for 7 hours.](image)

Figure 112: SEM images of Ni$_2$GaMo$_3$N post-reaction with 3:1 H$_2$/Ar at 700°C for 7 hours. a) 1000x magnification, b) 2000x magnification, c) 4000x magnification and d) 6000x magnification.
Figure 113: Element map for Ni_2GaMo_3N post-reaction with 3:1 H_2/Ar at 700°C for 7 hours. Elements: Ni (red), gallium (green), molybdenum (blue) and nitrogen (black).

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Table 27: EDX values for Ni_2GaMo_3N post-reaction with 3:1 H_2/Ar at 700°C.

3.2.4.2.3 Lattice Nitrogen Reactivity of Ni_2GaMo_3N at 900°C

In order to investigate the possible reactivity of lattice nitrogen in Ni_2GaMo_3N, the material was reduced at a higher temperature. The material was tested at 900°C under 3:1 H_2/Ar for 7 hours. As observed from the conductivity data in Figure 114, the production of ammonia was minimal, with the conductivity decreasing by only 18 µS/cm over the 7 hours. However, it must be noted that ammonia production is unfavourable at this temperature and will decompose [99] and, therefore, the lattice nitrogen may be lost as N_2. No N_2 analysis was undertaken.
Conductivity profile for Ni$_2$GaMo$_3$N reacted with 3:1 H$_2$/Ar at 900°C for 7 hours.

The XRD pattern displayed in Figure 115 shows that the η-carbide structured Ni$_2$GaMo$_3$N was maintained after the reaction. There does not appear to have been any major change in phase compared to pre-reaction or shift in XRD reflections as seen in Figure 116. This suggests that the material is not reduced and does not loss a large percentage of nitrogen under these conditions. The Mo$_3$N$_2$ impurity was reduced during the reaction as seen from the XRD pattern. The XRD pattern confirms that the bulk lattice nitrogen in the material was unreactive. Ni$_2$Mo$_3$N also has no shift in its XRD reflections when tested under Ar/H$_2$ at 900°C as seen in section 3.2.1.2.1.

The elemental analysis shows that the percentage of nitrogen had decreased after reduction with 3:1 H$_2$/Ar at 900°C (C: 0.00 wt. %, H: 0.00 wt. % and N: 3.34 wt. %) compared to pre-reaction (4.17 wt. %). The reduction of the Mo$_3$N$_2$ phase or some loss of nitrogen from the quaternary nitride could account for the decrease in nitrogen. Assuming the loss of nitrogen was due only to the Ni$_2$GaMo$_3$N, the percentage of lattice nitrogen lost that was converted to ammonia was 14.62%.

This result suggests that the structure does not influence the lattice nitrogen reactivity, as similar behaviour was observed between the filled β-Mn structured Ni$_2$Mo$_3$N and the η-carbide structured Ni$_2$GaMo$_3$N.
Figure 115: XRD pattern of Ni$_2$GaMo$_3$N post-reaction with 3:1 H$_2$/Ar at 900°C for 7 hours. Reflections marked: ■ Ni$_2$GaMo$_3$N (CIF file from Springer Materials [123]), ○ GaNi (JCPDS file number 01-071-8617) and ● GaMo$_3$ (JCPDS file number 03-065-3312).

Figure 116: Comparison of XRD patterns between Ni$_2$GaMo$_3$N pre- (black) and post-reaction (red) with 3:1 H$_2$/Ar at 900°C for 7 hours.
SEM analysis was conducted to see if the reaction had an effect on the morphology of the material. Typical SEM images of Ni$_2$GaMo$_3$N post-reaction with 1:3 Ar/H$_2$ at 900°C are shown in Figure 117. The material consisted of a porous structure, platelets and small needles and the morphology was retained from the pre-reaction material. The morphology was slightly different from the Ni$_2$Mo$_3$N that was tested under the same conditions (Figure 26). The Ni$_2$Mo$_3$N did not contain platelets and there was not as many small needles. Therefore, the lattice nitrogen reactivity is not affected by the morphology of the material.

![SEM images of Ni$_2$GaMo$_3$N post-reaction with 3:1 H$_2$/Ar at 900°C for 7 hours.

The element maps in Figure 118 illustrate that there was a fairly even distribution of nickel, gallium, molybdenum and nitrogen over the sample. Therefore, there had not been phase segregation during the reaction.
Figure 118: Element map for Ni$_2$GaMo$_3$N post-reaction with 3:1 H$_2$/Ar at 900°C for 7 hours. Elements: Ni (red), gallium (green), molybdenum (blue) and nitrogen (black).

The EDX data for the post-reaction sample is shown in Table 28. The stoichiometric percentage of nickel, gallium, molybdenum and nitrogen in Ni$_2$GaMo$_3$N is 24.01 wt. %, 14.26 wt. %, 58.87 wt. % and 2.86 wt. %, respectively. The nitrogen percentage had decreased compared to pre-reaction suggesting that some nitrogen was lost during the reaction. This agrees with the CHN analysis that showed the nitrogen percentage had decreased post-reaction. The percentage of nickel had decreased compared to pre-reaction and the amount of molybdenum had increased. Therefore, the ratio of the metals was closer to 2:1:3 compared to pre-reaction. This confirms that the Ni$_2$GaMo$_3$N phase had been retained as seen in the XRD pattern.

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Table 28: EDX values for Ni$_2$GaMo$_3$N post-reaction with 3:1 H$_2$/Ar at 900°C.
3.3 Conclusions

The filled $\beta$-Mn structured Ni$_2$Mo$_3$N and Ni$_2$Mo$_3$C$_x$N$_y$ and $\eta$-carbide structured Ni$_6$Mo$_6$C, Ni$_3$Mo$_3$C and Ni$_2$GaMo$_3$N were prepared and tested for ammonia synthesis activity and lattice nitrogen reactivity. Unfortunately, Ni$_2$Mo$_3$C could not be synthesised by topotactic routes from Ni$_2$Mo$_3$N even though different carburisation sources were used. These materials were prepared and tested to give information on the influence structure and composition has on ammonia synthesis activity. All of these phases have the interstitial element (nitrogen and/or carbon) coordinated to six molybdenum species.

Ni$_2$Mo$_3$N and Ni$_2$GaMo$_3$N were reacted under 3:1 H$_2$/Ar at 900°C to determine their lattice nitrogen reactivity. The materials were found to not be reduced under these conditions, suggesting that the bulk lattice nitrogen was unreactive. Therefore, it appears that structure does not have an effect on the activity but perhaps composition has a greater importance.

Nickel molybdenum carbonitride (Ni$_2$Mo$_3$C$_x$N$_y$) was found to be active for ammonia synthesis at 400°C and was observed to undergo nitridation during the reaction as evidenced from elemental analysis. An induction period was observed for this material when it was tested at 500°C but was not observed when tested at 400°C. The effect of the passivation layer on the ammonia synthesis activity and its possible influence on the induction period was investigated by ToF-SIMS. It was seen that nitrogen and carbon were both present near the surface of the material at a depth of 10 nm.

Both Ni$_6$Mo$_6$C and Ni$_3$Mo$_3$C have been prepared and tested for ammonia synthesis activity to help establish structure-activity and composition-activity relationships. Ni$_6$Mo$_6$C was synthesised by using citric acid to carburise nickel molybdate under Ar/H$_2$ at 700°C. Ni$_6$Mo$_6$C phase was converted to Ni$_3$Mo$_3$C when reacted with 20% CH$_4$/H$_2$. The materials consisted of two main segregated phases, the carbide and Ni$_2$Mo$_3$N. ‘Ni$_6$Mo$_6$C’ and ‘Ni$_3$Mo$_3$C’ were not active for ammonia synthesis when tested at 400°C or 500°C, respectively. However, they were both active at 700°C under 3:1 H$_2$/N$_2$ with ‘Ni$_6$Mo$_6$C’ having the higher activity. The two materials were shown to undergo nitridation during the reaction as confirmed by the XRD patterns and elemental analysis. The carbides formed Ni$_2$Mo$_3$N rather than carry out a topotactic exchange mechanism as reported for Co$_3$Mo$_3$C, suggesting that the Ni$_3$Mo$_3$N phase is less stable. Interestingly, Mo$_2$C and Mo$_{0.99}$Ni$_{0.91}$ had good ammonia synthesis activity and also combined to form Ni$_2$Mo$_3$N during the reaction. It is not understood if the activity arises due to the nitridation of these materials and
therefore, the presence of lattice nitrogen is required or whether lattice nitrogen incorporates into these materials as they are active for ammonia synthesis.

Ni$_2$GaMo$_3$N was shown to have a very low activity for ammonia synthesis when tested at 400°C and 500°C and a rate of 96 ± 12 µmol h$^{-1}$ g$^{-1}$ at 700°C. This rate is lower than the reported rates for Ni$_2$Mo$_3$N in the literature (395 ± 6 µmol h$^{-1}$ g$^{-1}$ at 400°C [36]) and for Ni$_2$Mo$_3$C$_x$N$_y$ in this work (197 ± 23 µmol h$^{-1}$ g$^{-1}$ at 400°C). Therefore, it could be suggested that there is a possible relationship between structure and ammonia synthesis activity for nickel containing nitrides. However, it has been shown that nickel impurities can lower the rate of Ni$_2$Mo$_3$N (< 15 µmol h$^{-1}$ g$^{-1}$ at 400°C [36]). Therefore, the presence of GaNi in Ni$_2$GaMo$_3$N may affect its rate and a definite conclusion cannot be drawn for the structure-activity relationship.

A summary of the major phase transformations of the nickel molybdenum materials investigated within this chapter is presented in Figure 119.

Figure 119: Phase transformations of the nickel molybdenum materials.
4. Cobalt Molybdenum Materials

4.1 Introduction

In order to continue to investigate the relationships between structure-ammonia synthesis activity and composition-activity, the filled β-Mn structured Co$_2$Mo$_3$N has been prepared. A comparison of the activity and lattice nitrogen reactivity of this nitride with the filled β-Mn structured Ni$_2$Mo$_3$N reported in Chapter 3 might give an insight into the role that metal composition has on the activity.

The η-carbide structured Co$_3$Mo$_3$N is a well known ammonia synthesis catalyst [35] [39] [54]. Co$_3$Mo$_3$N has been shown to have a higher activity than the Haber Bosch catalyst at ambient pressure [127] and also at more realistic Haber Bosch conditions [94]. The activity of Co$_3$Mo$_3$N can be enhanced by the addition of Cs$^+$ in low levels [128]. As this nitride has a high activity, most of the literature has focused upon it. Co$_3$Mo$_3$N has the η-6 carbide structure, which was explained in detail in Chapter 3 [59] [60].

In recent years, the filled β-Mn structured Co$_2$Mo$_3$N has been synthesised and investigated for its ammonia synthesis activity [129] [130]. In this structure, the Co atoms occupy the 8c sites and the Mo species are positioned on the 12d sites [73]. The N species are bonded to six Mo species as in the η-6 carbide structure. When this nitride is prepared, a mixture of Co$_2$Mo$_3$N and Co$_3$Mo$_3$N is formed, with the ratio of the two nitrides depending on the synthesis conditions. The activity of this material can be improved by the addition of potassium or chromium [129] [130]. These promoters alter the ratio of the Co$_2$Mo$_3$N/Co$_3$Mo$_3$N and increase the surface area [129] [131]. When potassium is added, the formation of the Co$_2$Mo$_3$N phase is favoured and the activity of this material can be increased by 2.4 times [129]. The activity of this material is also enhanced when the nitride is co-promoted with potassium and 1 wt. % Cr [130]. Adamski et al. state that the higher percentage of Co$_2$Mo$_3$N leads to a higher ammonia synthesis activity [132]. Therefore, it would be of interest to investigate the reason for the difference in activity between the two ternary nitrides. The difference in structure between the two nitrides may influence the activity and thus, this should be examined. The lattice nitrogen reactivity is one method that can be used to measure the activity of the materials.

The work in this chapter will aim to prepare the pure phase Co$_2$Mo$_3$N by using different preparation methods and different synthesis temperatures. The material was not doped in this chapter due to the complicating issues related to phase instability which are known to
occur for some related systems, such as Cs$^+$ on Co$_3$Mo$_3$N [39]. Furthermore, the initial aim was to understand the pure phase behaviour.

4.1.1 Lattice Nitrogen Reactivity

As discussed in more detail in Chapter 3, previous work has shown the lattice nitrogen of Co$_3$Mo$_3$N to be highly reactive, reversibly forming the Co$_6$Mo$_6$N phase [35] [50] [120] [77]. These results suggest that Co$_3$Mo$_3$N may operate via a Mars-van Krevelen mechanism for ammonia synthesis. This observation was further supported by work performed with the analogous Co$_3$Mo$_3$C phase [54].

In order to investigate the role structure has on the lattice nitrogen reactivity, a comparison of the filled $\beta$-Mn structured Co$_2$Mo$_3$N phase and the $\eta$-carbide structured Co$_3$Mo$_3$N phase would be of interest. Both the filled $\beta$-Mn structured Ni$_2$Mo$_3$N and $\eta$-carbide structured Ni$_2$GaMo$_3$N were stable and had minimal lattice nitrogen reactivity even at elevated temperature as discussed in Chapter 3. The study of the cobalt molybdenum nitrides would make a good comparison in order to see if this relationship is the same across the nitrides and to gain further insight into the structure-activity relationship in view of their similarity in composition but difference in structure. A mixture containing both Co$_2$Mo$_3$N and Co$_3$Mo$_3$N phases has been reduced under pure hydrogen at 700°C [133]. It was shown that Co$_3$Mo$_3$N was reduced to Co$_6$Mo$_6$N, as would be expected. However, Co$_2$Mo$_3$N was not reduced under these conditions and in-situ powder XRD showed that this phase was stable. Therefore, the lattice nitrogen in Co$_2$Mo$_3$N would appear to be less reactive than in Co$_3$Mo$_3$N. The work in this chapter will be performed in order to verify this previous observation and also to expand on the temperature conditions investigated to see whether a phase transition analogous to that for Co$_3$Mo$_3$N occurs at a higher temperature than 700 °C for Co$_2$Mo$_3$N. The cobalt molybdenum nitrides will be reduced under 3:1 H$_2$/Ar up to 900°C so that a comparison can be made with the nickel molybdenum nitrides reported in Chapter 3.

4.1.2 Synthesis of Co$_2$Mo$_3$N

Co$_2$Mo$_3$N was first synthesised by Prior and Battle [73]. This material was prepared by mixing MoO$_3$ and Co$_3$O$_4$ together and reacting under a flow of 10% H$_2$/N$_2$. A temperature programmed heating regime was used up to 1000°C and the material was ground together between each firing step. The XRD pattern of the resultant material showed that small amounts of molybdenum metal and Co$_3$Mo$_3$N were also present. The authors found that prolonged heating favoured the formation of Co$_3$Mo$_3$N and molybdenum metal.
Adamski et al. additionally observed that Co$_2$Mo$_3$N transforms to Co$_3$Mo$_3$N upon prolonged exposure to ammonia at 700°C through combination with an excess cobalt metal component [132]. They prepared the mixed phase Co$_2$Mo$_3$N/Co$_3$Mo$_3$N by first heating the oxide precursor to 700°C under pure nitrogen and then switching to either pure NH$_3$ [133] or 10% NH$_3$/N$_2$ [132]. This mixed phase Co$_2$Mo$_3$N/Co$_3$Mo$_3$N was also synthesised by heating the oxide under NH$_3$ to 700°C [129] [130] [131]. It was proposed that the time at which ammonia is introduced affects the composition of the nitride [132]. Through in-situ XRD studies, Adamski et al. showed that Co$_3$Mo$_3$N was the final product of the ammonolysis of CoMoO$_4$ precursor. The authors suggested the diffusion of Co atoms was the main factor in the final composition of the material and the restriction of this diffusion can be used to control the ratio of Co$_2$Mo$_3$N to Co$_3$Mo$_3$N. Moszynski et al. have observed that potassium encourages the formation of Co$_2$Mo$_3$N [129] and the addition of chromium prevents its development [131]. When potassium was added, the concentration of Co$_2$Mo$_3$N was observed to be 50 wt. %.

From comparing the XRD patterns of the mixed phase Co$_2$Mo$_3$N prepared by either N$_2$/H$_2$ or NH$_3$, it appears that the preparation of the nitride by N$_2$/H$_2$ resulted in the highest proportion of Co$_2$Mo$_3$N. Therefore, for this reason, a 3:1 H$_2$/N$_2$ mixture was used within this work.

4.2 Results and Discussion

4.2.1 Cobalt Molybdenum Nitride (Co$_2$Mo$_3$N)

3. Cobalt Molybdenum Oxide (Co$_2$Mo$_3$O$_x$)

Three preparation methods were applied to synthesise the cobalt molybdenum oxide. The modified Pechini method was the first method attempted as it had been used to successfully prepare the filled β-Mn structured Ni$_2$Mo$_3$N. The second method was similar to the one used to prepare Co$_3$Mo$_3$N [55] [53] and was based upon stoichiometric amounts of (NH$_4$)$_6$Mo$_7$O$_{24}$-4H$_2$O and Co(NO$_3$)$_2$·6H$_2$O being added together in deionised water. The final method was similar to the second method but the material was not calcined prior to phase transformation.

The XRD pattern of the material prepared by the modified Pechini method is displayed in Figure 120. It can be seen that the oxide precursor was a mixture of CoMoO$_4$ and MoO$_3$ phases. This observation is consistent with the mixture of oxides that were synthesised when the sol-gel method was used to prepare Ni$_2$Mo$_3$N. Unique reflections of MoO$_3$ can be observed at 12.76°, 25.68°, 27.31°, 35.47° and 49.25° 20. This mixture of oxides was targeted as the
difference in metal ratios of the Co and Mo between the CoMoO$_4$ (1:1) and the nitride (2:3) could lead to impurities of cobalt metal when the nitride is synthesised similar to the observation for Ni$_2$Mo$_3$N, where nickel metal impurities are formed [36]. The other two preparation methods also comprised a mixture of phases but the intensities of the MoO$_3$ reflections were lower.

The elemental analysis showed that the material contained trace amounts of carbon and hydrogen when prepared by the modified Pechini method (C: 0.21 wt. %, H: 0.05 wt. %, N: 0.00 wt. %), which might be reflective of residues of the citric acid employed in the synthesis. However, for the method where the oxide was uncalcined, the material contained a larger percentage of nitrogen and hydrogen (C: 0.00 wt. %, H: 0.58 wt. %, N: 1.30 wt. %). The nitrogen and hydrogen likely originate from the starting precursors used in the synthesis.

Figure 120: XRD pattern of cobalt molybdenum oxide (Co$_2$Mo$_3$O$_x$). Reflections marked: ▲ CoMoO$_4$ (JCPDS file number 00-021-0868) and X MoO$_3$ (JCPDS file number 01-074-7383).

Raman spectroscopy was used to determine the different oxide phases present in the material and to confirm that the two phases were present. A representative Raman spectrum of the mixed phase oxide is provided in Figure 121. The Raman spectrum of this
material was analysed by comparing it with the spectra of CoMoO₄ and MoO₃ in the literature.

![Raman spectrum of cobalt molybdenum oxide (Co₂Mo₃Oₓ).](image)

**Figure 121: Raman spectrum of cobalt molybdenum oxide (Co₂Mo₃Oₓ).**

The Raman bands at positions of 927, 868, 806 and 359 cm⁻¹ were attributed to β-CoMoO₄ [126]. These Raman shifts are in very good agreement with CoMoO₄ spectra reported in the literature [126]. The bands at 927, 868 and 359 cm⁻¹ have been assigned in the literature as the Mo-O-Co stretching vibrations in cobalt molybdate [126], with the strong band at 927 cm⁻¹ being due to the A1 mode of Mo=O in MoO₄ [134]. The band at 806 cm⁻¹ has also been reported as a band that occurs in the Raman spectrum for MoO₃ and is due to the Mo-O-Mo asymmetric stretching mode [67]. The Raman bands at 334 and 277 cm⁻¹ have also been assigned to MoO₃ and are due to the Mo-O bending and Mo-O-Mo deformation mode [90]. However, the other expected bands for MoO₃ at approximately 995 and 665 cm⁻¹ were not observed. This is unusual as the band at 995 cm⁻¹ has a moderate intensity in the Raman spectrum for MoO₃. However, this can be dependent upon the edge plane and therefore, may be reflective of morphology. The SEM images for the cobalt molybdenum oxide (Co₂Mo₃O₄ₓ) are provided in Appendix IV. Morphologies related to MoO₃ cannot be identified and it is speculated that the MoO₃ morphology would be very anisotropic.
The presence of bands for both CoMoO$_4$ and MoO$_3$ agrees with the XRD results, which showed that both these oxides were present in the material. Alshibane [55] observed similar bands for the CoMoO$_4$ precursor.

EDX analysis was performed in order to determine if the ratio of cobalt to molybdenum was as desired for the formation of the Co$_2$Mo$_3$N phase from the oxide. This analysis may indicate the method that was best for preparing the oxide with the required Co$_2$Mo$_3$O$_x$ stoichiometry.

The EDX data in Table 29 details the weight percentages for each element for the material prepared by the modified Pechini method. The XRD pattern showed that the material consisted of both CoMoO$_4$ and MoO$_3$. Therefore, the stoichiometric percentage of cobalt, molybdenum and oxygen expected for this mixture of phases would be 20.26 wt. % Co, 49.48 wt. % Mo and 30.26 wt. % O, respectively. From the table, it can be seen that the values obtained from EDX agree quite well with the expected stoichiometric values. However, as stated before, the measure of low atomic number elements, such as oxygen, by EDX analysis is not reliable. This material had the correct ratio of cobalt to molybdenum to give the Co$_2$Mo$_3$O$_x$ stoichiometry.

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Table 29: EDX values for cobalt molybdenum oxide (Co$_2$Mo$_3$O$_x$) prepared by modified Pechini method.

The EDX analysis in Table 30 provides the weight percentages for the material prepared by the second method. The stoichiometric percentage of cobalt, molybdenum and oxygen in the theoretical Co$_2$Mo$_3$O$_{11}$ is 20.26 wt. %, 49.48 wt. % and 30.26 wt. %, respectively. From the table, it can be seen that the oxygen weight percentage was higher than predicted. However, the oxygen analysis is not reliable in EDX. The weight ratio of cobalt to molybdenum in this material was not as expected as there was a much lower cobalt weight.
percentage. This is in contrast to the XRD pattern and Raman spectroscopic result for this material, which showed that CoMoO$_4$ was the majority phase, which would suggest that the Co percentage would be higher. This result suggests that the modified Pechini method was superior at preparing the desired mixed phased oxide as the ratio of cobalt to molybdenum for that material was as required. This was also confirmed by the XRD pattern as the modified Pechini method had a better mixture of the CoMoO$_4$ and MoO$_3$ phases.

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<td>41</td>
<td>54</td>
</tr>
<tr>
<td>2</td>
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</tr>
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<td>7</td>
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</tr>
<tr>
<td>8</td>
<td>19</td>
<td>40</td>
<td>41</td>
</tr>
<tr>
<td>Average</td>
<td>9</td>
<td>41</td>
<td>51</td>
</tr>
</tbody>
</table>

Table 30: EDX values for cobalt molybdenum oxide (Co$_2$Mo$_3$O$_x$) prepared from method 2.

4.2.1.2 Cobalt Molybdenum Nitride (Co$_2$Mo$_3$N)

The filled β-Mn structured Co$_2$Mo$_3$N was prepared via temperature programmed nitridation of the mixed oxides. A 1:3 N$_2$/H$_2$ gas mixture was used and the synthesis was performed at different temperatures in order to try to prepare the pure-phase nitride. The preparation of this material followed the method used to prepare relatively phase pure Ni$_2$Mo$_3$N as shown in Chapter 3. The mixed phase Co$_2$Mo$_3$N has previously been prepared by the reaction of MoO$_3$ and Co$_3$O$_4$ under 10% H$_2$/N$_2$ with a heating regime up to 1000°C [73]. As stated for Ni$_2$Mo$_3$N, an advantage of using N$_2$/H$_2$ gas mixture in the preparation is that it overcomes problems with using ammonia at a large scale [95].

Prior and Battle stated that prolonged heating favoured the formation of Co$_3$Mo$_3$N and molybdenum metal [73]. Therefore, it would be of interest to attempt to prepare the pure-phase Co$_2$Mo$_3$N by using different synthesis conditions, such as varying the length of time of the nitridation process.

Modified Pechini Method

The XRD patterns of the nitrides that were prepared by the modified Pechini method at either 600°C or 700°C reaction temperature are shown in Figure 122. The formation of Co$_3$Mo$_3$N is favoured at higher reaction temperatures under H$_2$/N$_2$ atmosphere and hence, a lower temperature was applied in order to try to prepare Co$_2$Mo$_3$N. Prior and Battle
observed that Co$_3$Mo$_3$N formation was favoured at higher temperature [73]. Furthermore, at 800°C and 900°C under 3:1 H$_2$/N$_2$ Co$_3$Mo$_3$N is favoured (Lucy Costley-Wood, 2019, personal communication). However, from the XRD pattern of the material prepared at 600°C, it can be seen that it contained a mixture of oxide phases and no evidence of any nitride phases and therefore, it appears that the reaction temperature was too low for the nitridation process to take place. Unique reflections for MoO$_2$ can be observed at 26.08°, 53.48°, 54.06° and 66.84° 2θ, for CoO at 42.72° 2θ and for CoMoO$_3$ at 56.29° 2θ. The elemental analysis in Table 31 shows that the material contained 1.37 wt. % of nitrogen. The expected percentage of nitrogen in Co$_2$Mo$_3$N based upon stoichiometry is 3.34 wt. % and for Co$_3$Mo$_3$N the stoichiometric amount of nitrogen is 2.93 wt. %. Therefore, it is suggested that a degree of nitridation of the material has occurred but the desired ternary phase was not synthesised at 600°C.

Figure 122: XRD pattern of Co$_2$Mo$_3$N prepared at 600°C for 2 hours and 700°C for 2 hours under 3:1 H$_2$/N$_2$. Reflections marked: ☆ MoO$_2$ (JCPDS file number 01-076-1807), ★ CoO (JCPDS file number 01-070-2855), ★ CoMoO$_3$ (JCPDS file number 00-021-0869), Co$_2$Mo$_3$N (JCPDS file number 01-072-6570), ● Co$_3$Mo$_3$N (JCPDS file number 01-089-7953) and ● β-Mo$_2$N$_{0.76}$ (JCPDS file number 03-065-6236).
At 700°C, a mixture of the filled β-Mn structured Co$_2$Mo$_3$N and η-carbide structured Co$_3$Mo$_3$N were observed in the XRD pattern. However, the intensities of the Co$_2$Mo$_3$N reflections were greater than the Co$_3$Mo$_3$N reflections, suggesting that Co$_2$Mo$_3$N was the majority phase. A molybdenum nitride impurity was also observed in the XRD pattern. As both phases are prepared, an excess of molybdenum would be expected from the stoichiometry as a 2:3 ratio of Co to Mo was used to prepare the oxide. A unique reflection matching β-Mo$_2$N$_{0.76}$ can be seen at 37.68° 20. The elemental analysis of this material revealed that it contained 3.71 wt. % of nitrogen. This value was slightly higher than the expected stoichiometric value for Co$_2$Mo$_3$N. However, NH$_x$ species formed on the surface of the material during the nitridation process may contribute to this value.

These results indicate that the preparation temperature needs to be higher than 600°C in order to form the nitride and that a mixture of phases is formed from the oxide prepared by the modified Pechini method.

<table>
<thead>
<tr>
<th>Material</th>
<th>Carbon Content from Elemental Analysis (wt. %)</th>
<th>Hydrogen Content from Elemental Analysis (wt. %)</th>
<th>Nitrogen Content from Elemental Analysis (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>600°C 2 h</td>
<td>0.11</td>
<td>0.19</td>
<td>1.37</td>
</tr>
<tr>
<td>700°C 2 h</td>
<td>0.14</td>
<td>0.09</td>
<td>3.71</td>
</tr>
</tbody>
</table>

Table 31: Elemental Analysis for the cobalt molybdenum materials prepared at different temperatures with 3:1 H$_2$/N$_2$.

Method where the Oxide was Uncalcined

The XRD patterns of the nitrides that were prepared from the uncalcined oxide at either 650°C or 700°C reaction temperatures are presented in Figure 123. As the nitridation process did not appear to occur at 600°C, as shown before, the lowest temperature employed was above 600°C. For the material prepared at 650°C, it can be seen from the XRD pattern that it contained a mixture of oxide phases, which were the same phases as the material prepared at 600°C. Therefore, it appears that the temperature needs to be at 700°C in order for the nitridation process to take place. The elemental analysis shows that the material prepared at 650°C contained 2.01 wt. % nitrogen, suggesting that some nitridation resulting in XRD amorphous phases may possibly have occurred. Unique XRD reflections for MoO$_2$ can be observed at 26.08°, 53.48°, 54.06° and 66.84° 20, for CoO at 42.72° 20 and for CoMoO$_3$ at 35.74° 20, which are indicative of reduction having commenced.
Figure 123: XRD pattern of Co$_2$Mo$_3$N prepared at 650°C for 3 hours, 700°C for 1 hour and 700°C for 2 hours under 3:1 H$_2$/N$_2$. Reflections marked: ☆ MoO$_2$ (JCPDS file number 01-076-1807), ▲ CoO (JCPDS file number 01-070-2855), ★ CoMoO$_3$ (JCPDS file number 00-021-0869), ● Co$_2$Mo$_3$N (JCPDS file number 01-072-6570), ● Co$_3$Mo$_3$N (JCPDS file number 01-089-7953), ◇ Co$_3$Mo (JCPDS file number 03-065-3519) and ◇ CoMoO$_4$ (JCPDS file number 00-021-0868).

In an attempt to prepare the desired pure-phase nitride, nitridation at 700°C for either 1 hour or 2 hours was undertaken. As stated previously, it has been suggested that prolonged heating favours the formation of Co$_3$Mo$_3$N. However, when the material was prepared for 1 hour, it contained a mixture of oxides and Co$_3$Mo as seen from the XRD pattern. Unique XRD reflections for Co$_3$Mo can be observed at 46.41º 2θ, for CoMoO$_4$ at 26.51º 2θ and for CoO at 36.77º 2θ. Therefore, it appears that the nitride needs to be prepared at 700°C employing a longer time duration. The elemental analysis in Table 32, showed that, as expected from the XRD pattern, the percentage of nitrogen (2.30 wt. %) was lower than the expected stoichiometric value for Co$_2$Mo$_3$N. The XRD pattern of this material comprised a higher degree of amorphous component as evident from the intensity of its background. However, Co fluoresces when a Cu X-ray source is used, which results in adding to the background of the pattern. Therefore, the increased background may be due to increased Co fluorescence and not amorphous material.

When the material was synthesised at 700°C for 2 hours, a mixture of the ternary nitride phases were observed in the XRD pattern. Co$_3$Mo$_3$N was the majority phase as the
intensity of the reflections were greater than those for Co₂Mo₃N. This is in contrast to the material that was prepared from the modified Pechini method and therefore, that method would appear to be better in terms of preparation of the desired Co₂Mo₃N target. The material contained 4.00 wt. % nitrogen, which is higher than the expected stoichiometric value for either Co₂Mo₃N or Co₃Mo₃N. However, possible NHₓ species on the surface of the material that result from the nitridation process would contribute to this percentage.

Table 32: Elemental Analysis for the cobalt molybdenum materials prepared at different temperatures with 3:1 H₂/N₂.

<table>
<thead>
<tr>
<th>Material</th>
<th>Carbon Content from Elemental Analysis (wt. %)</th>
<th>Hydrogen Content from Elemental Analysis (wt. %)</th>
<th>Nitrogen Content from Elemental Analysis (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>650°C 3 h</td>
<td>0.00</td>
<td>0.10</td>
<td>2.01</td>
</tr>
<tr>
<td>700°C 1 h</td>
<td>0.00</td>
<td>0.00</td>
<td>2.30</td>
</tr>
<tr>
<td>700°C 2 h</td>
<td>0.00</td>
<td>0.00</td>
<td>4.00</td>
</tr>
</tbody>
</table>

Second Method
For the material prepared by the second method, where stoichiometric amounts of (NH₄)₆Mo₇O₂₄·4H₂O and Co(NO₃)₂·6H₂O were added together in deionised water, Co₃Mo₃N appeared to be the majority phase and the intensity of the Co₂Mo₃N reflections were very small (the XRD pattern for this method is not provided).

Out of the three methods used, the oxide prepared by the modified Pechini route was the best method in order to prepare the desired Co₂Mo₃N phase in the highest ratio with respect to Co₂Mo₃N to Co₃Mo₃N. Therefore, the material that was synthesised by this route was investigated for its ammonia synthesis activity and lattice nitrogen reactivity.

Optimal Conditions for Preparing the Best Ratio of Co₂Mo₃N from the Oxide Prepared by the Modified Pechini Method

The filled β-Mn structured Co₂Mo₃N was prepared via temperature programmed nitridation of the mixed oxide at 700°C for three hours. These were found to be the optimal conditions to give the highest amount of Co₂Mo₃N. The XRD pattern of the material is displayed in Figure 124. The material also contained β-Mo₂N₀.₇₆ and Co₃Mo₃N. The elemental analysis showed that the material contained 3.82 wt. % of nitrogen (C: 0.00 wt. %, H: 0.00 wt. %, N: 3.82 wt. %). This value agrees quite well with the expected stoichiometric amount of nitrogen for Co₂Mo₃N despite the fact that it comprises mixed phases.
Figure 124: XRD pattern of cobalt molybdenum nitride (Co$_2$Mo$_3$N). Reflections marked: ● Co$_2$Mo$_3$N (JCPDS file number 01-072-6570), ● Co$_3$Mo$_3$N (JCPDS file number 01-089-7953) and ● β-Mo$_2$N$_{0.76}$ (JCPDS file number 03-065-6236).

The Raman spectrum for the material is shown in Figure 125. The spectrum was similar to the one for the oxide, suggesting that the surface of the material possessed a passivation layer as expected based upon the air-sensitivity of nitrides. The Raman bands at 934, 877, 814 and 362 cm$^{-1}$ were assigned to β-CoMoO$_4$ [126]. The bands at 934, 877 and 362 cm$^{-1}$ are stated to be due to the Mo-O-Co stretching vibrations in cobalt molybdate [126]. The bands at 806 and 341 cm$^{-1}$ have also been reported as bands that occur in the Raman spectrum for MoO$_3$ and are due to the Mo-O-Mo asymmetric stretching mode [67] and the Mo-O bending [90], respectively. The bands due to β-CoMoO$_4$ could be due to the surface oxide layer on Co$_2$Mo$_3$N and Co$_3$Mo$_3$N and the bands relating to MoO$_3$ could be due to a passivation layer on the molybdenum nitride impurity phase. Alshibane [55] and Alconchel et al. [105] observed similar bands for the Raman spectrum of Co$_3$Mo$_3$N.
Figure 125: Raman spectrum of cobalt molybdenum nitride (‘Co$_2$Mo$_3$N’).

The representative SEM images of the material given in Figure 126 show that the morphology was retained with respect to the oxide precursor (SEM for oxide is provided in Appendix IV). The material had a porous and uneven surface, with the pores ranging in size from 1 to 10 µm.

The EDX analysis in Table 33 gives the weight percentages for the material. The stoichiometric percentage of cobalt, molybdenum and nitrogen in Co$_2$Mo$_3$N is 28.08 wt. %, 68.58 wt. % and 3.34 wt. %, respectively. It can be seen that the values obtained from EDX agree well with the expected stoichiometric values, even though the XRD pattern showed that the material consisted of both Co$_5$Mo$_3$N and β-Mo$_2$N$_{0.76}$ impurities. Therefore, the material had the desired weight ratio for Co$_2$Mo$_3$N. The values of the cobalt and molybdenum had increased compared to the oxide precursor, which is to be expected when considering that oxygen has been replaced with nitrogen. The weight ratio of cobalt and molybdenum in the oxide and nitride were as would be expected for these materials.
Figure 126: SEM images of cobalt molybdenum nitride (‘Co$_2$Mo$_3$N’). a) 100x magnification, b) 500x magnification, c) 1000x magnification and d) 2000x magnification.

The elemental maps in Figure 127 indicate that the cobalt, molybdenum and nitrogen were fairly evenly disbursed across the material as would be expected.

Figure 127: Element Maps for ‘Co$_2$Mo$_3$N’. Elements: Co (red), Mo (green) and N (blue).

The number of EDX measurements for the samples are different and therefore, the samples with fewer measurements may not be as accurate due to the smaller sample size. There is also a significant variation in the nitrogen percentage between the areas examined. It has to be borne in mind that, in addition to being semi-quantitative, EDX analysis is not reliable in relation to nitrogen analysis.
<table>
<thead>
<tr>
<th>Area</th>
<th>Co weight (%)</th>
<th>Mo weight (%)</th>
<th>N weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>31</td>
<td>62</td>
<td>7</td>
</tr>
<tr>
<td>2</td>
<td>34</td>
<td>66</td>
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</tr>
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<td>3</td>
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<td>7</td>
</tr>
<tr>
<td>4</td>
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<tr>
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<td>66</td>
<td>10</td>
</tr>
<tr>
<td>13</td>
<td>32</td>
<td>68</td>
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</tr>
<tr>
<td>14</td>
<td>23</td>
<td>65</td>
<td>13</td>
</tr>
<tr>
<td>15</td>
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<td>65</td>
<td>0</td>
</tr>
<tr>
<td>Average</td>
<td>28</td>
<td>66</td>
<td>6</td>
</tr>
</tbody>
</table>

Table 33: EDX values for cobalt molybdenum nitride (‘Co$_2$Mo$_3$N’).

4.2.2 Ammonia Synthesis at 400°C for Co$_2$Mo$_3$N

Mixed phase Co$_2$Mo$_3$N and Co$_3$Mo$_3$N has previously been tested for ammonia synthesis and was found to have a rate as reported by the authors as approximately 5.8 g$_{\text{NH}_3}\text{MPa}^{0.5}$ g$_{\text{cat}}^{-1}$ h$^{-1}$ at 500°C and 10 MPa [130]. The quoted units for this rate are unusual and the origin is unclear from the reported literature. This rate was influenced by the addition of chromium and potassium, which altered the ratio of the ternary nitrides and the surface area [130] [131] [129].

The mixed phase Co$_2$Mo$_3$N prepared by the modified Pechini method in the current study was tested for ammonia synthesis at 400°C under 3:1 H$_2$/N$_2$ at atmospheric pressure for 8 hours. The material was first pre-treated at 700°C for 2 hours under the same gas mixture. The conductivity profile of the material is presented in Figure 128. The ammonia synthesis rate of ‘Co$_2$Mo$_3$N’ at 400°C was 208 µmol h$^{-1}$ g$^{-1}$ and at 700°C was 159 ± 8 µmol h$^{-1}$ g$^{-1}$. The rate at 700°C was obtained during the pre-treatment, therefore, any phase changes during this period may consequently influence the rate. However, the rate was steady state during the pre-treatment. The lower rate of the material at 700°C may be expected as ammonia decomposes at this temperature. Co$_3$Mo$_3$N was previously reported to exhibit a rate of 166 ± 2 µmol h$^{-1}$ g$^{-1}$ under comparable reaction conditions at 400°C [35]. However, a direct comparison cannot be made as the relative surface areas between the materials is not known. An added consideration is that the materials have different morphologies. Unfortunately, there is not a surface area measurement value for the mixed phase nitride in this work as there were pro-longed technical issues with the equipment required to make
this measurement. Moszynski et al. [129] have previously stated that there is a direct relationship between the Co₂Mo₃N content and the ammonia synthesis activity. However, surface area was also a factor in this reported relationship.

![Conductivity profile](image.png)

Figure 128: Conductivity profile for ‘Co₂Mo₃N’ reacted with 3:1 H₂/N₂ at 700°C for 2 hours and 400°C for 8 hours.

In the post-reaction XRD pattern (Figure 129) the ratio of Co₂Mo₃N to Co₃Mo₃N appeared to be the same as for the pre-reaction sample. This suggests that the material did not change phase during the reaction. The elemental analysis in Table 34 shows that the material had more nitrogen post-reaction and therefore, the pre-treatment may have further nitrided the material. The carbon present in the pre- and post-reaction material is most probably due to residues of citric acid used in the synthesis.

<table>
<thead>
<tr>
<th>Material</th>
<th>Calculated Stoichiometric Nitrogen Content (wt. %)</th>
<th>Calculated Stoichiometric Carbon Content (wt. %)</th>
<th>Nitrogen Content from Elemental Analysis (wt. %)</th>
<th>Carbon Content from Elemental Analysis (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>‘Co₂Mo₃N’ Pre-reaction</td>
<td>3.34</td>
<td>-</td>
<td>2.67</td>
<td>0.20</td>
</tr>
<tr>
<td>‘Co₂Mo₃N’ Post-reaction</td>
<td>3.34</td>
<td>-</td>
<td>3.25</td>
<td>0.18</td>
</tr>
</tbody>
</table>

Table 34: Elemental Analysis for ‘Co₂Mo₃N’ comparing pre- and post-reaction with 3:1 H₂/N₂ at 700°C for 2 hours and 400°C for 8 hours as shown in the reaction profile in Figure 128.
Figure 129: XRD pattern for 'Co₂Mo₃N' post-reaction with 3:1 H₂/N₂ at 400°C for 8 hours. Reflections marked: ● Co₂Mo₃N (JCPDS file number 01-072-6570), ● Co₃Mo₃N (JCPDS file number 01-089-7953) and ● β-Mo₂N₀.₇₆ (JCPDS file number 03-065-6236).

SEM analysis was conducted in order to investigate if there was any change in morphology and structure of ‘Co₂Mo₃N’ during the reaction. Figure 130 gives representative SEM images of the post-reaction material at different magnifications. The sample was porous and had an uneven surface. The pores ranged in diameter from approximately 1 µm to 10 µm. From the SEM images, it appears that the morphology had been retained compared to pre-reaction.

The cobalt, molybdenum and nitrogen were fairly evenly distributed across the material as evidenced by the element map in Figure 131. However, some areas appeared to have more cobalt, which suggests that there may have been some phase segregation of cobalt, although this was not evidenced in the XRD pattern. There did not appear to be any areas that had a larger percentage of cobalt in the EDX analysis (data not provided).
Figure 130: SEM images of ‘Co$_2$Mo$_3$N’ post reaction with 3:1 H$_2$/N$_2$ at 400°C for 8 hours. a) 1000x magnification, b) 1000x magnification, c) 2000x magnification and d) 4000x magnification.

Figure 131: Element Map for ‘Co$_2$Mo$_3$N’ post-reaction with 3:1 H$_2$/N$_2$ at 400°C. Elements: Co (red), Mo (green) and N (blue).

4.2.3 Lattice Nitrogen Reactivity of Co$_2$Mo$_3$N

4.2.3.1 Lattice Nitrogen Reactivity of Co$_2$Mo$_3$N at 700°C

In order to determine the lattice nitrogen reactivity in Co$_2$Mo$_3$N, the material was reduced at 700°C under a flow of 3:1 H$_2$/Ar at ambient pressure for 7 hours. As observed from the conductivity profile data in Figure 132, for the first 60 minutes the conductivity decreased in a non-steady state manner. After the first 60 minutes, the rate became steady state with
ammonia production occurring at a rate of 13 $\mu$mol h$^{-1}$ g$^{-1}$ although at this temperature ammonia is thermodynamically unstable with respect to its decomposition. There was a total decrease in conductivity of 51 $\mu$S/cm over the 7 hours at 700°C. Co$_3$Mo$_3$N has been shown to have a linear decrease at 700°C when tested at this temperature for 1 hour [135]. However, the ammonia production rate was not reported.

![Conductivity profile](image)

Figure 132: Conductivity profile for ‘Co$_2$Mo$_3$N’ reacted with 3:1 H$_2$/Ar at 700°C for 7 hours.

The XRD patterns of the pre- and post-reaction materials can be compared in Figure 133. The post-reaction XRD pattern shows a shift of the Co$_3$Mo$_3$N reflections to higher 2θ angles, which indicates that there was a decrease in the lattice nitrogen content of this phase as would be expected from its known phase transition to Co$_6$Mo$_6$N [55] [135] [35]. However, the analysis is complicated by the degree of overlap between reflections relating to the Co$_6$Mo$_6$N and Co$_2$Mo$_3$N phases. The reflections of Co$_2$Mo$_3$N did not appear to move to higher 2θ values post-reaction as clearly seen by the peak at approximately 45.08° 2θ. This suggests that this phase did not lose lattice nitrogen. This confirms the previous observations of Adamski et al. who have reported that the Co$_2$Mo$_3$N phase remains stable under pure hydrogen at 700°C [133], whereas Co$_3$Mo$_3$N does not. The molybdenum nitride impurity was reduced to molybdenum metal during the reaction, as would be expected on the basis of prior literature [135]. There are no unique reflections for molybdenum and hence, this phase cannot be completely established. However, the Raman spectrum for this material showed bands associated with MoO$_3$, suggesting that molybdenum metal, which oxidised upon standing in ambient air, was present in this material (spectrum not shown).
Figure 133: Comparison of XRD patterns for 'Co$_2$Mo$_3$N' pre- and post-reaction with 3:1 H$_2$/Ar at 700°C for 7 hours. Reflections marked: ● Co$_2$Mo$_3$N (JCPDS file number 01-072-6570), ○ Co$_3$Mo$_3$N (JCPDS file number 01-089-7953), ● β-Mo$_2$N$_{0.76}$ (JCPDS file number 03-065-6236), ○ Mo (JCPDS file number 01-071-4645) and ● Co$_6$Mo$_6$N (data from [55]).

In addition, the elemental analysis showed that there was a loss of more than half the nitrogen content compared to pre-reaction as seen in Table 35. As the material contains Co$_6$Mo$_6$N, Co$_2$Mo$_3$N and Mo, the expected stoichiometric percentage of nitrogen in this material is 1.92 wt. %, assuming a 1:1:1 ratio. The experimental value was quite close to this expected value. The percentage of the overall nitrogen that was lost from the material that was converted to ammonia was ca. 25% (as determined from the change in conductivity of the H$_2$SO$_4$ solution through which the reactor effluent is passed) with the remainder of the nitrogen lost presumably being in the form of dinitrogen.
The stability of the filled β-Mn structured Co$_2$Mo$_3$N is similar to the observations for the filled β-Mn structured Ni$_2$Mo$_3$N and η-carbide structured Ni$_2$GaMo$_3$N tested under the same conditions. This suggests that the lattice nitrogen reactivity of the ternary nitrides is a complex relationship between the metal composition and structure. The two nickel containing nitrides are stable, even though they have different structures, suggesting that the metal composition is more important than structure. However, this is not the case with the cobalt containing nitrides, suggesting that the structure also affects the stability. The local nitrogen environment between the two structures is similar with nitrogen coordinated to six molybdenum species in each case. Therefore, the influence of the other metal component on the Mo$_6$N species could possibly affect the lattice nitrogen reactivity. To the author’s knowledge, the bond distances in Co$_2$Mo$_3$N have not been reported in the literature and therefore, a comparison cannot be made with those for Co$_3$Mo$_3$N. In Co$_3$Mo$_3$N, the nitrogen relocates from the 16c site to the 8a site when the material transforms to Co$_6$Mo$_6$N. It could be suggested that for the filled β-Mn structure, nitrogen relocation within the crystallographic structure is less favourable and the Co$_2$Mo$_3$N phase is more stable. For the η-carbide structured Co$_3$Mo$_3$N, four Mo, six Co and two N species surround the molybdenum species, whereas in the filled β-Mn structure, the molybdenum species are bonded to six Co, six Mo and two N species [59]. Therefore, the Co atoms have a proportionately greater influence on the molybdenum species in the filled β-Mn structure and this in turn might affect the Mo-N interaction. This would suggest that the structure (i.e. η-carbide versus filled β-Mn) has some impact on the lattice nitrogen reactivity for materials of related composition (i.e. Co-Mo-N). The coordination diagrams of molybdenum in the η-carbide structured Co$_3$Mo$_3$N and the filled β-Mn structured Co$_2$Mo$_3$N are presented in Figure 134 and Figure 135, respectively.
The SEM images in Figure 136 show that the morphology was similar to the pre-reaction material. The particles had an irregular shape with a smooth surface and pores. The morphology of the post-reaction nitrides (Ni$_2$Mo$_3$N, Ni$_2$GaMo$_3$N and mixed phase ‘Co$_2$Mo$_3$N’) tested under 3:1 $\text{H}_2/\text{Ar}$ within this research are different.
Figure 136: SEM images of ‘Co$_2$Mo$_3$N’ post-reaction with 3:1 H$_2$/Ar. a) 200x magnification, b) 1000x magnification, c) 2000x magnification and d) 2000x magnification.

The element map in Figure 137 shows that there was a fairly even distribution of cobalt and molybdenum over the sample, although as with the post N$_2$/H$_2$ reaction sample, there were areas that contained less molybdenum. This suggests that there may have been phase segregation during the reaction. However, this was not evidenced in the EDX analysis (data not provided).

Figure 137: Element Map for ‘Co$_2$Mo$_3$N’ post-reaction with 3:1 H$_2$/Ar at 700°C. Elements: Co (red), Mo (green) and N (blue).
4.2.3.2 Lattice Nitrogen Reactivity of Co$_2$Mo$_3$N at 800°C and 900°C

The stability of Co$_2$Mo$_3$N and Co$_6$Mo$_6$N under reducing conditions and the possible lattice nitrogen reactivity of the material was investigated further by testing the material under 3:1 H$_2$/Ar at 800°C and 900°C. The material was tested at 900°C, in order to make a comparison with the other ternary nitrides examined elsewhere within this thesis. The conductivity data in Figure 138 for the 800°C reaction and in Figure 139 for the 900°C reaction show that the rate was non-steady state and the production of ammonia was minimal at both temperatures. There was a decrease in conductivity of 44 µS/cm at 800°C and of only 31 µS/cm at 900°C, over the 7 hours. This result is in accordance with the limited stability of ammonia under these conditions under which much of the lattice nitrogen would therefore be lost as N$_2$.

![Conductivity profile for Co$_2$Mo$_3$N reacted with 3:1 H$_2$/Ar at 800°C for 7 hours.](image1.png)

Figure 138: Conductivity profile for Co$_2$Mo$_3$N reacted with 3:1 H$_2$/Ar at 800°C for 7 hours.
4.2.3.2.1 XRD Pattern and Elemental Analysis of Co$_2$Mo$_3$N Post 800°C Reaction

The pre- and post-reaction XRD patterns are provided in Figure 140. As was observed before, the Co$_3$Mo$_3$N phase shifted to higher 2θ values. This was most clearly seen when comparing the peak at approximately 35.46° 2θ, pre- and post-reaction. Moreover, the XRD reflections for Co$_6$Mo$_6$N appear to have shifted to even higher 2θ values than expected, suggesting that this phase has lost even more nitrogen. The Co$_2$Mo$_3$N appears to remain stable at this temperature, with no shift in the peak positions observed for this phase. The peak for Co$_2$Mo$_3$N at approximately 45.08° 2θ does not change position compared to pre-reaction. This suggests that the lattice nitrogen in this phase was unreactive. As was seen at 700°C, the molybdenum nitride impurity was reduced to molybdenum metal during the reaction. However, as there are not unique reflections for Mo, this phase cannot be completely confirmed as is the case at 700°C. However, the reduction of molybdenum nitride to Mo has been reported to occur under 3:1 Ar/H$_2$ at 700°C [135] and therefore, would be assumed to occur in this case as well.

The elemental analysis displayed in Table 36 shows that the nitrogen percentage decreased significantly compared to pre-reaction. If the material contained Co$_6$Mo$_6$N, Co$_2$Mo$_3$N and Mo, the expected stoichiometric percentage of nitrogen in this material is 1.92 wt. %, assuming a 1:1:1 ratio. The material had a lower percentage of nitrogen than this value, however, as the XRD pattern showed that the reflections of Co$_6$Mo$_6$N had shifted to higher 2θ values, this lower value is to be expected. The XRD pattern showed that the reflections
of \( \text{Co}_2\text{Mo}_3\text{N} \) had not shifted positions and therefore, the lower nitrogen value is not due to a loss of some nitrogen from this phase. Therefore, the loss of nitrogen is expected to be only from the \( \text{Co}_2\text{Mo}_3\text{N} \) phase. The percentage of nitrogen that was lost from the material that was converted to ammonia was ca. 24%. This value was similar to the calculated amount for the material reacted at 700°C. However, \( \text{NH}_3 \) becomes less stable as the temperature is increased.

<table>
<thead>
<tr>
<th>Material</th>
<th>Calculated Stoichiometric Nitrogen Content (wt. %)</th>
<th>Calculated Stoichiometric Carbon Content (wt. %)</th>
<th>Nitrogen Content from Elemental Analysis (wt. %)</th>
<th>Carbon Content from Elemental Analysis (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td><code>\( \text{Co}_2\text{Mo}_3\text{N} \)</code> Pre-reaction</td>
<td>3.34</td>
<td>-</td>
<td>2.67</td>
<td>0.20</td>
</tr>
<tr>
<td><code>\( \text{Co}_2\text{Mo}_3\text{N} \)</code> Post-reaction</td>
<td>3.34</td>
<td>-</td>
<td>0.72</td>
<td>0.34</td>
</tr>
</tbody>
</table>

Table 36: Elemental Analysis for `\( \text{Co}_2\text{Mo}_3\text{N} \)` comparing pre- and post-reaction with 3:1 \( \text{H}_2/\text{Ar} \) at 800°C for 7 hours as shown in Figure 138.

![Figure 140](image-url): Comparison of XRD patterns for `\( \text{Co}_2\text{Mo}_3\text{N} \)` pre- and post-reaction with 3:1 \( \text{H}_2/\text{Ar} \) at 800°C for 7 hours. Reflections marked: – \( \text{Co}_2\text{Mo}_3\text{N} \) (JCPDS file number 01-072-6570), ● \( \text{Co}_3\text{Mo}_3\text{N} \) (JCPDS file number 01-089-7953), ■ \( \beta-\text{Mo}_2\text{N}_{0.76} \) (JCPDS file number 03-065-6236), ● Mo (JCPDS file number 01-071-4645) and ◆ \( \text{Co}_6\text{Mo}_6\text{N} \) (data from [55]).
4.2.3.2.2 XRD Pattern and Elemental Analysis of Co$_2$Mo$_3$N Post 900°C Reaction

The XRD pattern in Figure 141 shows that there was a significant change in the post-reaction material compared to pre-reaction. The material was observed to have completely decomposed to Co$_{0.08}$Mo$_{0.92}$, α-Co and either a cobalt nitride phase or a cobalt molybdenum alloy.

It could be suggested that there was a lattice shift of Co$_2$Mo$_3$N to higher 2θ values as evidenced by two reflections at 40.57° and 42.87° 2θ pre-reaction and 40.65° and 43.52° 2θ post-reaction. However, the other two expected reflections for Co$_{0.08}$Mo$_{0.92}$ are evident in the XRD pattern. In addition, the other reflections due to Co$_2$Mo$_3$N are not apparent in the XRD pattern. Therefore, it is proposed that the material had decomposed under these conditions.

Figure 141: Comparison of XRD patterns for 'Co$_2$Mo$_3$N' pre- and post-reaction with 3:1 H$_2$/Ar at 900°C for 7 hours. Reflections marked: • Co$_2$Mo$_3$N (JCPDS file number 01-072-6570), ● Co$_3$Mo$_3$N (JCPDS file number 01-089-7953), ● β-Mo$_2$N$_{0.76}$ (JCPDS file number 03-065-6236), ○ Co$_{0.08}$Mo$_{0.92}$ (JCPDS file number 01-071-7326), α-Co (JCPDS file number 01-089-4307), ▲ Co$_2$N (JCPDS file number 01-074-8393), + Co$_7$Mo$_6$ (JCPDS file number 00-029-0489).
This result suggests that the lattice nitrogen in the filled β-Mn structured Co₂Mo₃N was reactive at the elevated temperature and that the material was not as stable at 900°C compared to the filled β-Mn structured Ni₂Mo₃N and η-carbide structured Ni₂GaMo₃N. A possible explanation for this difference in stability and lattice nitrogen reactivity could be due to the bonding character of the M-Mo bond (M = Ni, Co) and its influence on the strength of the Mo-N interaction. The difference in electronegativity between Co (1.88) and Mo (2.16) is slightly greater than that for Ni (1.91) and therefore, the interaction is more ionic. The Mo-N bond distances in Co₃Mo₃N are calculated to be 2.113 Å [59] compared to 2.086 Å and 2.097 Å for Ni₂Mo₃N and Ni₂GaMo₃N, respectively [59] [121]. Unfortunately, the Mo-N distances in Co₂Mo₃N have not been reported in the literature to the writer’s knowledge.

The elemental analysis shows that the amount of nitrogen had decreased significantly after reduction at 900°C as presented in Table 37 and as expected. The majority of the lattice nitrogen would have been lost as N₂ as the conductivity did not decrease as would be expected for the decrease in nitrogen observed. The percentage of lattice nitrogen removed from the material that was converted to ammonia was ca. 13%. Carbon was not detected in this sample pre- and post-reaction, contrasting with the other reported samples. However, the weight percentage of carbon in the other samples was very low and therefore, was unlikely to have affected the reduction process.

<table>
<thead>
<tr>
<th>Material</th>
<th>Calculated Stoichiometric Nitrogen Content (%)</th>
<th>Calculated Stoichiometric Carbon Content (%)</th>
<th>Nitrogen Content from Elemental Analysis (%)</th>
<th>Carbon Content from Elemental Analysis (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>‘Co₂Mo₃N’ Pre-reaction</td>
<td>3.34</td>
<td>-</td>
<td>3.82</td>
<td>0.00</td>
</tr>
<tr>
<td>‘Co₂Mo₃N’ Post-reaction</td>
<td>3.34</td>
<td>-</td>
<td>0.48</td>
<td>0.00</td>
</tr>
</tbody>
</table>

*Table 37: Elemental Analysis for ‘Co₂Mo₃N’ comparing pre- and post-reaction with 3:1 H₂/Ar at 900°C for 7 hours.*

4.2.3.2.3 SEM Analysis of Co₂Mo₃N Post 800°C Reaction

The SEM images of the post 800°C material are displayed in Figure 142. The morphology of this material resembled the one for the pre-reaction material and it consisted of a porous material with a rough surface. The pores ranged in size from 1 µm to 70 µm, which is larger than the pre-reaction material, although this observation is statistically limited in view of the comparatively small number of observations.
Figure 142: SEM images of ‘Co$_2$Mo$_3$N’ post-reaction with 3:1 H$_2$/Ar at 800°C. a) 1000x magnification, b) 1000x magnification, c) 2000x magnification and d) 4000x magnification.

The elemental map of the material illustrates that the cobalt and molybdenum were evenly distributed across the sample, as shown in Figure 143. In this sample, there was not an area with higher cobalt concentration as seen for the post 700°C material. This suggests that the material did not undergo segregation at this temperature. The reason for this difference is not clear.

Figure 143: Element Map for ‘Co$_2$Mo$_3$N’ post-reaction with 3:1 H$_2$/Ar at 800°C. Elements: Co (red), Mo (green) and N (blue).
### 4.2.3.2.4 SEM Analysis of Co$_2$Mo$_3$N Post 900°C Reaction

SEM analysis was conducted on this sample to investigate if the decomposition of the material had an effect on the morphology. Previous materials that have decomposed under 3:1 H$_2$/Ar have been shown to have a porous nature after reduction [136], which might prove useful in terms of other applications. Therefore, it would be of interest to examine the morphology post-reaction. The morphology of the material was similar to the pre-reaction sample as observed from the SEM images displayed in Figure 144. The material contained pores and cracks that ranged in size from 1 µm to 100 µm, although as stated earlier, this observation is statistically limited. Therefore, although the material decomposed, there was not a large change in the morphology. However, the material did appear to be more porous post-reaction.

![SEM images](image_url)

**Figure 144:** SEM images of ‘Co$_2$Mo$_3$N’ post-reaction with 3:1 H$_2$/Ar at 900°C. a) 200x magnification, b) 500x magnification, c) 1000x magnification and d) 2000x magnification.

The elemental maps in Figure 145 show that the cobalt and molybdenum were fairly evenly distributed across the sample, although, some areas of the elemental map did not show the presence of molybdenum. This somewhat agrees with the XRD pattern, as although the material had decomposed, cobalt molybdenum alloy phases had been formed and some segregation was observed.
Figure 145: Element Maps for ‘Co\textsubscript{2}Mo\textsubscript{3}N’ post-reaction with 3:1 H\textsubscript{2}/Ar at 900°C. Elements: Co (red), Mo (green) and N (blue).

4.3 Conclusions

In this chapter, the filled $\beta$-Mn structured Co\textsubscript{2}Mo\textsubscript{3}N and the $\eta$-carbide structured Co\textsubscript{3}Mo\textsubscript{3}N were examined for their ammonia synthesis activity and lattice nitrogen reactivity. This was performed in order to analyse the effect the metal composition and crystal structure had on the activity. A comparison could also be made with the filled $\beta$-Mn structured Ni\textsubscript{2}Mo\textsubscript{3}N and $\eta$-carbide structured Ni\textsubscript{2}GaMo\textsubscript{3}N discussed in Chapter 3.

Pure phase Co\textsubscript{2}Mo\textsubscript{3}N could not be synthesised and instead the material was a mixture of the filled $\beta$-Mn structured Co\textsubscript{2}Mo\textsubscript{3}N and the $\eta$-carbide structured Co\textsubscript{3}Mo\textsubscript{3}N, which is consistent with previous literature reports. Three preparation methods were used to synthesise a cobalt molybdenum oxide precursor. This was performed in an attempt to prepare the single phase Co\textsubscript{2}Mo\textsubscript{3}N from the oxide. It was found that the modified Pechini method, that was used to prepare $\beta$-Mn structured Ni\textsubscript{2}Mo\textsubscript{3}N, was the best route to preparing the highest ratio of Co\textsubscript{2}Mo\textsubscript{3}N to Co\textsubscript{3}Mo\textsubscript{3}N as indicated by the relative intensities in the powder XRD patterns. The optimal nitridation conditions were observed to be at 700°C for 3 hours.

The mixed phase ‘Co\textsubscript{2}Mo\textsubscript{3}N’ was shown to be active for ammonia synthesis. It exhibited a comparatively high activity of 208 μmol h\textsuperscript{-1} g\textsuperscript{-1} at 400°C and 159 ± 8 μmol h\textsuperscript{-1} g\textsuperscript{-1} at 700°C. Pure phase Co\textsubscript{3}Mo\textsubscript{3}N has previously been reported to have a rate of 166 ± 2 μmol h\textsuperscript{-1} g\textsuperscript{-1} at 400°C [35].

‘Co\textsubscript{2}Mo\textsubscript{3}N’ was reacted under 3:1 H\textsubscript{2}/Ar at different temperatures to establish the lattice nitrogen reactivity and stability of the material. Co\textsubscript{2}Mo\textsubscript{3}N was shown to retain its structure up to 800°C. Co\textsubscript{3}Mo\textsubscript{3}N lost the majority of the lattice nitrogen at 700°C and 800°C yielding Co\textsubscript{6}Mo\textsubscript{6}N as expected. Therefore, the bulk lattice nitrogen in this phase was more reactive
than in Co<sub>2</sub>Mo<sub>3</sub>N. However, when reacted at 900°C, the mixed-phase material decomposed to the metal constituent components and most of the lattice nitrogen was lost. Therefore, it can be concluded that the Co<sub>2</sub>Mo<sub>3</sub>N, Co<sub>6</sub>Mo<sub>6</sub>N and Co<sub>3</sub>Mo<sub>3</sub>N phases were not stable under these conditions. In Chapter 3, it was shown that the filled β-Mn structured Ni<sub>2</sub>Mo<sub>3</sub>N and the η-carbide structured Ni<sub>2</sub>GaMo<sub>3</sub>N were not reduced at this temperature. Consequently, these results suggest that the lattice nitrogen reactivity of these ternary nitrides is a complex relationship between the metal composition and structure type.
5. Iron Molybdenum Materials

5.1 Introduction

As the lattice nitrogen reactivity of \( \eta \)-carbide \( \text{Co}_3\text{Mo}_3\text{N} \) and \( \text{Ni}_2\text{GaMo}_3\text{N} \) has been shown to be different, it would be of interest to investigate the activity and lattice nitrogen reactivity of another \( \eta \)-carbide structured nitride. If a nitride with a different metal composition was studied, it may be possible to gain yet further insight into the metal composition-activity relationship.

The \( \eta \)-carbide structured \( \text{Fe}_3\text{Mo}_3\text{N} \) is a known ammonia synthesis catalyst [35] [39] that has a lower activity than \( \text{Co}_3\text{Mo}_3\text{N} \) and therefore, has been less well studied [35] [135]. \( \text{Fe}_3\text{Mo}_3\text{N} \) is isostructural with \( \text{Co}_3\text{Mo}_3\text{N} \) as both have the \( \eta \)-6 carbide structure [59] [60]. The lattice nitrogen in \( \text{Co}_3\text{Mo}_3\text{N} \) has been shown to be highly reactive under Ar/H\(_2\) atmosphere. Although \( \text{Fe}_3\text{Mo}_3\text{N} \) is isostructural with \( \text{Co}_3\text{Mo}_3\text{N} \), the lattice nitrogen of this material has been revealed to be less reactive [35] [135]. Up to a temperature of 800°C, \( \text{Fe}_3\text{Mo}_3\text{N} \) has been observed to be stable under 3:1 H\(_2\)/Ar and the loss of lattice nitrogen was minimal. Powder neutron diffraction data showed that the nitride did not lose bulk nitrogen [135] and therefore, under 3:1 H\(_2\)/Ar, ammonia is not produced from the ternary nitride bulk lattice nitrogen. There is the possibility that the bulk nitrogen is not mobile within this system and that a surface Mars-van Krevelen type mechanism could still occur. In order to further investigate this possibility, \( \eta \)-carbide structured \( \text{Fe}_3\text{Mo}_3\text{N} \) and \( \text{Fe}_3\text{Mo}_3\text{C} \) have been synthesised and their comparative performance for ammonia synthesis is examined in this chapter.

5.1.1 Ammonia Synthesis Activity of \( \text{Co}_3\text{Mo}_3\text{C} \) and \( \text{Fe}_3\text{Mo}_3\text{C} \)

The replacement of lattice nitrogen with carbon is another method that can be used to investigate the activity of these materials. As stated in Chapter 3, there are two possible explanations for the high activity of \( \text{Co}_3\text{Mo}_3\text{N} \).

As mentioned in the introduction of Chapter 3, \( \text{Co}_3\text{Mo}_3\text{C} \) has been studied for ammonia synthesis activity in order to see if the lattice nitrogen is required in this material [54]. It was found that the activity of this material occurred at higher temperatures than for \( \text{Co}_3\text{Mo}_3\text{N} \) and was associated with the substitution of lattice carbon with nitrogen.

As \( \text{Fe}_3\text{Mo}_3\text{N} \) was found to be less reducible than \( \text{Co}_3\text{Mo}_3\text{N} \) [35], it would be of interest to investigate the role the lattice nitrogen has in the iron molybdenum material. The synthesis
and testing of Fe₃Mo₃C would give an insight into the part the lattice nitrogen plays and comparisons could be made between Fe₃Mo₃C and Co₃Mo₃C.

5.1.2 Synthesis of Fe₃Mo₃N
One of the most widely applied ways of preparing Fe₃Mo₃N was devised by Bem et al. [49]. In this method, a 0.25 M aqueous solution of FeCl₂ and a 0.55 M aqueous solution of Na₂MoO₄.2H₂O were mixed together and the resulting product was FeMoO₄. The nitride was then prepared by ammonolysis of the oxide precursor. Bem et al. also stated that the nitride can be formed by using a 5% H₂/N₂ nitridation mixture [49]. The XRD pattern of Fe₃Mo₃N revealed that the material was phase pure and therefore, this two-step method was shown to be successful. Other research that followed this method has also resulted in the formation of single phase Fe₃Mo₃N [135] [59] [74].

A modification of this method was investigated by McKay et al. [35], who used Fe(NO₃)₃.9H₂O as the starting material. Unsurprisingly, the oxide precursor formed from this material was different from when FeCl₂ was used. The XRD pattern showed that the Fe₂(MoO₄)₃ phase was prepared instead of FeMoO₄. After ammonolysis of the oxide precursor, the XRD pattern showed that the desired nitride was formed along with substantial amounts of γ-Mo₂N impurity [35] [137], which is a consequence of the 2/3 Fe/Mo stoichiometric ratio in the precursor phase [135].

Another method of preparing Fe₃Mo₃N involves plasma nitridation of the oxide precursor with N₂/H₂ [74]. However, an FeMo alloy impurity was also formed alongside the desired ternary nitride. It was stated that the alloy was formed as the temperature was too high and hard to control due to thermal runaway. Fe₃Mo₃N has also been prepared by ball-milling of Mo₂N with iron [138] and heating hydrolysed alkanolamine complexed precursors in ammonia at 950°C [139]. A one step synthesis of Fe₃Mo₃N has been proposed by heating Fe₂O₃, molybdenum and sodium azide in an autoclave at 750°C for 10 hours [140]. Fe₃Mo₃N was also synthesised by heating iron powder and molybdenum powder under 10% H₂/N₂ at 975°C for 36 hours [60]. However, a small amount of molybdenum metal was observed in the XRD pattern when this method was used.

5.1.3 Synthesis of Fe₃Mo₃C
As with the formation of Ni₂Mo₃C, issues arose when the TPR method was used to synthesise Fe₃Mo₃C from the oxide precursor under CH₄/H₂ [141] [105]. Oyama et al. noted that the resulting product was a mixture of phases with the major phase having a hexagonal structure, which was not definitively identified [141]. Alconchel also observed a
mixture of phases, with the products being $\beta$-Mo$_2$N and Mo$_{12}$Fe$_{22}$C$_{10}$ [105]. Therefore, Alconchel et al. decided to prepare Fe$_3$Mo$_3$C by carburisation of Fe$_3$Mo$_3$N with CH$_4$/H$_2$ via topotactic lattice exchange of N by C [105]. The XRD pattern of this material showed that the single-phase ternary carbide was formed up to a temperature of 980 K.

Other methods have been used in order to prepare Fe$_3$Mo$_3$C, for example the ball milling of Fe, Mo and carbon in vacuum for 194 hours [142]. However, iron metal was also formed alongside the ternary carbide. Tsuchida attempted to prepare single phase Fe$_3$Mo$_3$C by ball milling Fe, Mo and carbon for 30 minutes at 700°C to 900°C, after having ground the sample together for 3 hours [143]. The author stated that the preparation of the carbide depended on the homogeneity of the mixture. Nevertheless, a mixture of Fe$_3$Mo$_3$C and FeMoO$_3$ was observed in the XRD pattern of the resultant material.

Other sources of carbon have also been used to synthesise Fe$_3$Mo$_3$C. The single-phase carbide has been prepared using decolourising carbon at 950°C under argon gas [48]. Fe$_3$Mo$_3$C was also prepared by a sol-gel method using chitosan solution, FeCl$_2$ and (NH$_4$)$_2$MoO$_4$ to form FeMoO$_4$, which was subsequently heat treated under Ar/H$_2$ [144]. However, Mo$_2$C was formed as an impurity when this method was used.

5.2 Results and Discussion
5.2.1 Iron Molybdenum Nitride (Fe$_3$Mo$_3$N)
5.2.1.1 Iron Molybdenum Oxide (FeMoO$_4$)

The FeMoO$_4$ precursor was targeted in order to synthesise pure phase Fe$_3$Mo$_3$N by the nitridation of the oxide with 3:1 H$_2$/N$_2$ mixture. The XRD pattern of the oxide precursor prepared in this work is displayed in Figure 146. It can be seen that the resultant material comprised a mixture of FeMoO$_4$, Fe$_2$(MoO$_4$)$_3$ and Fe$_2$O$_3$. Therefore, although iron (II) chloride tetrahydrate was used as a starting material, a mixture of phases comprising iron in different oxidation states (+2 and +3) was still observed. The elemental analysis showed that, as expected, the material did not contain any carbon, hydrogen or nitrogen.
Figure 146: XRD pattern of iron molybdenum oxide (FeMoO₄). Reflections marked: ■ FeMoO₄ (JCPDS file number 00-028-0488), + Fe₂O₃ (JCPDS file number 01-076-4579) and ○ Fe₂(MoO₄)₃ (JCPDS file number 01-074-6404).

The Raman spectrum for the iron molybdenum oxide is presented in Figure 147. The Raman bands at positions of approximately 342, 775, 808, 921 and 967 cm⁻¹ were attributed to Fe₂(MoO₄)₃. These Raman shifts are in very good agreement with Fe₂(MoO₄)₃ spectra reported in the literature [105] [145]. The band at 808 cm⁻¹ is also observed in MoO₃ as a strong band. The bands at 921 and 967 cm⁻¹ are assigned to the symmetric stretching modes of MoO₄ units, the bands at 775 and 808 cm⁻¹ are the anti-symmetric stretching modes, the band at 342 cm⁻¹ is assigned to a bending mode and the bands below 280 cm⁻¹ are due to lattice modes [146]. The strong bands at 967 and 775 cm⁻¹ have been assigned in the literature as Mo in a tetrahedral coordination in Fe₂(MoO₄)₃ [145]. It has also been suggested that the band at 808 cm⁻¹ could be due to octahedrally coordinated Mo species, since MoO₃, which has octahedral Mo coordination, has a band at a similar wavenumber [145]. The bands at 593 and 212 cm⁻¹ are observed in the Raman spectrum for Fe₂O₃ and the bands at 921, 342 and 276 cm⁻¹ are seen in the Raman spectrum of β-FeMoO₄ [147], which corresponds to the XRD assignment presented above. However, the other bands expected for FeMoO₄ and Fe₂O₃ were not observed in the Raman spectrum in Figure 147. It is currently unclear why this is the case.
SEM analysis was performed in order to see if the different phases could be distinguished on the basis of, for example, differing morphology. The representative SEM images for the oxide precursor are shown in Figure 148. The material had an irregular morphology and appeared to consist of rounded particles. The material had a surface area of 1 m$^2$/g, a pore volume of 0.02 cc/g and an average pore radius of 20.31 Å. To the author’s knowledge, other groups that used a similar preparation method did not publish SEM images of the iron molybdenum oxide [59] [148]. Fe$_2$(MoO$_4$)$_3$, for example, has been shown to have different morphologies depending on the preparation method [149] [150]. The different oxides did not appear to have distinguishable morphologies.
The EDX weight percentages for each element in the oxide precursor are provided in Table 38. For FeMoO₄, the percentage of iron, molybdenum and oxygen in the sample should be 25.88 wt. %, 44.46 wt. % and 29.66 wt. % respectively. However, the XRD pattern showed that the material was a mixture of phases containing Fe₂(MoO₄)₃, FeMoO₄ and Fe₂O₃. From the EDX analysis, the calculated stoichiometry of this material is Fe₅Mo₄O₂₄. This suggests that the three oxides are present in equal proportions, although, the percentage of oxygen would be lower than the obtained value. Therefore, the three phases were present in the material, agreeing with the XRD pattern.

<table>
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<th>Area</th>
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<th>Mo weight (%)</th>
<th>O weight (%)</th>
</tr>
</thead>
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<td><strong>36</strong></td>
<td><strong>37</strong></td>
</tr>
</tbody>
</table>

Table 38: EDX values for iron molybdenum oxide (FeMoO₄).
5.2.1.2 Iron Molybdenum Nitride (Fe$_3$Mo$_3$N)

Although the XRD pattern of the oxide precursor showed it contained a mixture of Fe$_2$(MoO$_4$)$_3$, FeMoO$_4$, and Fe$_2$O$_3$, reasonably phase-pure Fe$_3$Mo$_3$N was formed after ammonolysis. However, small traces of MoN impurity were apparent in the XRD pattern as shown in Figure 149.

The elemental analysis showed that the material contained 4.27 wt. % nitrogen (C: 0.00 wt. %, H: 0.00 wt. %, N: 4.27 wt. %). The stoichiometric weight percentage of nitrogen in Fe$_3$Mo$_3$N is 2.98 wt. %. Therefore, the nitride contained a considerably higher percentage of nitrogen than the calculated stoichiometric content. However, the excess nitrogen will be due to the molybdenum nitride impurity and any NH$_x$ species on the surface of the material. From the XRD pattern, the MoN phase content appeared to be very low and therefore, the contribution from this phase would be small. Hence, the excess nitrogen is more likely due to the NH$_x$ species on the surface of the material.

![XRD pattern of iron molybdenum nitride (Fe$_3$Mo$_3$N).](image)

Figure 149: XRD pattern of iron molybdenum nitride (Fe$_3$Mo$_3$N). Reflections marked: ▼ Fe$_3$Mo$_3$N (JCPDS file number 00-048-1408) and MoN (JCPDS file number 01-073-9468).

Raman spectroscopy was used to characterise possible surface oxide species on the nitride. The presence of an oxide surface layer may affect the ammonia synthesis activity and
therefore, it is important to observe if one occurs on the surface of the material. The Raman spectra of Fe$_3$Mo$_3$N is presented in Figure 150. The Raman bands at positions of 967, 927, 806, 775 and 344 cm$^{-1}$ were attributed to Fe$_2$(MoO$_4$)$_3$ [145] [146]. These Raman bands match the spectrum observed for the oxide precursor in Figure 147. These bands have been assigned in the literature to the MoO$_4$ vibrations [146]. However, it has been shown that FeMoO$_4$ has a similar Raman spectrum when a high-power laser is used [151]. It has been suggested by Boucherit et al. that the Fe$^{2+}$ oxidises to Fe$^{3+}$ and possibly transforms to Fe$_2$(MoO$_4$)$_3$. However, iron would need to be lost from the material in order for this process to occur. The presence of Fe$_2$(MoO$_4$)$_3$ in the Raman spectrum of Fe$_3$Mo$_3$N has been reported previously in the literature [105]. It has been shown that Fe$_2$(MoO$_4$)$_3$ and Fe$_2$O$_3$ are the products of the oxidation of the nitride [59].

The results from the Raman spectrum demonstrate that, as expected in view of the passivation treatment conducted prior to discharge from the ammonolysis reactor, there was a non-XRD apparent oxide layer covering the surface of the nitride.

![Raman spectrum of iron molybdenum nitride (Fe$_3$Mo$_3$N).](image)

Figure 150: Raman spectrum of iron molybdenum nitride (Fe$_3$Mo$_3$N).

In order to compare the activity of the nitride and carbide, the morphology of the two materials has to be similar to remove any concerns that effects arising from structure sensitivity might be incorrectly ascribed to composition. Therefore, SEM analysis of the nitride was performed in order for a comparison with the topotactically synthesised carbide
to be discussed later to be made. Figure 151 shows representative SEM images for Fe₃Mo₃N. The SEM images show a similar morphology to that of the oxide precursor. It can be seen that the morphology of the sample appeared to consist of rounded particles. The material had a surface area of 13 m²/g, a pore volume of 0.07 cc/g and an average pore radius of 30.78 Å. In the literature, the surface area of the nitride ranges from 4 to 18 m²/g [148] [94] [152] and therefore, this result is in agreement with the published work. Since the sample had an oxide surface layer, the BET surface area may not be representative of the area exhibited by the sample during testing.

Previous studies by groups that used a similar preparation method had a different morphology. Their images showed smooth, rounded particles with an irregular morphology [59] [148] [137]. The η-carbide structured Co₃Mo₃N was shown to consist of needles when prepared by ammonolysis [54]. However, ammonolysis of an oxide precursor generally results in a pseudomorphic transformation. As there were three phases present in the oxide precursor, this transformation is complicated. However, there did not appear to be different morphologies in the oxide precursor.

![Figure 151: SEM images of iron molybdenum nitride (Fe₃Mo₃N). a) 1000x magnification, b) 2000x magnification, c) 6000x magnification and d) 6000x magnification.](image)

An iron only containing component was observed in the XRD pattern for the oxide precursor and a molybdenum nitride impurity was seen in the XRD pattern of the nitride. Therefore, an elemental map was performed for this material in order to see if there were
areas of phase separation. The elemental map in Figure 152 shows that the iron, molybdenum and nitrogen were evenly dispersed across the sample.

Figure 152: Element Map for Fe₃Mo₃N. Elements: Fe (red), Mo (green) and N (blue).

The EDX analysis for Fe₃Mo₃N is given in Table 39. The stoichiometric percentage of iron, molybdenum and nitrogen in the sample is 35.69 wt. %, 61.32 wt. % and 2.98 wt. %, respectively. The nitrogen weight percentage was greater than expected and was highly variable. However, the limitations of EDX for light element analysis should be taken into consideration. As with the oxide precursor, the percentage of molybdenum and iron were approximately the same as the expected stoichiometric values.

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Table 39: EDX values for iron molybdenum nitride (Fe₃Mo₃N).
5.2.1.3 Ammonia Synthesis at 400°C for Fe₃Mo₃N

Fe₃Mo₃N has previously been examined for its ammonia synthesis activity [35] [39] [94] and lattice nitrogen reactivity [35]. The highest ammonia synthesis rates for Fe₃Mo₃N at 400°C and ambient pressure which have been reported are 143 µmol h⁻¹ g⁻¹ [39] and 95 µmol h⁻¹ g⁻¹ [35]. However, these materials contained impurities, including γ-Mo₂N. The γ-Mo₂N phase is a known ammonia synthesis catalyst and therefore, it would be expected to contribute to the ammonia synthesis activity. The pure phase Fe₃Mo₃N has previously been reported to have a rate of 91 µmol h⁻¹ g⁻¹ at 400°C [135]. Therefore, it appears that the nitride has a similar activity to the material containing the impurity.

Fe₃Mo₃N was tested at 400°C under 1:3 ratio N₂/H₂ at atmospheric pressure for 7.75 hours in order to confirm the activity of the material and to make a comparison with the related carbide (as presented later in the chapter). The material was first pre-treated at 700°C for 2 hours under 1:3 ratio N₂/H₂ to remove the passivation layer, before the temperature was reduced to the reaction temperature. The conductivity profile of the material is shown in Figure 153. The ammonia synthesis rate of Fe₃Mo₃N at 400°C was 74 ± 1 µmol h⁻¹ g⁻¹ and at 700°C was 137 ± 7 µmol h⁻¹ g⁻¹. This rate was lower than the ones reported previously and this may be due to the difference in morphology.

Figure 153: Conductivity profile for Fe₃Mo₃N reacted with 3:1 H₂/N₂ at 700°C for 2 hours and 400°C for 7.75 hours.
The XRD pattern in Figure 154 shows that there did not appear to be any major change in the Fe$_3$Mo$_3$N phase upon reaction. However, the MoN impurity present in the material was reduced to Mo$_2$N during the reaction. The elemental analysis in Table 40 shows that the percentage of nitrogen present in the material had decreased compared to pre-reaction. The percentage of nitrogen present in the material was comparable to the expected stoichiometric value of 2.98 wt. % for Fe$_3$Mo$_3$N. The decrease in nitrogen could be due to the reduction of the molybdenum nitride or the loss of some surface nitrogen from the ternary nitride. The total amount of N lost compared to the total amount of ammonia produced was ca. 55 %. Therefore, there is definitely a catalytic component to the results for Fe$_3$Mo$_3$N.

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<th>Material</th>
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<th>Calculated Stoichiometric Carbon Content (wt. %)</th>
<th>Nitrogen Content from Elemental Analysis (wt. %)</th>
<th>Carbon Content from Elemental Analysis (wt. %)</th>
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<td>Fe$_3$Mo$_3$N Post-reaction</td>
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<td>2.86</td>
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Table 40: Elemental Analysis for Fe$_3$Mo$_3$N post-reaction with 3:1 H$_2$/N$_2$ at 700°C for 2 hours and 400°C for 7.75 hours.

Figure 154: XRD pattern for Fe$_3$Mo$_3$N post-reaction with 3:1 H$_2$/N$_2$ at 400°C for 7.75 hours. Reflections marked: ▼ Fe$_3$Mo$_3$N (JCPDS file number 00-048-1408) and ♦ Mo$_2$N (JCPDS file number 00-025-1368).
SEM analysis was performed in order to examine if any changes occurred to the morphology or structure of Fe₃Mo₃N during the ammonia synthesis reaction. The representative SEM images of the post-reaction material are displayed in Figure 155. The material had an irregular structure and the morphology was similar to the pre-reaction material. The element map in Figure 156 shows that the even iron and molybdenum distribution had been retained from the pre-reaction sample.

Figure 155: SEM images of Fe₃Mo₃N post reaction with 3:1 H₂/N₂ at 400°C for 7.75 hours. a) 1000x magnification, b) 2000x magnification, c) 4000x magnification and d) 6000x magnification.

Figure 156: Element Map for Fe₃Mo₃N post-reaction with 3:1 H₂/N₂ at 400°C. Elements: Fe (red), Mo (green) and N (blue).
5.2.1.4 Ammonia Synthesis at 500°C for Fe$_3$Mo$_3$N

Fe$_3$Mo$_3$N was tested for ammonia synthesis activity at 500°C and atmospheric pressure under 3:1 H$_2$/N$_2$ in order to compare the activity of the nitride with the ternary carbide (as presented later). As before, the material was pre-treated at 700°C for 2 hours under 1:3 ratio N$_2$/H$_2$, before the temperature was reduced to 500°C. The reaction profile showed a linear decrease in conductivity over time and there was no induction period as seen in Figure 157. The ammonia synthesis rate of Fe$_3$Mo$_3$N was determined to be 403 µmol h$^{-1}$ g$^{-1}$ at 500°C. The material had a rate of 74 ± 1 µmol h$^{-1}$ g$^{-1}$ at 400°C. Therefore, the material was much more active at the higher temperature as might be expected. In comparison, Co$_3$Mo$_3$N has a rate of 489 ± 17 µmol h$^{-1}$ g$^{-1}$ [54] at 500°C and ambient pressure. This suggests that these two nitrides have similar specific activities as they have similar surface areas (Co$_3$Mo$_3$N: 18 m$^2$/g [55] and Fe$_3$Mo$_3$N: 13 m$^2$/g).

![Conductivity profile for Fe$_3$Mo$_3$N reacted with 3:1 H$_2$/N$_2$ at 700°C for 2 hours and 500°C for 6 hours.](image)

The XRD pattern in Figure 158 illustrates that the Fe$_3$Mo$_3$N did not change phase. However, as with the post 400°C reaction material, the MoN impurity present in the pre-reaction material was reduced during the reaction. The elemental analysis shows that there was a significant decrease in the percentage of nitrogen compared to the pre-reaction sample. This decrease in nitrogen could be due to the reduction of the molybdenum nitride or, more likely, the loss of NH$_x$ species from the surface of the material. The post-reaction material had a similar percentage of nitrogen (2.91 wt. %) to the expected stoichiometric
value of 2.98 wt. % for Fe₃Mo₃N. The total amount of N lost versus the total amount of NH₃ produced was ca. 42 % and therefore, there was a catalytic component to the result. Additionally, the treatment stage at 700°C would be expected to lead to the loss of NHₓ surface groups to form N₂.

Figure 158: XRD pattern for Fe₃Mo₃N post-reaction with 3:1 H₂/N₂ at 500°C for 6 hours. Reflections marked: ▼ Fe₃Mo₃N (JCPDS file number 00-048-1408) and ◀ Mo₁₆N₇ (JCPDS file number 00-023-1256).

The SEM images of the material post 500°C reaction are exhibited in Figure 159. The morphology of the material was similar to the pre-reaction material. The material consisted of rounded particles.
Figure 159: SEM images of Fe$_3$Mo$_3$N post reaction with 3:1 H$_2$/N$_2$ at 500°C. a) 1000x magnification, b) 2000x magnification, c) 4000x magnification and d) 6000x magnification.

The elemental map in Figure 160 shows that the iron and molybdenum were fairly evenly distributed across the sample.

Figure 160: Element Map for Fe$_3$Mo$_3$N post-reaction with 3:1 H$_2$/N$_2$ at 500°C. Elements: Fe (red), Mo (green) and N (blue).

5.2.1.5 Lattice Nitrogen Reactivity of Fe$_3$Mo$_3$N at 900°C

In order to determine the reactivity of lattice nitrogen in Fe$_3$Mo$_3$N, the material has been reacted under 3:1 H$_2$/Ar at 900°C. The material has previously been investigated from 400°C to 800°C for its lattice nitrogen reactivity and it was found to be less reducible than
Co$_3$Mo$_3$N [35], even though they have the same structure. It was found that the molybdenum nitride component in the mixture of FeMo$_3$N and γ-MoN decomposed to Mo metal whereas there was no shift in peak positions of the Fe$_3$Mo$_3$N in the resultant XRD pattern [135]. If the bulk lattice nitrogen was active for ammonia synthesis via a Mars-van Krevelen mechanism, it would be expected that a reduction in the bulk nitrogen content of Fe$_3$Mo$_3$N might occur when reduced under Ar/H$_2$.

Figure 161 shows that only a small amount of ammonia was produced and therefore, the lattice nitrogen was relatively unreactive in terms of ammonia production under Ar/H$_2$ at 900°C. There was a decrease in conductivity of 48 µS/cm over the 7 hours. However, as discussed in the previous chapter, ammonia synthesis is unfavourable at this temperature and ammonia will decompose [99] and, therefore, some lattice nitrogen may be lost as N$_2$.

![Figure 161: Conductivity profile for Fe$_3$Mo$_3$N reacted with 3:1 H$_2$/Ar at 900°C for 7 hours.](image)

The XRD pattern in Figure 162 shows that the material decomposed to Mo metal and α-Fe and that there was an iron nitride phase. Minuscule peaks due to Fe$_3$Mo$_3$N can also be observed at 42° and 72° 20. This suggests that the lattice nitrogen was mainly lost as dinitrogen and that this loss is associated with the phase decomposition. In a number of respects, the XRD pattern of this material is reminiscent of the one for Co$_2$Mo$_3$N/Co$_3$Mo$_3$N post 900°C reaction, which was presented in Figure 141 in the previous chapter. Both Fe$_3$Mo$_3$N and Co$_2$Mo$_3$N/Co$_3$Mo$_3$N were not as stable at 900°C as Ni$_2$Mo$_3$N and Ni$_2$GaMo$_3$N. As stated for ‘Co$_2$Mo$_3$N’, one possible reason for this difference in stability
could be due to the bonding character in the materials. It has been shown that the bonding between the M-Mo (M = Ni, Fe, Co) is covalent in character [59]. In the case of Fe$_3$Mo$_3$N, the difference in electronegativity between Fe (1.83 on the Pauling scale) and Mo (2.16 on the Pauling scale) is larger than that of Ni (1.91 on the Pauling scale). This suggests that the Fe-Mo bond is more ionic than the Ni-Mo bond in Ni$_2$Mo$_3$N. Furthermore, the Mo-N bond distances in Fe$_3$Mo$_3$N, Ni$_2$Mo$_3$N and Ni$_2$GaMo$_3$N were calculated to be 2.111 Å, 2.086 Å and 2.097 Å, respectively [135] [59] [121]. Therefore, the difference in lattice nitrogen reactivity could be due to the secondary effect the iron, cobalt or nickel may have on the Mo-N sub-lattice.

Figure 162: Comparison of XRD patterns for Fe$_3$Mo$_3$N pre- and post-reaction with 3:1 H$_2$/Ar at 900°C for 7 hours. Reflections marked: ▼ Fe$_3$Mo$_3$N (JCPDS file number 00-048-1408), ○ α-Fe (JCPDS file number 01-085-1410), ● Mo (JCPDS file number 01-089-5023) and ▲ ε-Fe$_3$N (JCPDS file number 01-073-2101).

The elemental analysis shows that the percentage of nitrogen had significantly decreased after reduction with 3:1 H$_2$/Ar at 900°C compared to pre-reaction as shown in Table 41 as would be expected for the decomposition of the material. The percentage of lattice nitrogen that was lost from Fe$_3$Mo$_3$N that was converted to ammonia was ca. 5.6%. 

216
<table>
<thead>
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<th>Material</th>
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<th>Carbon Content from Elemental Analysis (%)</th>
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Table 41: Elemental Analysis for Fe₃Mo₃N post-reaction with 3:1 H₂/Ar at 900°C for 7 hours.

The Raman spectrum of the post reduction material, displayed in Figure 163, appears to be somewhat different compared to the pre-reaction spectrum as would be expected due to the material decomposing. The bands at 816 and 273 cm⁻¹ could be due to MoO₃ [90]. This could result from a surface oxide layer on the molybdenum metal. The Raman bands at positions of 970, 924, 780 and 369 cm⁻¹ could be attributed to Fe₂(MoO₄)₃ [146]. Although the XRD pattern only showed trace amounts of Fe₃Mo₃N were present in the material.

![Raman spectrum of Fe₃Mo₃N post-reaction with 3:1 H₂/Ar at 900°C.](image)

**Figure 163:** Raman spectrum of Fe₃Mo₃N post-reaction with 3:1 H₂/Ar at 900°C.

SEM analysis was conducted to see if the reduction of the material had an effect on the morphology. Typical SEM images of Fe₃Mo₃N post-reaction with 3:1 H₂/Ar are presented in Figure 164. The morphology was retained from the pre-reaction material and consisted of an irregular morphology and rounded particles. The morphology of the Fe₃Mo₃N, ‘Co₂Mo₃N’, Ni₂Mo₃N and Ni₂GaMo₃N post-reaction with 3:1 H₂/Ar were different.
between each other, suggesting that the lattice nitrogen reactivity was not affected by the morphology of the material.

Figure 164: SEM images of Fe$_3$Mo$_3$N post-reaction with 3:1 H$_2$/Ar at 900°C. a) 1000x magnification, b) 2000x magnification, c) 4000x magnification and d) 6000x magnification.

The element maps in Figure 165 show that there was a fairly even distribution of nickel and molybdenum over the sample, even though the material decomposed.

Figure 165: Element Maps for Fe$_3$Mo$_3$N post-reaction with 3:1 H$_2$/Ar at 900°C. Elements: Fe (red), Mo (green) and N (blue).

The EDX data for the post-reaction sample is provided in Table 42. Nitrogen was not detected in the areas measured by EDX. However, the elemental maps in Figure 165 detected some nitrogen, suggesting that it was present in the material in small amounts.
This agrees with the CHN analysis that showed a small amount of nitrogen remained in the material post-reaction. The ratio of iron to molybdenum is approximately as would be expected for this material.

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Table 42: EDX values for Fe$_3$Mo$_3$N post-reaction with 3:1 H$_2$/Ar at 900°C.

The decomposition of Fe$_3$Mo$_3$N was investigated by thermogravimetric analysis of the pre-reaction material under 3:1 H$_2$/Ar. The TGA curve and first derivative weight change of the material heated from room temperature to 1000°C at a ramp rate of 10°C/min under 3:1 H$_2$/Ar is provided in Figure 166. The first feature of the TGA curve is a weight loss of approximately 1.29 wt. % at 408°C and the second is a weight loss of 2.68 wt. % at 496°C. These could be due to the removal of the passivation layer or the loss of adsorbed water and needs to be investigated further.

At 668°C, a small feature is observed and results from a weight loss of 0.96 wt. %. This could be due to the decomposition of the molybdenum nitride to Mo metal as it has been previously shown to be reduced at this temperature under 1:3 Ar/H$_2$ [135]. The feature at 816°C is due to a weight loss of 3.25 wt. % and could be due to the decomposition of the material. It has previously been shown by in-situ powder neutron diffraction that the Fe$_3$Mo$_3$N does not decompose at 800°C under 1:3 Ar/H$_2$ and the nitrogen content remained unchanged [135]. Hence, the decomposition must occur between 800°C and 900°C. The expected weight loss due to the removal of nitrogen from the material and the decomposition of Fe$_3$Mo$_3$N to Fe and Mo metal is 2.98 wt. %. Therefore, this value agrees quite well with the weight loss of 3.25 wt. % that was observed.

The final feature at 929°C results in a weight loss of 6.94 wt. % and could be due to removal of some Mo metal from the material as it is volatile at high temperatures. However, this would need to be investigated further.
Figure 166: TGA and derivative weight profile of Fe$_3$Mo$_3$N under 75% H$_2$/Ar in the range from room temperature to 1000°C.

5.2.2 Iron Molybdenum Carbide (Fe$_3$Mo$_3$C)

Fe$_3$Mo$_3$C was prepared by carburisation of Fe$_3$Mo$_3$N with 20% CH$_4$/H$_2$ at 560°C. At this carburisation temperature, the η-carbide structure of the iron molybdenum material was maintained as seen in Figure 167.
Figure 167: XRD pattern of iron molybdenum carbide (Fe$_3$Mo$_3$C). Reflections marked: ▼ Fe$_3$Mo$_3$C (JCPDS file number 00-047-1191), ● α-Fe (JCPDS file number 01-089-7194) and ○ η-MoC (JCPDS file number 01-089-4305).

There appears to have been a shift in position of the peaks associated with the Fe$_3$Mo$_3$N to lower 2θ values as shown in Figures 168 and 169. This suggests that there was replacement of the lattice nitrogen with carbon and the formation of either Fe$_3$Mo$_3$C or a carbonitride phase. The atomic radii of carbon and nitrogen are 70 pm and 65 pm, respectively [125] and therefore, there is an increase in the unit cell size when carbon is incorporated. This carburisation process is topotactic and pseudomorphic in nature and therefore, the potentially complicating issue of changed morphology should not be a concern in this case. The MoN impurity had also undergone carburisation to form η-MoC. However, an iron phase was detected in the carburised material that was not present in the nitride sample. This suggests that there may have been a minor degree of phase instability, although the intensity of the reflections associated with the iron phase were very low. Reflections for Mo metal were not observed at 40.52° or 58.61° 2θ.

The elemental analysis showed that carbon was present in the material after carburisation and there was no nitrogen detected (C: 3.48%, H: 0.00% and N: 0.00%). Therefore, this would suggest that the material had been converted to the carbide. The expected stoichiometric value for carbon in Fe$_3$Mo$_3$C is 2.57%. The carbon content of the material
was greater than the calculated stoichiometric ratio. This could be a concern if the carbon encapsulates the ternary phase covering active sites.

Figure 168: Comparison of XRD patterns for Fe₃Mo₃N and Fe₃Mo₃C showing shift in peaks associated with Fe₃Mo₃N.

Figure 169: Comparison of XRD patterns between Fe₃Mo₃N (black) and Fe₃Mo₃C (red).
Raman spectroscopy was undertaken to investigate the nature of the excess carbon which was generated from carburisation. Bands associated with graphitic like carbon, which would be expected to occur at approximately 1320 and 1575 cm\(^{-1}\) were not observed in the spectrum, as shown in Figure 170. The bands at 973, 778 and 350 cm\(^{-1}\) were observed in the nitride and are assigned to Fe\(_2\)(MoO\(_4\))\(_3\) [146]. Therefore, an oxide layer was covering the surface of the carbide. Alconchel et al. did not detect any bands in the Raman spectrum of Fe\(_3\)Mo\(_3\)C [105]. However, these authors applied a lower laser power in their measurement. It has previously been shown that as the carbon content of a material increases, the fluorescence of the background increases [153]. Therefore, the fluorescence observed for this material may be due to the presence of carbon.

![Raman spectrum of iron molybdenum carbide (Fe\(_3\)Mo\(_3\)C).](image)

**Figure 170:** Raman spectrum of iron molybdenum carbide (Fe\(_3\)Mo\(_3\)C).

In order to compare the activity of the carbide with the nitride, it is important that the carburisation process was topotactic as reported. SEM images of the carbide have been taken in order to compare the morphology of the material with the nitride. Representative SEM images of Fe\(_3\)Mo\(_3\)C are displayed in Figure 171. These SEM images show the material had a very similar morphology to both the oxide precursor and the nitride as the material had an irregular morphology and contained rounded particles. The carburisation process is known to be topotactic and pseudomorphic for the iron molybdenum material [105]. It is important that the morphology of the nitride and carbide are the same, so that any differences in activity between the two materials cannot be related simply to a change...
in morphology. There was no evidence that any additional structures, such as carbon nanotubes, had been formed, which is consistent with the Raman spectroscopic analysis presented above.

Figure 171: SEM images of iron molybdenum carbide (Fe₃Mo₃C). a) 1000x magnification, b) 2000x magnification, c) 6000x magnification and d) 6000x magnification.

The EDX analysis for Fe₃Mo₃C is provided in Table 43. The stoichiometric percentage of iron, molybdenum and carbon in the sample is 35.85 wt. %, 61.58 wt. % and 2.57 wt. %, respectively. The carbon weight percentage was greater than the expected stoichiometric percentage of carbon in Fe₃Mo₃C. However, EDX can be limited in analysing light elements and also it should be noted that in addition carbon stubs are used to mount the samples. Both the iron and molybdenum percentages were lower than the expected stoichiometric values due to the higher percentage of carbon.

<table>
<thead>
<tr>
<th>Area</th>
<th>Fe weight (%)</th>
<th>Mo weight (%)</th>
<th>C weight (%)</th>
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<td><strong>51</strong></td>
<td><strong>20</strong></td>
</tr>
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</table>

Table 43: EDX values for iron molybdenum carbide (Fe₃Mo₃C).
5.2.2.1 Ammonia Synthesis for Fe₃Mo₃C

Fe₃Mo₃C was tested for ammonia synthesis activity at 400°C and 500°C at atmospheric pressure under 3:1 H₂/N₂. This was performed to establish the influence the phase composition had upon ammonia synthesis activity. The material was not pre-treated before the reaction at 700°C as this would result in nitridation of the carbide and therefore, the activity would not be as a result of the carbide. Once the reaction had reached 400°C the conductivity values were recorded. The activity of the material at 400°C was very low and consequently, after 4 hours at 400°C, the temperature was increased to 500°C as shown in Figure 172.

The η-carbide structured Fe₃Mo₃C was not active for ammonia synthesis at 400 °C, unlike its corresponding nitride. The material became active at 500 °C and exhibited a steady state rate of 373 ± 55 µmol h⁻¹ g⁻¹. There was an induction period of approximately 45 minutes before the material developed steady state ammonia synthesis activity when the reaction temperature was at 500°C. The Fe₃Mo₃N precursor was observed to have a rate of 403 µmol h⁻¹ g⁻¹ at 500°C. Therefore, these two materials have similar activities at this temperature. This behaviour is comparable to that reported for the isostructural Co₃Mo₃C [54]. Co₃Mo₃C required a temperature of 500°C and it also had an induction period that lasted for 40 minutes before it became active [54]. It was observed to undergo nitridation to form a carbonitride phase during the reaction. The carbonitride phase had a similar activity to its nitride at 500°C reaction temperature, with a rate of 461 ± 17 µmol h⁻¹ g⁻¹ [54].

The filled β-Mn structured Ni₂Mo₃CₓNᵧ showed very different behaviour at 400°C reaction temperature. However, it is difficult to make comparisons between Fe₃Mo₃C and Ni₂Mo₃CₓNᵧ as one of the materials contained lattice nitrogen prior to the determination of its activity for ammonia synthesis.
Figure 172: Conductivity profile for Fe₃Mo₃C reacted with 3:1 H₂/N₂ at 400°C for 4 hours and 500°C for 32 hours.

The XRD pattern in Figure 173 shows that the η-carbide structure was retained after the reaction and that the reflections had shifted to higher 2θ values. This can be more clearly seen in Figure 174. This suggests that some of the lattice carbon was replaced with nitrogen during the reaction, as this corresponds to a reduction in lattice parameter since nitrogen has a smaller atomic radius than carbon as discussed previously.
Figure 173: Comparison of XRD patterns for Fe$_3$Mo$_3$C pre- and post-reaction with 3:1 H$_2$/N$_2$ at 400°C for 4 hours and 500°C for 32 hours. Reflections marked: ▼ Fe$_3$Mo$_3$C (JCPDS file number 00-047-1191).

Figure 174: Comparison of XRD patterns between Fe$_3$Mo$_3$C pre- (black) and post-reaction (red) with 3:1 H$_2$/N$_2$ at 400°C for 4 hours and 500°C for 32 hours.
The elemental analysis presented in Table 44 for the material run in Figure 172 shows that there was substitution of lattice carbon by nitrogen during the reaction and therefore, a carbonitride phase had been formed. The stoichiometry calculated for the bulk sample post-reaction was Fe$_3$Mo$_3$C$_{0.41}$N$_{0.65}$. Therefore, it could be suggested that the induction period was due to the material not containing lattice nitrogen and once the material had enough lattice nitrogen, it became active. However, it is not clear whether the material was active because there was lattice nitrogen present or if lattice nitrogen resulted from the material being active for ammonia synthesis. The removal of the passivation layer and surface segregation/restructuring are also possible reasons for the induction period, which need to be taken into consideration.

<table>
<thead>
<tr>
<th>Material</th>
<th>Calculated Stoichiometric Nitrogen Content (wt. %)</th>
<th>Calculated Stoichiometric Carbon Content (wt. %)</th>
<th>Nitrogen Content from Elemental Analysis (wt. %)</th>
<th>Carbon Content from Elemental Analysis (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_3$Mo$_3$C Pre-reaction</td>
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</tr>
<tr>
<td>Fe$_3$Mo$_3$C Post-reaction</td>
<td>-</td>
<td>2.57</td>
<td>1.94</td>
<td>1.05</td>
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</table>

Table 44: Elemental Analysis for Fe$_3$Mo$_3$C comparing pre- and post-reaction with 3:1 H$_2$/N$_2$ at 400°C for 4 hours and 500°C for 32 hours.

The representative SEM images of Fe$_3$Mo$_3$C post-reaction are given in Figure 175. The SEM images show a similar morphology to the oxide precursor, the nitride and the carbide pre-reaction. Therefore, the nitridation process did not result in a change in morphology. The material had a surface area of 3 m$^2$/g post-reaction, a pore volume of 0.03 cc/g and an average pore radius of 1002 Å.
Figure 175: SEM images of Fe₃Mo₃C post-reaction with 3:1 H₂/N₂ at 400°C for 4 hours and 500°C for 32 hours. a) 1000x magnification, b) 2000x magnification, c) 4000x magnification and d) 6000x magnification.

The iron, molybdenum, carbon and nitrogen were evenly distributed across the sample as seen in the element map in Figure 176.

Figure 176: Element Maps for Fe₃Mo₃C post-reaction with 3:1 H₂/N₂ at 500°C. Elements: Fe (red), Mo (green), C (blue) and N (black).

Table 45 displays the weight percentage for each element given by the EDX analysis. From CHN analysis, the stoichiometry calculated for the bulk sample post 36 hour reaction at 500°C is Fe₃Mo₃C₀.₄₁N₀.₆₅. The stoichiometric percentage of iron, molybdenum, carbon and nitrogen in the sample should be 35.69 wt. %, 61.32 wt. %, 1.05 wt. % and 1.94 wt. %
respectively. As with the pre-reaction sample, the carbon percentage was higher than expected and the molybdenum percentage was lower. Nitrogen was detected in the post-reaction sample and this agrees with the elemental analysis that showed some lattice carbon had been replaced with nitrogen.

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<tr>
<th>Area</th>
<th>Fe weight (%)</th>
<th>Mo weight (%)</th>
<th>C weight (%)</th>
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<td>33</td>
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Table 45: EDX values for Fe₃Mo₃C post-reaction with 3:1 H₂/N₂ at 500°C.

The extent to which development of activity required the removal of the surface oxide layer and/or restructuring of the near surface region was investigated by ToF-SIMS. Analysis was performed on the pre- and post- 32 hour reaction materials. The ToF-SIMS data is provided in Appendix V. In Fe₃Mo₃C, the carbon is bonded to six molybdenum species and therefore, the mass fragments for this material would contain MoC species. As discussed before, the depth profiling of ⁹²MoC and ⁹²MoN mass fragments was used to determine if carbon and nitrogen were present near the surface of this material. For the pre-reaction carbide, nitrogen was detected, suggesting that the material may not have been completely carburised. However, the ToF-SIMS measurement has a sensitivity of the ppm/ppb range, which is far below that of the elemental analysis explaining the apparent discrepancy between the two techniques. Carbon was present in the material at a depth of 10 nm in both the pre- and post-reaction materials, suggesting that although there was an oxide layer, carbon was present near the surface.

For the post- 32 hour reaction material, the intensity of the ⁹²MoN fragment was approximately twice that of the pre-reaction material, which suggests that there was more nitrogen present near the surface of the material post-reaction. Furthermore, the intensity of the ⁹²MoC peak had decreased compared to pre-reaction. Although the intensities of the mass fragments were different compared to the pre-reaction material, there was no other change in the mass spectra, suggesting that the material had not undergone restructuring during the reaction.
As expected, oxygen was present in the pre- and post-reaction materials. The intensity of the oxygen mass fragments appeared to decrease as the depth increased, which is consistent with this being a surface oxide layer.

From the ToF-SIMS analysis, it can be stated that although there was a passivation layer, carbon and nitrogen were detected close to the surface of the material.

5.2.2.1.1 Ammonia Synthesis for Fe₃Mo₃C at 400°C
To examine the difference in activity between Fe₃Mo₃C and Fe₃Mo₃N at 400°C, the carbide has been investigated further post 400°C reaction. From the XRD pattern presented in Figure 177, it can be seen that the reflections have remained in the same position between pre- and post-reaction. This suggests that the lattice carbon had not been replaced with nitrogen during the reaction, although this conflicts with post-reaction CHN analysis which does indicate the introduction of 0.63 wt. % N content after reaction. This origin of this apparent contradiction is not clear and requires further investigation.

Figure 177: Comparison of XRD patterns for Fe₃Mo₃C pre- and post-reaction with 3:1 H₂/N₂ at 400°C for 7.5 hours. Reflections marked: ▼ Fe₃Mo₃C (JCPDS file number 00-047-1191).

The reduction of the carbide was investigated by thermogravimetric analysis of the pre-reaction material under 3:1 H₂/Ar. The TGA of the reduction of the carbide was performed
in order to investigate the difference in activity of the nitride and carbide and the reduction of the passivated layer. The TGA curve and first derivative weight change of Fe₃Mo₃C heated from room temperature to 1000°C at a ramp rate of 10°C/min under 3:1 H₂/Ar is displayed in Figure 178. Several weight loss steps are observed for Fe₃Mo₃C. The TGA curve appears to be similar to the TGA curve for Fe₃Mo₃N up to 750°C under the same conditions (Figure 166).

The first feature of the TGA curve is a weight loss of 0.63 wt. % at approximately 100°C and this possibly relates to the loss of water from the material. The second is a weight loss of 1.16 wt. % at 275°C. The mass spectra ion curve of m/z 44 shows a peak at this temperature as seen in Figure 179, suggesting the loss of either CO₂ or C₃H₈. The weight loss could be due to the reaction of lattice carbon to form propane or it could correspond to the removal of the passivation layer. The initial expectation would be that the removal of the passivation layer would generate water. However, the production of a mass spectral features with m/z 18 or 17 were not observed. CO₂ or C₃H₈ have different fragmentation pathways. Unfortunately, m/z 29, that would be observed as a mass fragment of propane, was not followed. However, the other m/z signals that were followed did not show any features. Therefore, the unique fragmentation pathways for both species were not observed and the species associated with the weight loss feature cannot be determined with any degree of certainty.

The third and fourth features of the TGA curve are weight losses of approximately 1.37 wt. % at 413°C and a weight loss of 1.99 wt. % at 493°C. These could be due to the reduction of an oxide surface layer producing water. M/z values of 2, 14, 15, 16, 17, 18, 28, 30, 32, 44 and 46 m/z were scanned but they did not show any features at these temperatures. When the reaction is run at 400°C, these features may not be removed from the material and this could explain the inactivity of the material at this temperature. However, the ToF-SIMS analysis for the pre-reaction material showed that carbon and nitrogen were observed near the surface of the material. Therefore, these features need to be investigated further.

A feature is observed at 662°C, which corresponds to a weight loss of 1.37 wt. %. The TGA profile of Co₃Mo₃C under H₂/Ar showed that the lattice carbon reacted to form methane resulting in a weight loss at 616°C [55]. Therefore, the weight loss at 662°C for Fe₃Mo₃C may be due to the loss of some lattice carbon from the ternary carbide. There was a mass feature for 44 m/z as shown in Figure 179 at a higher temperature at approximately 730°C.
The final feature that is observed above 900°C results in a weight loss of 1.97 wt. %. It is not clear what the weight loss corresponds to, as mass spectra of 2, 14, 15, 16, 17, 18, 28, 30, 32, 44 and 46 m/z did not show any features at this temperature. However, the weight loss above 900°C may be associated with decomposition of the material.

Figure 178: TGA and derivative weight profile of Fe₃Mo₃C under 75% H₂/Ar in the range from room temperature to 1000°C.

Figure 179: The mass spectrum ion curve for 44 m/z and the derivative weight profile.
5.3 Conclusions

In this chapter, the \( \eta \)-carbide structured \( \text{Fe}_3\text{Mo}_3\text{N} \) and \( \text{Fe}_3\text{Mo}_3\text{C} \) were examined for their ammonia synthesis activity. The lattice nitrogen reactivity of \( \text{Fe}_3\text{Mo}_3\text{N} \) was also investigated. The intention of this work was to gain a further insight into the effect the composition had on the activity. Although the bulk lattice nitrogen of \( \text{Fe}_3\text{Mo}_3\text{N} \) has previously been reported to be unreactive, the bulk mobility of the nitrogen may be limited and a Mars-van Krevelen type mechanism may still occur for the surface lattice nitrogen.

\( \text{Fe}_3\text{Mo}_3\text{N} \) was active for ammonia synthesis at 400\(^\circ\)C and 500\(^\circ\)C under 3:1 \( \text{H}_2/\text{N}_2 \). The nitride had a rate of \( 74 \pm 1 \) \( \mu \text{mol h}^{-1} \text{g}^{-1} \) at 400\(^\circ\)C and \( 403 \) \( \mu \text{mol h}^{-1} \text{g}^{-1} \) at 500\(^\circ\)C. To determine the lattice nitrogen reactivity and stability of \( \text{Fe}_3\text{Mo}_3\text{N} \), the nitride was reacted under 3:1 \( \text{H}_2/\text{Ar} \) at 900\(^\circ\)C. The material decomposed and therefore, \( \text{Fe}_3\text{Mo}_3\text{N} \) was not stable under these conditions. In Chapter 4, the filled \( \beta \)-Mn structured \( \text{Co}_2\text{Mo}_3\text{N} \) and the \( \eta \)-carbide structured \( \text{Co}_3\text{Mo}_3\text{N} \) were shown to have a similar instability at 900\(^\circ\)C.

The \( \eta \)-carbide structured \( \text{Fe}_3\text{Mo}_3\text{C} \) was also analysed for ammonia synthesis activity, to investigate the role the lattice nitrogen plays in \( \text{Fe}_3\text{Mo}_3\text{N} \). The carbide was not active for ammonia synthesis at 400\(^\circ\)C. A reaction temperature of 500\(^\circ\)C was required and after an induction period, the material developed activity. The post-reaction XRD pattern and elemental analysis confirmed that the material underwent nitridation at 500\(^\circ\)C and the material formed a carbonitride phase via a topotactic mechanism. These results were similar to those reported for the isostructural \( \text{Co}_3\text{Mo}_3\text{N} \) [55]. The difference in activity of \( \text{Fe}_3\text{Mo}_3\text{N} \) and \( \text{Fe}_3\text{Mo}_3\text{C} \) at 400\(^\circ\)C suggests that the lattice nitrogen may be required in order for the material to be active. However, this needs to be investigated further as it is currently unknown whether the activity of \( \text{Fe}_3\text{Mo}_3\text{C} \) at 500\(^\circ\)C occurs due to the nitridation of the carbide. There were a number of inconsistencies for the carbide tested at 400\(^\circ\)C and therefore, this work should be repeated and this temperature would have to be investigated further. ToF-SIMS analysis was performed on the pre- and post-reaction \( \text{Fe}_3\text{Mo}_3\text{C} \) to investigate the effect the passivation layer had on the ammonia synthesis activity. Both carbon and nitrogen were detected in the near surface region of the material and therefore, it could be proposed that the passivation layer may have only a limited impact on the activity.
6. Osmium Based Compounds and Supported Mixed Metal Clusters

6.1 Introduction

6.1.1 Osmium

Osmium was discovered in 1803 by Smithson Tennant, who noticed that when platinum was added to dilute aqua regia, some powder remained. By using different acid and alkali treatments, Tennant separated the powder into two new elements, which he named osmium and iridium [154]. Osmium is a silver blue metal that is a member of the platinum group. The platinum group metals consist of six transition metals, which have high melting points and are corrosion resistant [11]. Osmium is the densest element with a value of 22.587 ± 0.009 g/cm³ as calculated from X-ray diffraction [155]. It has a hexagonal close packed structure. In powdered form, osmium can be oxidised at room temperature to give osmium tetroxide. Due to the toxicity of the tetroxide, alloys of osmium are more commonly used than the pure metal. The metal can be used in pen nibs and needles of gramophones and also has applications as a catalyst [156] [157].

Osmium is found mainly with the other platinum group metals in mineral deposits, for example osmiridium, which consists of an alloy with iridium [11]. Osmium is obtained mostly from nickel refining and copper ores. It is estimated that only 10% of osmium is recovered from copper ore [158].

6.1.2 Osmium for Ammonia Synthesis

Osmium has had great historical interest as an ammonia synthesis catalyst, although there has been very little work in this area in recent years. In 1909, Haber discovered that osmium had a high activity towards ammonia synthesis with an 8% yield under reaction conditions of 175 atmospheres pressure and 600°C [159]. Further work carried out by Mittasch [15] found that promoting the osmium with alkali metal oxides increased the yield from 2% ammonia to 4% at 550°C and 100 atmospheres pressure. However, osmium was a rare resource with approximately only 100 kg of it available in the world at that time [160]. Therefore, it was vital to find another catalyst that was cheaper as well as having a high ammonia synthesis rate. This led to the development of the promoted Fe catalyst that is used today in essentially unchanged form in the Haber-Bosch Process.

In 1982, Rambeau et al. [161] [162] reported their studies on the hydrogenation of nitrogen on an osmium powder at atmospheric pressure and over the temperature range 100 to 500°C. They concluded that catalytic ammonia synthesis over osmium is limited by
adsorption of nitrogen and is inhibited by both hydrogen and ammonia. A decrease in the nitrogen pressure resulted in a decrease in the ammonia produced. The reaction order with respect to nitrogen was shown to be one. As hydrogen pressure decreased, both the ammonia pressure and inhibition due to ammonia, increased. A negative first order was observed for the hydrogen, which suggests hydrogen inhibition that is strong. As hydrogen inhibition affected the activity of osmium, Rambeau et al. proposed a cyclic operation for ammonia synthesis to overcome this problem [162]. Firstly, they saturated the surface of the osmium with pure nitrogen. Then, the adsorbed nitrogen was hydrogenated under pure hydrogen. By using this method, it was proposed that rates of industrial relevance could be achieved at atmospheric pressure. When 3:1 H₂/N₂ was used, a rate of approximately 0.5 x 10⁻⁶ mole NH₃/min was reported at 400°C and when the cyclic procedure was used the rate was approximately 0.9 x 10⁻⁴ mole NH₃/min [162].

Ozaki et al. [163] investigated the ammonia synthesis activity of different transition metals including osmium. The catalyst was prepared by supporting osmium tetroxide on coconut carbon and promoting it with potassium. A stoichiometric ammonia synthesis reactant mixture and a pressure of 0.79 atmospheres were utilised. The rate of ammonia synthesis was determined over a temperature range of 100 – 400°C. Of the transition metals tested, both ruthenium and osmium ranked highest for their activity. At 253°C, osmium had a reported rate of approximately 4 mL STP NH₃/hr and ruthenium had a rate of approximately 10 mL STP NH₃/hr [163]. It is interesting to note that the materials were inactive in the absence of potassium promotion. It was concluded that this effect was due to the potassium transferring electron density to the transition metal causing the adsorbed nitrogen to be converted to an anionic intermediate. When potassium was replaced with sodium, the activity decreased, which was explained as resulting from sodium’s higher ionisation potential.

A recent DFT study by Ishikawa et al. examined the catalytic performance of osmium for ammonia synthesis [164]. It was proposed that the most active sites are step sites with an increase in turnover frequency of 10⁴ for these sites compared to the sites on the (0001) surface terrace plane. The maximum concentration of the active step sites was expected to occur at an osmium particle diameter of 3-4 nm. However, it was proposed that NH₂ species can block these active sites, which prevents N₂ dissociation and results in a lower TOF (turnover frequency) than predicted. Ru has a similar value to Os for the activation barrier for N₂ dissociation at the step sites. Conversely, Ru has a higher catalytic activity than Os due to it having a higher number of vacant sites [164].
6.1.3 Comparison of Osmium with Iron and Ruthenium for Ammonia Synthesis

Osmium is located in the same group as iron and ruthenium in the periodic table. These two elements are used as commercial ammonia synthesis catalysts and therefore, it would be of interest to compare the activity and behaviour of osmium with them. The activity of ruthenium has been found to be higher than iron and hence, with osmium below ruthenium in the group, it would be of interest to further compare these three elements.

Ruthenium is considered to have the close to optimal binding energy for nitrogen [24], explaining the high activity of this metal. The metal is structure sensitive for ammonia synthesis, with $B_5$ sites being the active site for the reaction [165]. $B_5$ step sites are associated with three Ru atoms in one layer and two Ru atoms in the layer above, with some of the Ru having low-coordination, for example edge atoms. The $B_5$ sites have a particle size dependence, where particles of 1.8–2.5 nm have the optimum number of $B_5$ sites [165]. Therefore, Ru is the most active when it is supported as shown by the KAAP Process using Ru based catalyst supported on carbon. The choice of support is known to play an important role in the number of $B_5$ sites due to the support controlling the Ru morphology [165].

Ammonia synthesis on iron is also a structure sensitive reaction [166], with the Fe (111) plane having a much higher activity than the Fe (100) and the Fe (110) planes [167] [168] [169]. It was suggested that $C_7$ sites were the most active in iron catalysts [169]. $C_7$ sites consist of surface iron atoms with seven neighbours. Iron has been observed to have a higher activity when it is in bulk form [166]. Iron was shown to have a higher TOF when the iron particle size was large, showing a dependence on metal particle size.

Since, as stated above, osmium is in the same group as iron and ruthenium, it would be of interest to examine the nature of any potential structure sensitivity for osmium, which to the author’s knowledge has not been investigated, to suggest potential strategies for further enhancing its catalytic performance. In order to undertake this, preliminary comparisons have been made between the performance of bulk metallic osmium and that for supported osmium prepared from a well-defined cluster compound precursor.

6.1.4 Osmium Carbonyl Clusters

Cotton first referred to a metal cluster as a material that contains metal-metal bonds [170]. A more specific definition is a collection of two or more metal atoms, which are bonded directly. Metal clusters are considered to be intermediate between mononuclear and polynuclear complexes. This means that they have similar properties to both; for example,
similar to mononuclear complexes, the clusters can be isolated and characterised by spectroscopy but they can also have delocalised metal to metal bonds. A common type of metal cluster is a metal carbonyl cluster. These are compounds that have two or more metals connected by metal bonds where the ligands are either entirely or predominately carbon monoxide. The nuclearity of the metal carbonyl clusters can vary greatly, with Os$_3$(CO)$_{12}$ being the compound of interest within this chapter. The structure of Os$_3$(CO)$_{12}$ is presented in Figure 180.

Figure 180: Structure of Os$_3$(CO)$_{12}$ at low temperature [171].

During the 1970s and 80s, there was growing interest in the application of metal carbonyl clusters as catalysts [36]. Metal carbonyl clusters have been utilised as heterogeneous catalysts by being used as precursors which can be impregnated onto supports such as silica and alumina. This provides some advantages over conventional heterogeneous catalysts. For example, if the cluster is retained on the support, there is extra control over its composition and nuclearity, which can have an effect on its activity and selectivity. Another advantage supported carbonyl clusters may have over conventional catalysts, is that their activity may sometimes be retained after being exposed to air, as is seen for supported osmium and ruthenium carbonyl clusters in the reaction of ethane hydrogenolysis [172]. When osmium on silica is exposed to air, an induction stage of a number of minutes is required before activity is restored. There is no such induction stage necessary for the cluster materials. Although the oxygen dissociates on adsorption, a reason for the catalysts not being affected by exposure to air could be due to the adsorption of oxygen being weak such that it is still reversible at 152°C.
As they are small molecules, the catalytic behaviour of clusters can be seriously affected by how they interact with the support. This strong interaction between the cluster and the support is of great interest and has been studied for Os$_3$(CO)$_{12}$ and Os$_6$(CO)$_{18}$ on silica, alumina and titania [51]. Previously, the osmium cluster compounds were thought to be reduced to monometallic species during the preparation of the precursor onto the oxide support [173]. The interaction of the support with the cluster was believed to occur through the hydroxyl groups. However, if the support is severely dehydroxylated before the precursor is impregnated, it has been shown from IR and UV-visible spectroscopy, that clusters remain intact on the support [51].

Yunusov et al have studied some carbonyl clusters for their ammonia synthesis activities [174]. They prepared K$_2$[Ru$_4$(CO)$_{13}$], K$_2$[Fe$_2$(CO)$_8$] and K$_2$[Os$_3$(CO)$_{11}$] on two different carbon supports. The first carbon support was a commercial SKT and the second was an active carbon called sibunit. Sibunit was prepared from carbon black and differs from the other carbon support as it has a mainly mesoporous structure [175]. In addition, it has a very low amount of impurities with a carbon content of 99.4 wt. % compared to the 85.9 wt. % for SKT. The type of metal and carbon support had a great influence on the rate of ammonia produced. The ruthenium compound on sibunit was found to be the most active, with ammonia being produced from as low a temperature as 250°C. Next active was the osmium on sibunit and the iron on sibunit was discovered to have the lowest activity. K$_2$[Ru$_4$(CO)$_{13}$] , K$_2$[Os$_3$(CO)$_{11}$] and K$_2$[Fe$_2$(CO)$_8$] on sibunit had a reported ammonia synthesis rate of 14.9 mL NH$_3$ h$^{-1}$ g$^{-1}$ cat., 11.3 mL NH$_3$ h$^{-1}$ g$^{-1}$ cat. and 0.7 mL NH$_3$ h$^{-1}$ g$^{-1}$ cat., respectively at 400°C and atmospheric pressure [174]. When the SKT carbon was used, ammonia was only produced at 400°C and the catalyst deactivated with the activity rapidly decreasing within the first hour of testing.

6.1.5 Mixed Metal Carbonyl Clusters
A variety of mixed metal carbonyl clusters can be formed from the Group 8 elements. Generally, these materials are prepared as part of a mixture of products, which need to be separated by chromatography techniques [176] [177]. Therefore, the percentage yield of the desired product can vary from low to reasonable yields depending on the synthesis method used [178] [179]. In a typical synthesis, the monometallic metal carbonyls are dissolved in a solvent and left for a period of time. After this, column chromatography or thin layer chromatography are used to isolate the mixed metal carbonyl cluster. For example, Os$_2$Ru(CO)$_{12}$ and OsRu$_2$(CO)$_{12}$ can be synthesised from thermal decomposition of Ru$_3$(CO)$_{12}$ and Os$_3$(CO)$_{12}$ in xylene [180].
The mixed metal carbonyl clusters are usually isostructural with one of the starting monometallic metal carbonyl precursors as observed by XRD and IR measurements [176] [178] [181]. For example, FeOs₂(CO)₁₂ has been suggested to be isostructural with Os₃(CO)₁₂, with one of the osmium being replaced with iron [176].

Kulkarni and Gates [52] have proposed that supported bimetallic clusters can be formed by heating metal carbonyls, resulting in decarbonylation and metal-metal bond formation. This was shown by supporting Os₃(CO)₁₂ and Ru₃(CO)₁₂ on MgO and heating the material under H₂. Through IR and EXAFS spectroscopy, it was observed that Ru-Os bond formation occurred at 125°C after partial decarbonylation of the two precursors. This is a promising method for forming supported mixed metal carbonyl clusters and overcomes the issue of separating the desired product by chromatography.

6.2 Results and Discussion

6.2.1 Bulk Osmium Metal

The XRD pattern in Figure 181 shows that only osmium metal was present, as expected. This demonstrates that the metal had not formed bulk osmium tetroxide while being in contact with air. However, a surface oxide layer may have formed, which would not be detectable by XRD analysis.

![Figure 181: XRD pattern of osmium metal. Reflections marked: Os (JCPDS file number 00-006-0662).](image)
The BET surface area of the osmium was measured to be 2 m$^2$/g. According to Pinto and Paniego [182], osmium tetroxide can be formed when osmium is in the presence of oxygen or air. When the sample is in contact with air for a short time, a monolayer of oxygen is adsorbed onto the surface. If this is the case, then the BET surface area value for the osmium powder might not be a truly representative measurement in relation to that exhibited under reaction conditions.

The SEM images for osmium metal at different magnifications are presented in Figure 182. The material had an irregular structure with an agglomeration of small rounded crystallites. Some areas had a smoother surface as can be seen in Figure 182 (b). Only osmium was detected by EDX analysis for this material and no other element was observed.

![SEM images of the bulk osmium sample. a) 2000x magnification, b) 4000x magnification and c) 4000x magnification.](image)

Figure 182: SEM images of the bulk osmium sample. a) 2000x magnification, b) 4000x magnification and c) 4000x magnification.

The bulk osmium sample was pre-treated with different gas mixtures to examine the potential inhibition of nitrogen and hydrogen on the surface. As stated in the introduction of this chapter, hydrogen was shown to inhibit the reaction and nitrogen coverage can also affect the rate [162]. These factors may therefore affect the ammonia synthesis rate of the osmium sample tested.
The metal was first pre-treated at 500°C for 2 hours with one of the following gas mixtures: 1:3 N2/H2, 1:3 Ar/H2 or pure N2. This pre-treatment temperature was employed to replicate the conditions used by Rambeau et al. [161] [162]. The temperature was then decreased to 400°C and the ammonia synthesis reaction was performed under 1:3 N2/H2. The ammonia production reaction profile for the osmium metal at 400°C after the three pre-treatments is presented in Figure 183. When 1:3 Ar/H2 and pure N2 were used as the pre-treatment gas, a lag period of approximately 20 minutes was observed before the material became active. However, when using a N2/H2 pre-treatment, this was not observed and the decrease in conductivity versus time resulted in a linear profile over the 12.5 hours of testing. Line flushing tests were undertaken to ensure that the lag period was not due to any experimental artefacts. For the 1:3 Ar/H2 and N2 pre-treated samples, beyond the induction period, the activity was observed to be steady state.

One possible explanation is that N2, in the case of the N2 pre-treatment, and H2, in the case of the Ar/H2 pre-treatment, cover the surface of the osmium during the pre-treatment. Hydrogen has been shown to inhibit the ammonia synthesis reaction for osmium and therefore, the coverage could block the active sites. The coverage of nitrogen may also block the active sites and thus delay the start of the reaction. The hydrogen may also reduce the osmium to an active phase and hence, would be required in the pre-treatment step. It might also be the case that the surface facets to an active form in the presence of the reactant mixture under these reaction conditions. The origin of this lag period, to eliminate any other potential artefacts, should be investigated further.
Figure 183: Conductivity profiles for osmium reacted with 3:1 H₂/N₂ at 400°C after different pre-treatments. Labels: 1:3 N₂/H₂ pre-treatment (blue), 1:3 Ar/H₂ pre-treatment (orange) and N₂ pre-treatment (grey).

The steady state ammonia synthesis rates relating to the tests employing the bulk osmium sample at 400°C are displayed in Table 46. In comparison, the rate of osmium metal at 500°C under 1:3 N₂/H₂ during the pre-treatment was 262 ± 21 μmol h⁻¹ g⁻¹.

It can be seen that the pre-treatment gas possibly had a small effect on the ammonia synthesis activity of osmium. The metal had the highest activity at 400°C when the 1:3 N₂/H₂ pre-treatment was used. However, the three values for the different pre-treatment samples are within experimental error. In comparison, the promoted iron Haber Bosch catalyst has been reported to exhibit a rate of 330 μmol h⁻¹ g⁻¹ under comparable conditions [127]. A previous study on the comparative ammonia synthesis activity of Os and Fe, suggested that the activity of osmium was 100 times lower than iron powder at 1 atmosphere pressure and 400°C, when a stoichiometric ratio of N₂:H₂ was used [161]. The inhibition by hydrogen on osmium was proposed as the explanation for the lower activity compared to iron, which does not suffer from inhibition by hydrogen [161]. The rate of N₂ chemisorption on a bare osmium surface was reported to be 100 times higher than that for Fe and 100 times lower than that for Ru [161]. However, it is important to note that other studies show that osmium metal has a higher activity than iron [24] [15] [183].
Table 46: Ammonia synthesis rates of osmium under 3:1 H\textsubscript{2}/N\textsubscript{2} at 400°C after different pre-treatments.

<table>
<thead>
<tr>
<th>Pre-treatment</th>
<th>NH\textsubscript{3} Synthesis Rate (\textmu mol h\textsuperscript{-1} g\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:3 N\textsubscript{2}/H\textsubscript{2}</td>
<td>79 ± 1</td>
</tr>
<tr>
<td>1:3 Ar/H\textsubscript{2}</td>
<td>64 ± 16</td>
</tr>
<tr>
<td>N\textsubscript{2}</td>
<td>69 ± 3</td>
</tr>
</tbody>
</table>

The post-reaction XRD patterns for osmium that had undergone different pre-treatments are displayed in Figure 184. The XRD patterns were found to display only the pattern for osmium metal. CHN analyses undertaken for the pre-reaction and all the post-reaction samples did not evidence the formation of any bulk nitrogen or hydrogen content.

![XRD patterns of osmium metal post-reaction with different pre-treatments.](image)

Figure 184: XRD patterns of osmium metal post-reaction with different pre-treatments. Reflections marked: • Os (JCPDS file number 00-006-0662).

Compared to pre-reaction, there did not appear to be a change in morphology of the osmium post-reaction for all three pre-treatments. Representative SEM images of osmium that had undergone the three pre-treatments are shown in Figure 185. The samples consisted of an irregular morphology, with small rounded crystallites. Therefore, the lag period did not appear to be due to a change in morphology between the pre-reaction and Ar/H\textsubscript{2} and N\textsubscript{2} pre-treated samples. Whilst the post-reaction material that was pre-treated with 3:1 H\textsubscript{2}/N\textsubscript{2} had a surface area of 3 m\textsuperscript{2}/g, the small difference with respect to the pre-reaction material is not significant particularly in view of the uncertainties associated with the determination of such low BET surface areas.
Due to the possible inhibition of nitrogen and hydrogen on the surface of the osmium metal, a cyclic procedure was performed based upon the method reported by Rambeau et al. [162]. The osmium was first pre-treated at 500°C with 3:1 H₂/N₂ for 2 hours and then the temperature was decreased to 400°C. The line was switched to pure N₂ only and the nitrogen was flowed over the sample for 5 minutes. The line was then switched to a flow of pure H₂ and this was passed over the osmium for 5 minutes. This five minute cycling procedure was repeatedly performed for 1 h 30 min. After this, the cycling was switched to every two minutes for a further hour to explore the possible role of pulsing duration and
then to every eight minutes for another hour. Each time \( \text{N}_2 \) gas was the first gas to flow in the cycling step. Finally, the temperature was increased to 500\( ^\circ \text{C} \) and the cyclic procedure was performed every five minutes for 1 h 30 min.

The decrease in conductivity over time for the different stages outlined above is presented in Figure 186.

![Figure 186: Conductivity profile for osmium cyclic procedure with 3:1 \( \text{H}_2/\text{N}_2 \) pre-treatment at 500\( ^\circ \text{C} \).

The amount of ammonia produced in one hour for the different stages of the osmium cyclic procedure, detailed in Figure 186, is provided in Table 47. For the 5 min cycling at 400\( ^\circ \text{C} \) and 500\( ^\circ \text{C} \), the values were calculated from when the conductivity had reached a steady decrease. When a continuous feed of 3:1 \( \text{H}_2/\text{N}_2 \) was used, the osmium that had been pre-treated with 3:1 \( \text{H}_2/\text{N}_2 \) produced 34.6 \( \mu \)moles of ammonia in one hour at 400\( ^\circ \text{C} \). These results suggest that the cyclic procedure was having a negative impact on the amount of ammonia produced at both 400\( ^\circ \text{C} \) and 500\( ^\circ \text{C} \) compared to when a continuous feed was used. It appears that the 5 minute cycling stage was the most effective at producing ammonia of the three stages investigated.
Conditions | Ammonia Produced in One Hour (µmoles) | Number of Cycles of H₂ Treatment
--- | --- | ---
500°C 1:3 N₂/H₂ Pre-Treatment | 108.0 | -
400°C: Every 5 min | 10.8 | 6
400°C: Every 2 min | 5.8 | 15
400°C: Every 8 min | 4.3 | 4
500°C: Every 5 min | 11.5 | 6

Table 47: Amount of ammonia produced in one hour for each stage of the osmium cyclic procedure.

Rambeau et al. noted that at 400°C, the best conditions were when osmium was exposed to 10 s of nitrogen and 5 s of hydrogen [162]. Therefore, this would suggest that the cycling time needed to be shorter. However, this was not possible in this experimental setup. On the other hand, however, Rambeau et al. achieved satisfactory rates when the material was exposed to 5 minutes of nitrogen and 1 minute of hydrogen [162]. It would therefore be expected that the osmium should have a steady state rate in this work at these longer cycling times.

The ammonia synthesis rates of the osmium during the different cycling stages are provided in Table 48. During the pre-treatment stage at 500°C shown in Figure 186, beyond the lag period, the rate of ammonia production for the osmium was as expected according to the previous rate obtained. However, when the cycling procedure was performed at this temperature, the rate was significantly lower at 28 µmol h⁻¹ g⁻¹. This suggests that the cycling procedure was having a negative effect on the ammonia synthesis process for osmium. This was also observed at 400°C when a 2 minute cycling period was used, with the rate of 15 µmol h⁻¹ g⁻¹ being much lower than the rates reported in Table 46 at the same temperature employing continuous feeding of reaction mixture. Therefore, these observations were not consistent with those reported by Rambeau et al. [162] who suggested that the rate could be increased by a factor of 5 at 400°C when the cyclic procedure was used.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>NH₃ Synthesis Rate (µmol h⁻¹ g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500°C 1:3 N₂/H₂ Pre-Treatment</td>
<td>261</td>
</tr>
<tr>
<td>400°C: Every 2 min</td>
<td>15</td>
</tr>
<tr>
<td>500°C: Every 5 min</td>
<td>28</td>
</tr>
</tbody>
</table>

Table 48: Ammonia synthesis rates of osmium under different conditions.
The XRD pattern for the post-reaction osmium that underwent a cyclic procedure is shown in Figure 187. Only osmium metal was observed in the pattern, as expected on the basis of the observations reported previously.

![XRD pattern](image)

Figure 187: XRD patterns of osmium post cyclic procedure reaction. Reflections marked: • Os (JCPDS file number 00-006-0662).

Representative SEM images for the osmium post cyclic procedure showed that the material had a similar morphology to the pre-reaction material. Therefore, the cyclic procedure did not affect the morphology of the osmium.

6.2.2 Supported Osmium Compounds

6.2.2.1 Os3(CO)12 on Silica

To investigate potential structure sensitivity in the case of osmium catalysed ammonia synthesis, Os3(CO)12 was supported on amorphous silica. The material was prepared to give a 5 wt. % loading of osmium. In the literature, a 5 wt. % loading is used to prepare these materials and therefore, the same loading was used in this work. As the silica was not treated in order to remove hydroxyl groups, the silica support is referred to as hydroxylated. The XRD pattern of the 5% Os3(CO)12/silica hydroxylated is displayed in Figure 188. Reflections due to Os3(CO)12 can be observed in the pattern as well as a broad peak between 15-35° 20 that is due to amorphous silica. The crystalline reflections related to the Os3(CO)12 suggest that there was not monolayer dispersion initially.
The elemental analysis of the silica showed that there was trace amounts of carbon and significant amounts of hydrogen, as to be expected due to the hydroxyl groups on the surface (C: 0.04 wt. %, H: 0.87 wt. %, N: 0.00 wt. %). For the 5% Os$_3$(CO)$_{12}$/silica, the elemental analysis indicated that there was carbon and hydrogen present in the material (C: 0.98 wt. %, H: 0.77 wt. %, N: 0.00 wt. %). As there was a 5 wt. % loading of osmium metal, the expected percentage of carbon in this supported material is 1.26 wt. %. Therefore, the percentage of carbon was lower than expected.

Figure 188: XRD pattern of 5% Os$_3$(CO)$_{12}$/silica hydroxylated. Reflections marked: Os$_3$(CO)$_{12}$ (JCPDS file number 01-070-0415).

FTIR spectroscopy was performed in the carbonyl region for the supported Os$_3$(CO)$_{12}$ material. The FTIR spectrum is provided in Figure 189. For the 5% Os$_3$(CO)$_{12}$/silica, IR frequencies were noted at 2068 cm$^{-1}$ (s), 2035 cm$^{-1}$ (m), 2014 cm$^{-1}$ (w) and 2000 cm$^{-1}$ (w). From the literature, Os$_3$(CO)$_{12}$ stretching frequencies have been reported to occur at 2068 cm$^{-1}$ (s), 2035 cm$^{-1}$ (s), 2014 cm$^{-1}$ (m) and 2002 cm$^{-1}$ (m) [181] [184]. Therefore, these results agree well with the literature values.
The silica supported Os$_3$(CO)$_{12}$/silica hydroxylated was investigated for ammonia synthesis activity at 400°C and 500°C, in order to compare the rate of the material with the osmium metal. The reaction profile for this material is displayed in Figure 190. The material was reduced for 2 hours under N$_2$/H$_2$ at 500°C. This was performed in order to replicate the conditions used for the osmium metal. After 2 hours, the furnace was cooled to 400°C and kept at this temperature for 2 h 15 minutes. The temperature was then increased to 500°C, due to the low activity of the material at 400°C. The furnace was kept at 500°C for 4 hours. Finally, the furnace was cooled down again to 400°C and was kept at this temperature for 2 h and 25 minutes. The temperature was decreased to 400°C for a second time in order to investigate if there had been a change in the material when it was run at 500°C for a longer time. When the 5% Os$_3$(CO)$_{12}$/silica hydroxylated was run at 500°C for 36 hours, there was no indication of the material deactivating as seen in Figure 191.

The ammonia synthesis rate of the material at 400°C was 39 ± 6 μmol h$^{-1}$ g$^{-1}$. The rate was calculated for the catalyst weight and was not normalised to osmium content. In comparison, the rate of the N$_2$/H$_2$ pre-treated osmium metal at 400°C was 79 ± 1 μmol h$^{-1}$ g$^{-1}$. Therefore, the osmium metal was more active than the supported material at the lower temperature. However, when the activity is normalised to the mass of osmium, the supported material is much more active (770 ± 114 μmol h$^{-1}$ g$_{Os}$$^{-1}$). The 5%
Os₃(CO)₁₂/silica hydroxylated had a rate of 265 ± 48 µmol h⁻¹ g⁻¹ at 500°C. Comparing this with the ammonia synthesis rate of the osmium metal at 500°C (262 ± 21 µmol h⁻¹ g⁻¹), the rate was very similar, suggesting that osmium has the same activity whether in the bulk or supported form. However, a rate of 5306 ± 954 µmol h⁻¹ g₉⁻¹ is obtained for the supported material when the rate is normalised to metal content. Therefore, the Os content is more efficient in the supported material and is much more active per unit mass of osmium. This possibly suggests that osmium is structure sensitive for ammonia synthesis. Osmium appears to possess structure sensitivity more similar to ruthenium, with osmium being more active when it is more highly dispersed.

Figure 190: Conductivity profile for 5% Os₃(CO)₁₂/silica hydroxylated reacted with 3:1 H₂/N₂ at 400°C and 500°C.
It has previously been suggested that Os₃(CO)₁₂ decomposes through a hydride intermediate when under hydrogen and supported on carbon [185]. At 400°C, it was shown that the Os₃(CO)₁₂ had decomposed to give well dispersed Os on the carbon support. A similar hydride intermediate has also been proposed for Os₃(CO)₁₂ supported on hydroxylated silica and alumina [186]. The retention of the Os-Os nuclearity has been questioned when the supported osmium carbonyl cluster decomposes [186] [187]. However, Collier et al. have claimed that Os-Os bonding is retained on dehydroxylated silica and alumina [51]. They observed that above 250°C, there were no spectral features of Os₃(CO)₁₂, suggesting that the carbonyl had decomposed.

The XRD pattern of the material post-reaction is displayed in Figure 192 and shows that, unlike the pre-reaction case, there were no reflections corresponding to Os₃(CO)₁₂. The broad peak between 15-35° 20 due to amorphous silica was observed. An amorphous peak between 40 – 45° 20 is observed that was not present in the pre-reaction material. This peak could be due to osmium as the metal has three high intensity reflections at this position. However, silica can also have similar features and therefore, some caution has to be taken. The XRD pattern indicates that Os₃(CO)₁₂ had decomposed during the reaction.

The elemental analysis of the post-reaction material showed that the amount of carbon and hydrogen had significantly decreased compared to pre-reaction (C: 0.04 wt.%, H: 0.26 wt. %, N: 0.07 wt.%). The loss of carbon is to be expected, if the Os₃(CO)₁₂ had decomposed.

Figure 191: Conductivity profile for 5% Os₃(CO)₁₂/silica hydroxylated reacted with 3:1 H₂/N₂ at 500°C for 36 hours.
Figure 192: XRD patterns of 5% Os$_3$(CO)$_{12}$/silica hydroxylated: (a) pre-reaction and (b) post-reaction with 3:1 H$_2$/N$_2$. Reflections marked: Os$_3$(CO)$_{12}$ (JCPDS file number 01-070-0415).

An FTIR spectrum was taken for the post-reaction material, in order to see the effect the reaction had on the Os$_3$(CO)$_{12}$ structure and it is displayed in Figure 193. After the reaction, frequencies were recorded at 2043 cm$^{-1}$ (vw), 2018 cm$^{-1}$ (vw) and 1992 cm$^{-1}$ (vw) in the carbonyl region. These bands are different from the literature values and those of the pre-reaction material. However, the bands are very weak and may be due to background noise. The intensity of the bands decreased after the ammonia synthesis reaction, suggesting that the Os$_3$(CO)$_{12}$ had largely decomposed. Such decomposition has been recorded in previous literature [188] and agrees with the information obtained from the XRD pattern and elemental analysis.
Figure 193: FTIR spectrum of 5% Os$_3$(CO)$_{12}$/silica hydroxylated post-reaction with 3:1 H$_2$/N$_2$ at 500°C for 36 hours.

EDX analysis of the Os$_3$(CO)$_{12}$/silica showed that it consisted of 1.27 wt. % Os, 14.27 wt. % C, 52.36 wt. % O and 32.09 wt. % Si. The post-reaction material consisted of 1.76 wt. % Os, 14.33 wt. % C, 46.44 wt. % O and 37.47 wt. % Si. The pre-reaction osmium percentage was lower than the 5 wt. % of osmium used to prepare the material. However, the osmium was not uniformly dispersed across the surface, as the EDX data showed a variation in the areas examined. The osmium was more evenly dispersed in the post-reaction material and the percentage had apparently increased compared to pre-reaction. However, as there was a variation in osmium content pre-reaction, this increase may be due to the higher dispersion. To calculate the coverage of the silica support with Os triangles, the bond lengths and angles of Os-Os in Os$_3$(CO)$_{12}$ [171] were used to calculate the cross-sectional area of the Os triangle. The cross-sectional area of the Os$_3$ complex was calculated to be $3.594 \times 10^{-20}$ m$^2$ and the silica had a BET surface area of 427 m$^2$/g. Then, assuming the Os$_3$ structure lies flat on the silica support and that a monolayer was formed, the coverage of the silica support was calculated to be 0.44%.
To improve the activity of the silica supported Os$_3$(CO)$_{12}$, the material was modified in four different ways:

(1) The first method was the preparation of 5% Os$_3$(CO)$_{12}$/silica hydroxylated under a nitrogen atmosphere. This was to confirm that the metal carbonyl was not air sensitive as stated in the introduction. The sample was transferred into the reactor under nitrogen atmosphere and therefore, did not come into contact with air before the reaction.

(2) The second method resulted in the silica support being treated with nitrogen prior to being supported in order to remove surface hydroxyl groups. As Collier et al. suggested that there was retention of the cluster structure on dehydroxylated supports, a comparison of hydroxylated and dehydroxylated silica would be of interest.

(3) In the third method, the metal loading of osmium on the hydroxylated silica was increased to 7 wt. %.

(4) Finally, the 5% Os$_3$(CO)$_{12}$/silica hydroxylated was doped with 1% KOH as the ammonia synthesis activity of Ru/Al$_2$O$_3$ has been shown to increase when it is doped with alkali metals [26].

The ammonia synthesis activity of these materials at 400°C and 500°C are shown in Table 49. The activity of the “standard” 5% Os$_3$(CO)$_{12}$/silica hydroxylated material has been provided as a comparison. Only the materials that had a steady state rate at 400°C are listed in Table 49. For the sample prepared under N$_2$, there appeared to be minimal difference in activity compared to the 5% Os$_3$(CO)$_{12}$/silica hydroxylated material suggesting that the supported Os$_3$(CO)$_{12}$ material is not very air sensitive.

When comparing the hydroxylated and dehydroxylated silica supports, the hydroxylated silica supported material was more active at 400°C, with 5% Os$_3$(CO)$_{12}$/dehydroxylated silica not exhibiting a steady state rate at this temperature. However, at 500°C, there appeared to be an enhancement of the rate on the dehydroxylated system. Therefore, it could be suggested that the hydroxyl groups on the silica have an effect on the rate.

At 400°C, the 7% Os$_3$(CO)$_{12}$/silica hydroxylated had a lower activity than the 5% loaded material. When the catalyst weight was used to calculate the rate, the 7% loaded material was observed to be more active at 500°C. However, when the rate is normalised to the mass of osmium, the activity of the 5% Os$_3$(CO)$_{12}$/silica hydroxylated and 7% Os$_3$(CO)$_{12}$/silica hydroxylated were similar. If there was uniform dispersion of the
Os₃(CO)₁₂ on the silica surface, the rate should be 7/5 of the 5% Os₃(CO)₁₂/silica hydroxylated. Therefore, the rate is expected to be 7428 µmol h⁻¹ g⁻¹ Os⁻¹ for the 7 wt. % loading material. The osmium mass normalised rate was lower than this expected value.

The Os supported material was not promoted by KOH at either 400°C or 500°C. At 400°C, the rate was non-steady state and at 500°C the rate was significantly reduced. These results suggest, surprisingly, that the KOH had a negative effect on the activity for this system.

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature (°C)</th>
<th>NH₃ Synthesis Rate (µmol h⁻¹ g⁻¹)</th>
<th>NH₃ Synthesis Rate (µmol h⁻¹ g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5% Os₃(CO)₁₂/silica hydroxylated</td>
<td>400</td>
<td>39 ± 6</td>
<td>770 ± 114</td>
</tr>
<tr>
<td>5% Os₃(CO)₁₂/silica hydroxylated</td>
<td>500</td>
<td>265 ± 48</td>
<td>5306 ± 954</td>
</tr>
<tr>
<td>5% Os₃(CO)₁₂/silica hydroxylated prepared under N₂ (1)</td>
<td>400</td>
<td>34</td>
<td>680</td>
</tr>
<tr>
<td>5% Os₃(CO)₁₂/silica hydroxylated prepared under N₂ (1)</td>
<td>500</td>
<td>284</td>
<td>5676</td>
</tr>
<tr>
<td>5% Os₃(CO)₁₂/silica dehydroxylated (2)</td>
<td>500</td>
<td>355 ± 19</td>
<td>7096 ± 385</td>
</tr>
<tr>
<td>7% Os₃(CO)₁₂/silica hydroxylated (3)</td>
<td>400</td>
<td>22</td>
<td>313</td>
</tr>
<tr>
<td>7% Os₃(CO)₁₂/silica hydroxylated (3)</td>
<td>500</td>
<td>349 ± 9</td>
<td>4972 ± 126</td>
</tr>
<tr>
<td>5% Os₃(CO)₁₂/silica hydroxylated + 1% KOH (4)</td>
<td>500</td>
<td>174 ± 11</td>
<td>3470 ± 202</td>
</tr>
</tbody>
</table>

Table 49: Ammonia synthesis rates of different Os₃(CO)₁₂/silica materials reacted with 3:1 H₂/N₂. (1), (2), (3) and (4) refers to the four different modifications detailed above.

6.2.2.1.1 5% Os₃(CO)₁₂/silica hydroxylated Prepared Under N₂

The XRD patterns of the material pre- and post-reaction are shown in Figure 194. The pattern was very similar to the material not prepared under nitrogen, with the reflections due to Os₃(CO)₁₂ not being present in the XRD pattern post-reaction. This indicates that Os₃(CO)₁₂ decomposed during the reaction. As before, the crystalline reflections of Os₃(CO)₁₂ suggests that there was not a monolayer dispersion.
Figure 194: XRD patterns of 5% Os\textsubscript{3}(CO)\textsubscript{12}/silica hydroxylated: (a) pre-reaction, (b) post-reaction and (c) post-reaction prepared under N\textsubscript{2}. Reflections marked: + Os\textsubscript{3}(CO)\textsubscript{12} (JCPDS file number 01-070-0415).

6.2.2.1.2 5% Os\textsubscript{3}(CO)\textsubscript{12}/silica dehydroxylated

The XRD patterns of the dehydroxylated material pre- and post-reaction appear to be very similar to the XRD patterns for the hydroxylated material as observed in Figure 195.

The silica post nitrogen treatment was shown to still contain some hydrogen (C: 0.03 wt. %, H: 0.20 wt. %, N: 0.00 wt. %). However, the amount was significantly lower than the sample that was not treated to remove hydroxyl groups, as would be expected. A degree of rehydroxylation may have occurred when the silica was in contact with air. The elemental analysis for the material pre- and post-reaction is provided in Table 50. The amount of carbon had significantly decreased post-reaction, which agrees with the XRD pattern that showed the Os\textsubscript{3}(CO)\textsubscript{12} had decomposed.
Figure 195: XRD patterns of 5% Os$_3$(CO)$_{12}$/silica dehydroxylated: (a) pre-reaction, (b) post-reaction at 400°C and (c) post-reaction at 500°C. Reflections marked: + Os$_3$(CO)$_{12}$ (JCPDS file number 01-070-0415).

<table>
<thead>
<tr>
<th>Material</th>
<th>Carbon Content from Elemental Analysis (wt. %)</th>
<th>Hydrogen Content from Elemental Analysis (wt. %)</th>
<th>Nitrogen Content from Elemental Analysis (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-reaction</td>
<td>2.42</td>
<td>0.52</td>
<td>0.03</td>
</tr>
<tr>
<td>Post-reaction</td>
<td>0.06</td>
<td>0.24</td>
<td>0.11</td>
</tr>
</tbody>
</table>

Table 50: Elemental Analysis for pre- and post-reaction 5% Os$_3$(CO)$_{12}$/silica dehydroxylated.

6.2.2.1.3 7% Os$_3$(CO)$_{12}$/silica hydroxylated

The XRD patterns of the material pre- and post-reaction are displayed in Figure 196. The Os$_3$(CO)$_{12}$ is not observed in the post-reaction pattern and therefore, it appears to have decomposed during the reaction. The pre- and post-reaction XRD patterns are similar to those for the 5% loaded material.

The elemental analysis of the 7% Os$_3$(CO)$_{12}$/silica hydroxylated is given in Table 51. For a 7 wt. % loading of osmium metal, the expected percentage of carbon in the supported material would be 1.76 wt. %. The carbon percentage of the pre-reaction material agrees quite well with this expected value. As observed with the other materials, the carbon content decreased after the reaction and therefore, this confirms that the Os$_3$(CO)$_{12}$ decomposed.
Figure 196: XRD patterns of 7% Os$_3$(CO)$_{12}$/silica hydroxylated: (a) pre-reaction and (b) post-reaction at 500°C. Reflections marked: + Os$_3$(CO)$_{12}$ (JCPDS file number 01-070-0415).

<table>
<thead>
<tr>
<th>Material</th>
<th>Carbon Content from Elemental Analysis (wt. %)</th>
<th>Hydrogen Content from Elemental Analysis (wt. %)</th>
<th>Nitrogen Content from Elemental Analysis (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-reaction</td>
<td>1.58</td>
<td>0.69</td>
<td>0.00</td>
</tr>
<tr>
<td>Post-reaction</td>
<td>0.03</td>
<td>0.33</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Table 51: Elemental Analysis for pre- and post-reaction 7% Os$_3$(CO)$_{12}$/silica hydroxylated.

6.2.2.1.4 5% Os$_3$(CO)$_{12}$/silica hydroxylated + 1% KOH

The XRD patterns of the doped material were different to the undoped sample pre- and post-reaction as observed in Figure 197. For the pre-reaction sample, reflections due to Os$_3$(CO)$_{12}$ were not observed, with the only observed reflection being due to silica. In the post-reaction sample, the XRD pattern showed that osmium metal was present in the material. These differences in the XRD pattern of the doped material may provide an explanation for the lower activity compared to the undoped sample. The reflection widths of the osmium are large, suggesting that the osmium is highly dispersed consisting of small and/or disordered crystallites. As the osmium is more highly dispersed compared to the bulk osmium, this would suggest that there was a greater proportion of surface atoms.
Although Os₃(CO)₁₂ was not observed in the pre-reaction XRD pattern, the elemental analysis showed that there was carbon present in the material, suggesting that Os₃(CO)₁₂ was present pre-reaction. The carbon percentage was lower than expected, suggesting that the Os₃(CO)₁₂ percentage was also lower. This may be another reason for the lower activity of this material. The elemental analysis for the material pre- and post-reaction is provided in Table 52.

![XRD patterns of 5% Os₃(CO)₁₂/silica hydroxylated + 1% KOH: (a) pre-reaction and (b) post-reaction at 500°C. Reflections marked: Os (JCPDS file number 00-006-0662).](image)

Table 52: Elemental Analysis for pre- and post-reaction 5% Os₃(CO)₁₂/silica hydroxylated + 1% KOH.

<table>
<thead>
<tr>
<th>Material</th>
<th>Carbon Content from Elemental Analysis (wt. %)</th>
<th>Hydrogen Content from Elemental Analysis (wt. %)</th>
<th>Nitrogen Content from Elemental Analysis (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-reaction</td>
<td>0.75</td>
<td>0.78</td>
<td>0.01</td>
</tr>
<tr>
<td>Post-reaction</td>
<td>0.04</td>
<td>0.32</td>
<td>0.00</td>
</tr>
</tbody>
</table>

The elemental maps of osmium for the four samples is presented in Figure 198. The osmium appears to be evenly distributed across all four materials.
The EDX analysis of the four materials post-reaction is provided in Table 53. The osmium percentage for all four samples was higher than for the 5% Os₃(CO)₁₂/silica hydroxylated material discussed earlier, which contained 1.76 wt. % Os. There are a few interesting things to note. Firstly, although the doped material had a lower activity, this does not seem to be due to a lower percentage of osmium in the material. Next, as the 5% Os₃(CO)₁₂ on dehydroxylated silica apparently contained a higher percentage of osmium, this may explain the higher activity compared to the 5% Os₃(CO)₁₂/silica hydroxylated material. The osmium was not uniformly dispersed across the surface for all four samples, with variation in the osmium content observed in the EDX analysis. However, these results are statistically limited and this needs to be borne in mind. The lower loading may possibly suggest that the Os₃(CO)₁₂ was not completely loaded onto the support. However, as the Os was not evenly dispersed across the support, there were limitations to measuring the Os content by EDX analysis. Also, the monolayer coverage of Os₃ on silica was calculated to be only 0.44%.

Figure 198: Elemental maps of osmium for Os₃(CO)₁₂/silica post-reaction with 3:1 H₂/N₂. a) 5% Os₃(CO)₁₂/silica hydroxylated prepared under N₂, b) 5% Os₃(CO)₁₂/silica dehydroxylated, c) 7% Os₃(CO)₁₂/silica hydroxylated and d) 5% Os₃(CO)₁₂/silica hydroxylated + 1% KOH.
Table 53: EDX values for Os$_3$(CO)$_{12}$/silica post-reaction with 3:1 H$_2$/N$_2$.

<table>
<thead>
<tr>
<th>Material</th>
<th>Os weight (%)</th>
<th>C weight (%)</th>
<th>O weight (%)</th>
<th>Si weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5% Os$<em>3$(CO)$</em>{12}$/silica Hydroxylated prepared under N$_2$. Average from 4 measurements</td>
<td>2</td>
<td>20</td>
<td>51</td>
<td>26</td>
</tr>
<tr>
<td>5% Os$<em>3$(CO)$</em>{12}$/silica Dehydroxylated. Average from 10 measurements</td>
<td>4</td>
<td>22</td>
<td>31</td>
<td>43</td>
</tr>
<tr>
<td>7% Os$<em>3$(CO)$</em>{12}$/silica Hydroxylated. Average from 15 measurements</td>
<td>3</td>
<td>23</td>
<td>34</td>
<td>40</td>
</tr>
<tr>
<td>5% Os$<em>3$(CO)$</em>{12}$/silica Hydroxylated + 1% KOH. Average from 11 measurements</td>
<td>4</td>
<td>18</td>
<td>31</td>
<td>47</td>
</tr>
</tbody>
</table>

6.2.2.2 Os$_3$(CO)$_{12}$ on Gamma Alumina

Os$_3$(CO)$_{12}$ was supported on γ-alumina in order to investigate the effect the support may have on the ammonia synthesis activity. Os$_3$(CO)$_{12}$ was prepared on gamma alumina to give a percentage loading of 5% by weight of osmium. The material was first pre-treated at 500°C for 2 hours with N$_2$/H$_2$. Then, the temperature was decreased to 400°C. The temperature was subsequently changed as shown in Figure 199.

The material yielded an ammonia synthesis rate of 191 ± 43 µmol h$^{-1}$ g$^{-1}$ at 500°C when calculated from the catalyst weight. The rate was 3825 ± 860 µmol h$^{-1}$ g$_{Os}$ at 400°C. Although the material produced some ammonia at 400°C, it did not exhibit steady state activity. The performance of the material at 400°C did not change after being run at 500°C as can be seen in Figure 199.

The material was run at 500°C for 36 hours as shown in Figure 200 and was found to exhibit a steady-state ammonia synthesis rate throughout the reaction, with no indication of deactivation. The Os$_3$(CO)$_{12}$ supported on silica possessed a higher ammonia synthesis rate than the gamma alumina equivalent. Although alumina is amphoteric [189] and therefore
the acidic sites of the support might retain some of the ammonia that is produced, this did not seem to be a significant issue.

Aika et al. prepared 2% Ru$_3$(CO)$_{12}$/alumina and 5% Ru$_3$(CO)$_{12}$/alumina and obtained a rate of 62 µmol h$^{-1}$ g$^{-1}$ and 202 µmol h$^{-1}$ g$^{-1}$, respectively at 400°C and atmospheric pressure [25]. The mass was normalised to the total material weight. This suggests that the Ru metal is more active than the osmium at lower temperatures, even with a lower metal loading. This is to be expected as Ru has been shown to be more active than Os for ammonia synthesis [162] [163].

Figure 199: Conductivity profile for 5% Os$_3$(CO)$_{12}$/γ-alumina reacted with 3:1 H$_2$/N$_2$ at 400°C and 500°C.
Figure 200: Conductivity profile for 5% Os$_3$(CO)$_{12}$/γ-alumina reacted with 3:1 H$_2$/N$_2$ at 500°C for 36 hours.

The FTIR spectrum of the 5% Os$_3$(CO)$_{12}$/γ-alumina pre-reaction is provided in Figure 201. An FTIR spectrum was taken of the post-reaction material in order to see the effect the reaction had on the Os$_3$(CO)$_{12}$ structure. For the pre-reaction 5% Os$_3$(CO)$_{12}$/γ-alumina, IR frequencies were recorded in the carbonyl region at 2068 cm$^{-1}$ (m), 2033 cm$^{-1}$ (w) 2014 cm$^{-1}$ (vw) and 2003 cm$^{-1}$ (vw). These values are similar to those for the silica supported Os$_3$(CO)$_{12}$ and those reported in the literature [181] [184].
Os\textsubscript{3}(CO)\textsubscript{12} and $\gamma$-alumina can be seen in the XRD pattern of the supported gamma alumina material pre-reaction as shown in Figure 202. However, there is no evidence of Os\textsubscript{3}(CO)\textsubscript{12} present in the material post-reaction, with reflections due to $\gamma$-alumina being the only peaks observed. Therefore, this suggests that Os\textsubscript{3}(CO)\textsubscript{12} decomposed during the ammonia synthesis testing procedure. There does not appear to be a monolayer dispersion of Os\textsubscript{3}(CO)\textsubscript{12} in the pre-reaction material as the reflections for Os\textsubscript{3}(CO)\textsubscript{12} are crystalline.
Figure 202: XRD patterns of 5% Os$_3$(CO)$_{12}$/γ-alumina: (a) pre-reaction and (b) post-reaction with 3:1 H$_2$/N$_2$ at 500°C for 36 hours. Reflections marked: Os$_3$(CO)$_{12}$ (JCPDS file number 01-070-0415) and γ-Al$_2$O$_3$ (JCPDS file number 00-001-1303).

The FTIR spectrum of the post-reaction material is displayed in Figure 203. There were no distinct bands in the post-reaction spectrum. As before, this indicates that the Os$_3$(CO)$_{12}$ has decomposed on the support. A similar observation has been previously reported by Knözinger and Zhao [190], who observed that Os$_3$(CO)$_{12}$ on alumina, experienced thermal degradation by loss of CO at temperatures as low as 200°C. The decomposition of the material agrees with the analysis from the XRD pattern.
The EDX analysis showed that the pre-reaction material consisted of 3.7 wt. % Os, 13 wt.% C, 54 wt.% O and 29 wt.% Al. For the post-reaction material, the EDX analysis indicated that the sample consisted of 2.1 wt. % Os, 12 wt.% C, 53 wt.% O and 32 wt.% Al. The osmium percentage of 3.7 wt.% was slightly lower than the targeted 5% osmium. However, there did not appear to be uniform dispersion of osmium on the catalyst surface. The coverage of γ-alumina with triangular Os complex was calculated to be 0.91% as the γ-alumina had a BET surface area of 208 m²/g.

6.2.3 Supported Mixed Metal, Iron and Ruthenium Compounds

The other Group 8 metal carbonyls were investigated for ammonia synthesis activity, in order to make a comparison with the osmium compounds. The ammonia synthesis rates of the supported mixed metal, iron and ruthenium materials at 400°C and 500°C are presented in Table 54. Only those that had a steady state rate at these temperatures are provided. As can be observed, more materials were active at 500°C compared to 400°C.
<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature (°C)</th>
<th>NH₃ Synthesis Rate (µmol h⁻¹ g⁻¹)</th>
<th>NH₃ Synthesis Rate (µmol h⁻¹ g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5% Ru/Al₂O₃ + 1% KOH</td>
<td>400</td>
<td>461 ± 52</td>
<td>9207 ± 1038</td>
</tr>
<tr>
<td>5% Ru/Al₂O₃</td>
<td>400</td>
<td>42 ± 1</td>
<td>846 ± 21</td>
</tr>
<tr>
<td>2% Ru₃(CO)₁₂/γ-alumina</td>
<td>400</td>
<td>41 ± 5</td>
<td>2043 ± 265</td>
</tr>
<tr>
<td>2% Ru₃(CO)₁₂/silica hydroxylated</td>
<td>400</td>
<td>33 ± 6</td>
<td>1614 ± 274</td>
</tr>
<tr>
<td>1% Fe₃(CO)₁₂/γ-alumina</td>
<td>400</td>
<td>18 ± 2</td>
<td>1802 ± 228</td>
</tr>
<tr>
<td>5% Ru/Al₂O₃ + 1% KOH</td>
<td>500</td>
<td>544 ± 49</td>
<td>10875 ± 969</td>
</tr>
<tr>
<td>5% Ru/Al₂O₃</td>
<td>500</td>
<td>446 ± 63</td>
<td>8919 ± 1266</td>
</tr>
<tr>
<td>5% Os₃(CO)₁₂ + 2% Ru₃(CO)₁₂/silica hydroxylated</td>
<td>500</td>
<td>385 ± 34</td>
<td>5502 ± 491</td>
</tr>
<tr>
<td>2% Ru₃(CO)₁₂/γ-alumina</td>
<td>500</td>
<td>302 ± 19</td>
<td>15101 ± 934</td>
</tr>
<tr>
<td>2% Ru₃(CO)₁₂/silica hydroxylated</td>
<td>500</td>
<td>140 ± 51</td>
<td>6995 ± 2538</td>
</tr>
<tr>
<td>5% Os₃(CO)₁₂ + 1% Fe₃(CO)₁₂/silica hydroxylated</td>
<td>500</td>
<td>69 ± 1</td>
<td>1151 ± 14</td>
</tr>
<tr>
<td>1% Fe₃(CO)₁₂/γ-alumina</td>
<td>500</td>
<td>39 ± 10</td>
<td>3830 ± 944</td>
</tr>
<tr>
<td>2% Ru₃(CO)₁₂ + 1% Fe₃(CO)₁₂/silica hydroxylated</td>
<td>500</td>
<td>18 ± 3</td>
<td>587 ± 100</td>
</tr>
<tr>
<td>1% Fe₃(CO)₁₂/silica hydroxylated</td>
<td>500</td>
<td>4 ± 3</td>
<td>417 ± 317</td>
</tr>
</tbody>
</table>

Table 54: Ammonia synthesis rates of different mixed metal, iron and ruthenium supported materials reacted with 3:1 H₂/N₂ at 400°C and 500°C.

As supported Ru has previously been reported as having a high activity and is used in the KAAP process [29], Ru has been studied to give a reference. Commercial Ru/Al₂O₃ promoted with KOH gave the highest activity out of the materials studied at both 400°C and 500°C. In the literature, Ru is reported to have high activity as it is proposed to exhibit close to optimum nitrogen binding energy for ammonia synthesis [24]. At 400°C, there is a clearly evident enhancement due to the doping with KOH. This is in agreement with the literature, which states that doping of ruthenium with alkali metals increases activity via electron donation [26]. The promotional effect of KOH is less evident at 500°C, which could be due to loss of KOH at the elevated temperature. The choice of the support is also an important factor in enhancing the activity for Ru catalysts [191] [165]. It is suggested that the support controls the morphology of the Ru and therefore, the number of B₃ sites. In this study, the alumina supported Ru catalysts were more active than the
silica supported Ru catalyst at both 400°C and 500°C. This is in contrast to the Os₃(CO)₁₂, which exhibited better activity when supported on silica.

The supported iron based materials were shown to have the lowest activity of the samples investigated. As with the Ru based materials, the alumina supported Fe was more active at both 400°C and 500°C compared to when supported on silica. The higher activity of Os and Ru based materials compared to Fe is to be expected [24], although it must be noted that the loading of Fe was lower than for the other two metals. As stated in the introduction, iron has a higher activity when in the bulk form [192] [166] and therefore, the results of the supported Fe are as expected.

### 6.2.3.1 Supported Mixed Metal Compounds

Mixed metal supported materials were investigated in order to potentially optimise the ammonia synthesis activity and may provide the opportunity of tuning the activity of the dispersed clusters. The method performed by Kulkarni and Gates [52] was replicated in order to try and form supported mixed metal catalysts. As stated in the introduction, in this published work, mixed metal bonds were formed when the metal carbonyls underwent decarbonylation. Three mixed metal materials supported on hydroxylated silica have been prepared in this study: 5% Os₃(CO)₁₂ + 2% Ru₃(CO)₁₂, 5% Os₃(CO)₁₂ + 1% Fe₃(CO)₁₂ and 2% Ru₃(CO)₁₂ + 1% Fe₃(CO)₁₂.

None of the three materials were observed to exhibit a steady state ammonia synthesis rate at 400°C. As both 5% Os₃(CO)₁₂/silica hydroxylated and 2% Ru₃(CO)₁₂/silica hydroxylated were active at 400°C, it would possibly be expected that 5% Os₃(CO)₁₂ + 2% Ru₃(CO)₁₂/silica hydroxylated would also be active at this temperature. These results suggest that the metals were mixing due to the different effects on the rate.

At 500°C, the 5% Os₃(CO)₁₂ + 2% Ru₃(CO)₁₂/silica hydroxylated had the highest activity of the three mixed metal materials examined. This is possibly to be expected as the Os and Ru based materials displayed the highest activity. The activity of the mixed metal based material was higher than for both the 5% Os₃(CO)₁₂/silica hydroxylated (265 ± 48 µmol h⁻¹ g⁻¹) and 2% Ru₃(CO)₁₂/silica hydroxylated (140 ± 51 µmol h⁻¹ g⁻¹). The rate of the two separate monometallic materials added together is similar to the rate for the 5% Os₃(CO)₁₂ + 2% Ru₃(CO)₁₂/silica hydroxylated (385 ± 34 µmol h⁻¹ g⁻¹). Therefore, it is difficult at this stage to confirm whether the higher rate is due to the possible Os-Ru bond formation. However, when the rate is normalised to the targeted metal content, the rate for 5% Os₃(CO)₁₂ + 2% Ru₃(CO)₁₂/silica hydroxylated is lower than for 2% Ru₃(CO)₁₂/silica...
hydroxylated and is similar to the rate for 5\% Os$_3$(CO)$_{12}$/silica hydroxylated. This suggests that the rate is not as a result of adding the two metals together and could suggest the formation of Os-Ru bonds.

Both the 5\% Os$_3$(CO)$_{12}$ + 1\% Fe$_3$(CO)$_{12}$/silica hydroxylated and 2\% Ru$_3$(CO)$_{12}$ + 1\% Fe$_3$(CO)$_{12}$/silica hydroxylated had lower activities than the monometallic Os based and Ru based silica supported materials at 500\(^\circ\)C. This could possibly suggest that there was mixing of the metals, which had an adverse effect on the catalytic performance. Ru-Fe bimetallic catalyst has previously been reported to have a lower ammonia synthesis rate than Ru and Fe [193].

The XRD patterns of the mixed metal supported samples pre- and post-reaction are provided in Figures 204, 205 and 206. The crystalline reflections for Os$_3$(CO)$_{12}$, Ru$_3$(CO)$_{12}$ and Fe$_3$(CO)$_{12}$ in the pre-reaction XRD patterns indicates that there was not a monolayer dispersion of the metal complexes. For all three samples, it can be observed that the reflections due to the starting metal carbonyls are not present in the post-reaction patterns. In the XRD post-reaction patterns of the 5\% Os$_3$(CO)$_{12}$ + 2\% Ru$_3$(CO)$_{12}$/silica hydroxylated and 5\% Os$_3$(CO)$_{12}$ + 1\% Fe$_3$(CO)$_{12}$/silica hydroxylated, the broad band between 40 – 45\(^\circ\) 20 is observed. Furthermore, a reflection assigned to Ru metal can also be observed at 44\(^\circ\) 20 in the XRD pattern for 5\% Os$_3$(CO)$_{12}$ + 2\% Ru$_3$(CO)$_{12}$/silica hydroxylated. Therefore, it is suggested that the metal carbonyls decomposed to their corresponding metal components. However, in the post-reaction XRD pattern of 2\% Ru$_3$(CO)$_{12}$ + 1\% Fe$_3$(CO)$_{12}$/silica hydroxylated, there were no reflections corresponding to Ru or Fe metal. This cannot be due to a lower metal loading, as Ru with the same loading was observed in the XRD pattern for 5\% Os$_3$(CO)$_{12}$ + 2\% Ru$_3$(CO)$_{12}$/silica hydroxylated. This may explain the reason for this material having the lowest activity of the three samples.
Figure 204: XRD patterns of 5% Os\(_3\)(CO)\(_{12}\) + 2% Ru\(_3\)(CO)\(_{12}\)/silica hydroxylated pre- (black) and post-reaction (red) with 3:1 H\(_2\)/N\(_2\). Reflections marked: ⭐ Os\(_3\)(CO)\(_{12}\) (JCPDS file number 01-070-0415), • Ru\(_3\)(CO)\(_{12}\) (JCPDS file number 01-070-0553) and ♦ Ru (JCPDS file number 01-070-0274).

Figure 205: XRD patterns of 5% Os\(_3\)(CO)\(_{12}\) + 1% Fe\(_3\)(CO)\(_{12}\)/silica hydroxylated pre- (black) and post-reaction (red) with 3:1 H\(_2\)/N\(_2\). Reflections marked: ⭐ Os\(_3\)(CO)\(_{12}\) (JCPDS file number 01-070-0415) and + Fe\(_3\)(CO)\(_{12}\) (JCPDS file number 01-082-2196).
Figure 206: XRD patterns of 2% Ru$_3$(CO)$_{12}$ + 1% Fe$_3$(CO)$_{12}$/silica hydroxylated pre- (black) and post-reaction (red) with 3:1 H$_2$/N$_2$. Reflections marked: • Ru$_3$(CO)$_{12}$ (JCPDS file number 01-070-0553) and • Fe$_3$(CO)$_{12}$ (JCPDS file number 01-082-2196).

The FTIR spectra of the three supported mixed metal materials pre- and post-reaction are displayed in Figures 207, 208 and 209. For the 5% Os$_3$(CO)$_{12}$ + 2% Ru$_3$(CO)$_{12}$/silica hydroxylated pre-reaction spectrum, bands similar to those in the 5% Os$_3$(CO)$_{12}$/silica hydroxylated spectrum are observed. However, the IR bands for Ru$_3$(CO)$_{12}$ are at similar frequencies to those for Os$_3$(CO)$_{12}$ [184] [194]. Hence, overlapping of the bands due to Os$_3$(CO)$_{12}$ and Ru$_3$(CO)$_{12}$ may occur and will be difficult to distinguish.

The FTIR spectrum of 5% Os$_3$(CO)$_{12}$ + 1% Fe$_3$(CO)$_{12}$/silica hydroxylated pre-reaction is similar to the spectrum for 5% Os$_3$(CO)$_{12}$/silica hydroxylated. However, an additional band at 2046 (w) is also observed, which has been reported in the literature as a band for Fe$_3$(CO)$_{12}$ [195]. The expected bridging bands for Fe$_3$(CO)$_{12}$ between 1800 – 1900 cm$^{-1}$ may be present in the spectrum in Figure 208. However, as there appears to be background noise in this region it was difficult to distinguish the bands.

The bands in the pre-reaction FTIR spectrum for 2% Ru$_3$(CO)$_{12}$ + 1% Fe$_3$(CO)$_{12}$/silica hydroxylated were very weak and therefore, difficult to differentiate from the background noise. This could possibly suggest that the content of the two metal carbonyls was low in the material and thus, may explain the low activity of this material.
For all three samples, no clear bands were observed in the spectra post-reaction. This is to be expected as the metal carbonyls will have decomposed during the reaction. Therefore, the metal carbonyls underwent decarbonylation as observed by Kulkarni and Gates [52].

Figure 207: FTIR spectra of 5% Os₃(CO)₁₂ + 2% Ru₃(CO)₁₂/silica hydroxylated: a) pre-reaction and b) post-reaction.

Figure 208: FTIR spectra of 5% Os₃(CO)₁₂ + 1% Fe₃(CO)₁₂/silica hydroxylated: a) pre-reaction and b) post-reaction.
The pre and post-reaction EDX analysis is given in Table 55. The osmium percentage for 5% Os\textsubscript{3}(CO)\textsubscript{12} + 2% Ru\textsubscript{3}(CO)\textsubscript{12}/silica hydroxylated was higher than for 5% Os\textsubscript{3}(CO)\textsubscript{12} + 1% Fe\textsubscript{3}(CO)\textsubscript{12}/silica hydroxylated, which may explain the higher activity of this material. The osmium, ruthenium and iron percentages were observed to be higher post-reaction. The metal percentages were more varied across the areas examined in the pre-reaction materials and hence, this may suggest that there was better dispersion of the metals after the reaction.
### Material Composition and Analysis

<table>
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<tr>
<th>Material</th>
<th>Os weight (%)</th>
<th>Ru weight (%)</th>
<th>Fe weight (%)</th>
<th>C weight (%)</th>
<th>O weight (%)</th>
<th>Si weight (%)</th>
</tr>
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<tr>
<td>5% Os$<em>3$(CO)$</em>{12}$ + 2% Ru$<em>3$(CO)$</em>{12}$/silica Pre-reaction. Average from 6 measurements.</td>
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<td>0.5</td>
<td>-</td>
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<td>29</td>
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<tr>
<td>5% Os$<em>3$(CO)$</em>{12}$ + 2% Ru$<em>3$(CO)$</em>{12}$/silica Post-reaction. Average from 19 measurements.</td>
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<tr>
<td>5% Os$<em>3$(CO)$</em>{12}$ + 1% Fe$<em>3$(CO)$</em>{12}$/silica Pre-reaction. Average from 10 measurements.</td>
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<td>59</td>
<td>33</td>
</tr>
<tr>
<td>5% Os$<em>3$(CO)$</em>{12}$ + 1% Fe$<em>3$(CO)$</em>{12}$/silica Post-reaction. Average from 11 measurements.</td>
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<td>-</td>
<td>0.6</td>
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<td>52</td>
<td>35</td>
</tr>
</tbody>
</table>

Table 55: EDX values for 5% Os$_3$(CO)$_{12}$ + 2% Ru$_3$(CO)$_{12}$/silica hydroxylated and 5% Os$_3$(CO)$_{12}$ + 1% Fe$_3$(CO)$_{12}$/silica hydroxylated pre- and post-reaction with 3:1 H$_2$/N$_2$.

### 6.3 Conclusions

In this chapter the activity of the bulk and supported osmium was compared. The osmium metal (262 ± 21 µmol h$^{-1}$ g$^{-1}$) was found to have a similar activity as the supported Os$_3$(CO)$_{12}$ on silica (265 ± 48 µmol h$^{-1}$ g$^{-1}$) at 500°C. However, when the rate is normalised to the metal content, the supported material is more efficient. Therefore, it appears that osmium was structure sensitive for ammonia synthesis. The area of the supported metal particles is not known and therefore, a conclusion based upon comparative turnover frequencies cannot be made.

When osmium metal was pre-treated with H$_2$/Ar or N$_2$, a lag period was observed before the material became active. This was not the case when H$_2$/N$_2$ was used as the pre-treatment mixture. The inhibition of hydrogen and nitrogen coverage of the surface may explain this lag period, as might surface restructuring under the reaction atmosphere. The osmium metal had steady state activity for all three pre-treatments after the lag periods. A cycling procedure was performed in order to try and overcome the possible inhibition of
hydrogen on the surface of the osmium. However, the cycling procedure resulted in the activity being reduced. Shorter cycling times appeared to be the most promising and therefore, this may be an avenue to be explored in future work.

Os$_3$(CO)$_{12}$ was supported on both silica and $\gamma$-alumina to give a 5 wt. % loading of osmium. 5% Os$_3$(CO)$_{12}$/silica hydroxylated and 5% Os$_3$(CO)$_{12}$/γ-alumina were observed to be stable when tested for 36 hours. The material was found to have the highest activity when supported on silica. To optimise the activity of the Os$_3$(CO)$_{12}$/silica hydroxylated, the material was modified by four different methods. It was found that the material had the highest activity when the silica was dehydroxylated. Promoting the material with KOH was shown to have a negative effect on the activity. The metal carbonyl was observed to largely decompose as a consequence of the reaction procedure. Further studies need to be performed in order to confirm if the Os nuclearity was preserved upon decomposition.

As the supported mixed metal materials had different activities compared to their monometallic equivalents, this may suggest that there was possible metal-metal bond formation between the different metals. However, this would need to be investigated further in order to gain an insight into the nature of the active phases. This study suggests that it may be possible to optimise these materials and this method may provide the opportunity of altering the activity of the metal particles. Furthermore, different sized metal carbonyl precursors could be used to control ensemble size.

A summary of the performance of the supported materials investigated within this chapter is provided in Figures 210 and 211.
Figure 210: Ammonia synthesis activity of the supported materials reacted with 3:1 H<sub>2</sub>/N<sub>2</sub> at 400°C.

Figure 211: Ammonia synthesis activity of the supported materials reacted with 3:1 H<sub>2</sub>/N<sub>2</sub> at 500°C.
7. Conclusions and Future Work

7.1 Conclusions

The main aim of this work was to investigate the role composition and structure type had on the ammonia synthesis activity of ternary and quaternary molybdenum containing materials and also the potential structure sensitivity of Group 8 metals. As a result, nitrides (Ni$_2$Mo$_3$N, Ni$_2$GaMo$_3$N, Co$_2$Mo$_3$N and Fe$_3$Mo$_3$N), a carbonitride (Ni$_2$Mo$_3$C$_x$N$_y$) and carbides (Ni$_6$Mo$_6$C, Ni$_3$Mo$_3$C and Fe$_3$Mo$_3$C) were synthesised that had different metal compositions and either a η-carbide structure or a filled β-manganese structure. Furthermore, the structure sensitivity of osmium was examined and compared with the other Group 8 metals.

The synthesis of some of the pure phase nitrides and carbides proved to be challenging. In the case of Co$_2$Mo$_3$N, the Co$_3$Mo$_3$N phase was also present and therefore, the optimal conditions had to be identified to give the highest ratio of Co$_2$Mo$_3$N to Co$_3$Mo$_3$N. For some other phases, minor impurities of monometallic nitrides/carbides or metal phases were observed. Hence, the careful choice of the synthesis conditions was required, with precursors, temperature and synthesis atmosphere all having an effect on the resulting product. The four nitrides investigated in this work were active for ammonia synthesis, with ‘Co$_2$Mo$_3$N’ having the highest activity of 208 µmol h$^{-1}$ g$^{-1}$ at 400°C.

The lattice nitrogen reactivity of the different nitrides was investigated up to 900°C, in order to examine the effect the crystal structure and metal composition had on the nitrogen mobility. The bulk lattice nitrogen in the filled β-manganese structured Ni$_2$Mo$_3$N and η-carbide structured Ni$_2$GaMo$_3$N were observed to be unreactive. However, the filled β-manganese structured Co$_2$Mo$_3$N and η-carbide structured Fe$_3$Mo$_3$N were shown to decompose when reacted under 3:1 H$_2$/Ar at 900°C. As the two filled β-manganese structured nitrides and the two filled η-carbide structured nitrides were shown to have different reactivities from one another, this could possibly suggest that the metal composition has a greater effect on the reactivity than the structure type. However, since the filled β-manganese structured Co$_2$Mo$_3$N and the η-carbide structured Co$_3$Mo$_3$N were observed to have different reactivities under 3:1 H$_2$/Ar up to 800°C, both structure and metal composition seem to play a role in the reactivity of the lattice nitrogen.

The effect of the interstitial element composition on the ammonia synthesis activity of the nickel molybdenum and iron molybdenum materials was also investigated. Preparation of Ni$_2$Mo$_3$C by nitridation of Ni$_2$Mo$_3$N proved to be unsuccessful, with instead a carbonitride
phase being formed. \( \text{Ni}_2\text{Mo}_3\text{C}_x\text{N}_y \) was active for ammonia synthesis at 400°C and some replacement of lattice carbon was observed by elemental analysis. \( \text{Ni}_6\text{Mo}_6\text{C} \), \( \text{Ni}_3\text{Mo}_2\text{C} \) and \( \text{Fe}_3\text{Mo}_3\text{C} \) were not active at this temperature. For \( \text{Fe}_3\text{Mo}_3\text{C} \), unlike its corresponding nitride, a reaction temperature of 500°C was required before it developed activity. An induction period of 45 minutes was observed and through elemental analysis and analysis of the XRD patterns, it was discovered that substitution of some lattice carbon with nitrogen had taken place. This result may possibly suggest that the activity of \( \text{Fe}_3\text{Mo}_3\text{N} \) is due to the lattice nitrogen and therefore, the material may operate via a Mars-van Krevelen mechanism. The effect the passivation layer has on the reactivity of this system needs to be examined further but initial ToF-SIMS analysis suggests that this may have limited impact.

\( \text{Ni}_6\text{Mo}_6\text{C} \) and \( \text{Ni}_3\text{Mo}_2\text{C} \) required a much higher reaction temperature of 700°C before they were active. A small induction period was observed for both materials before there was development of activity. The two carbides were shown to undergo nitridation during the reaction. However, unlike \( \text{Fe}_3\text{Mo}_3\text{C} \), the nitridation process did not occur through a topotactic exchange mechanism, with both carbides instead forming \( \text{Ni}_2\text{Mo}_3\text{N} \). This possibly suggests that the \( \text{Ni}_3\text{Mo}_2\text{N} \) phase is unstable which is consistent with failed attempts to prepare it to date. This nitridation did not occur at the lower reaction temperatures examined and therefore, this may be the reason for the inactivity of these materials at these temperatures. Hence, it is possible that lattice nitrogen is required in order for these materials to be active.

The structure sensitivity of osmium was examined by comparing the ammonia synthesis activity of bulk osmium metal with triosmium dodecacarbonyl supported on silica and alumina. It was found that the bulk and supported osmium had similar activities at 500°C under 3:1 \( \text{H}_2/\text{N}_2 \). However, when the rate was normalised to take account of the differing mass of osmium present, the supported osmium materials were more active. This possibly suggests that the osmium is structure sensitive for ammonia synthesis, with the material being more active when the particle size is small. A comparison based upon turnover frequency is desirable. A cycling procedure was performed for osmium metal in order to try and improve ammonia production. Although production appeared to be reduced when this was implemented, shorter cycling times showed that there may be a benefit to this method.

Initial attempts were also performed in order to synthesise supported mixed metal clusters. Two of the osmium, ruthenium and iron metal carbonyl clusters were supported on silica and through FTIR analysis and analysis of the XRD patterns it was observed that the
materials underwent decarbonylation when reacted under 3:1 H₂/N₂. More detailed analysis using other techniques would need to be performed in order to determine if heterometallic bonds had formed. However, as the supported mixed metal materials had different activities to the supported monometallic equivalents, this possibly suggests that there may have been heterometallic bond formation. Therefore, this may be an interesting avenue to explore further.

7.2 Future Work

The formation of the η-carbide structured Ni₃Mo₃N, which is unprecedented to date, would give an interesting comparison to the isostructural Fe₃Mo₃N and Co₃Mo₃N. This would allow a further insight into the composition-activity relationship for ammonia synthesis and lattice nitrogen reactivity, which might be useful to feed into computational modelling for example. Furthermore, the comparison in performance between Ni₃Mo₃N and Ni₂Mo₃N would provide information on the structure-activity relationship. The study of anti-perovskites comprising the same elements but in different spatial and stoichiometric relationships could also provide information on the effect structure type has on activity.

The application of other complementary techniques such as X-ray photoelectron spectroscopy (XPS) and X-ray absorbance spectroscopy (XAS) could provide information on the effect structure and composition have on activity. XPS could also provide further information on the impact the passivation layer has on the activity of the carbides. XAS could be used to examine the possible heterometallic bond formation of the supported mixed metal clusters. This information could help towards the design of materials with high activity for ammonia synthesis.
Bibliography


[Fe2Ru(CO)12], [FeRu2(CO)12], [H2FeRu3(CO)13], [H2Ru4(CO)13], and Related Compounds,” *Journal of Organometallic Chemistry*, vol. 448, no. 1-2, pp. 157-166, 1993.


Appendices

Appendix I

The following calculation was used to determine the ammonia synthesis rate for each reaction that had a steady state reaction profile. The change in conductivity of 200 mL of 0.00108 mol/L sulfuric acid solution was used to measure the production of ammonia.

The first stage was to calculate the number of moles of $\text{H}_2\text{SO}_4$ within the flask.

$$\text{Moles (H}_2\text{SO}_4) = 0.00108 \text{ mol/L} \times 200 \text{ mL}$$

$$= 2.16 \times 10^{-4} \text{ moles}$$

This value is then multiplied by 2 to account for the equivalent $\text{H}^+$ in the ammonia needed to react with $\text{H}_2\text{SO}_4$.

$$= 4.32 \times 10^{-4} \text{ moles of ammonia required}$$

The mean conductivity change of the 0.00108 mol/L sulfuric acid solution for complete consumption by reaction with ammonia was observed to be 600 $\mu$S/cm.

The number of moles of ammonia required is divided by the mean conductivity to give the number of moles of $\text{H}_2\text{SO}_4$ used.

$$= 4.32 \times 10^{-4} \text{ moles/600} = 7.20 \times 10^{-7} \text{ mol/µScm}^{-1}$$

The gradient of the conductivity vs. time graph is multiplied by 60, to convert the value from minutes to hours, and $7.20 \times 10^{-7} \text{ mol/µScm}^{-1}$ to give a value $X$. Then, this value is divided by the mass of the material to obtain the ammonia synthesis rate in units of $\mu$mol hr$^{-1}$ g$^{-1}$ catalyst.
Appendix II

EDX Tables for Nickel Molybdenum Materials Prepared at Different Carburisation Temperatures with 20% CH\(_4\)/H\(_2\)

**Table 56:** EDX values for nickel molybdenum material prepared at 560°C with 20% CH\(_4\)/H\(_2\)

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<th>C weight (%)</th>
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**Table 57:** EDX values for nickel molybdenum material prepared at 600°C with 20% CH\(_4\)/H\(_2\)

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**Average**

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Table 58: EDX values for nickel molybdenum material prepared at 650°C with 20% CH₄/H₂

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Table 59: EDX values for nickel molybdenum material prepared at 700°C with 20% CH₄/H₂
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Table 60: EDX values for nickel molybdenum material prepared at 725°C with 20% CH₄/H₂
Appendix III

ToF-SIMS Data for Ni$_2$Mo$_3$C$_x$N$_y$

Figure 212: ToF-SIMS analysis from 100 – 120 m/z for Ni$_2$Mo$_3$C$_x$N$_y$

Figure 213: Depth profile for $^{92}$MoN from Ni$_2$Mo$_3$C$_x$N$_y$
Figure 214: Depth profiles for MoO\textsuperscript{3+} (red) and CN\textsuperscript{-} (orange) from Ni\textsubscript{2}Mo\textsubscript{3}C\textsubscript{x}N\textsubscript{y}.

Figure 215: Depth profiles for NiMoO\textsubscript{4} (red), \textsuperscript{92}MoC\textsuperscript{-} (green), \textsuperscript{94}MoC (purple), Mo\textsubscript{2}N (pink) and \textsuperscript{92}MoMoN (blue) from Ni\textsubscript{2}Mo\textsubscript{3}C\textsubscript{x}N\textsubscript{y}.
ToF-SIMS Data for Ni$_2$Mo$_3$C$_x$N$_y$ Post-Reaction with 3:1 H$_2$/N$_2$ at 400°C for 36 Hours

Figure 216: ToF-SIMS analysis from 100 – 120 m/z for Ni$_2$Mo$_3$C$_x$N$_y$ post reaction with 3:1 H$_2$/N$_2$ at 400°C for 36 hours.

Figure 217: Depth profile for $^{92}$MoN from Ni$_2$Mo$_3$C$_x$N$_y$ post reaction with 3:1 H$_2$/N$_2$ at 400°C for 36 hours.
Figure 218: Depth profiles for MoO$_3$ (red) and CN$^-$ (green) from Ni$_2$Mo$_3$C$_x$N$_y$ post reaction with 3:1 H$_2$/N$_2$ at 400°C for 36 hours.

Figure 219: Depth profiles for NiMoO$_4$ (red), $^{92}$MoC$^-$ (green), $^{94}$MoC (light blue), Mo$_3$N (pink) and $^{94}$Mo$^{96}$MoN (blue) from Ni$_2$Mo$_3$C$_x$N$_y$ post reaction with 3:1 H$_2$/N$_2$ at 400°C for 36 hours.
ToF-SIMS Data for Ni$_2$Mo$_3$C$_x$N$_y$ Post-Reaction with 3:1 H$_2$/N$_2$ at 500°C for 7.5 Hours

Figure 220: ToF-SIMS analysis from 100 – 120 m/z for Ni$_2$Mo$_3$C$_x$N$_y$ post-reaction with 3:1 H$_2$/N$_2$ at 500°C for 7.5 hours. Measurement was taken in static mode.
Appendix IV

SEM Images for Cobalt Molybdenum Oxide Prepared by Modified Pechini Method

Figure 221: SEM images of cobalt molybdenum oxide prepared by modified Pechini method (Co$_2$Mo$_3$O$_x$). a) 1000x magnification, b) 1000x magnification, c) 2000x magnification and d) 4000x magnification.

Figure 222: Element Map for cobalt molybdenum oxide (Co$_2$Mo$_3$O$_x$) prepared by modified Pechini method. Elements: Co (red), Mo (green) and O (blue).
SEM Images for Cobalt Molybdenum Oxide Prepared from Mixing of (NH₄)₆Mo₇O₂₄·4H₂O and Co(NO₃)₂·6H₂O (Method 2)

Figure 223: SEM images of cobalt molybdenum oxide (Co₂Mo₉Oₓ) prepared from method 2. a) 1000x magnification, b) 2000x magnification, c) 4000x magnification and d) 4000x magnification.
Appendix V

ToF-SIMS Data for Fe$_3$Mo$_3$C

Figure 224: ToF-SIMS analysis from 100 – 120 m/z for Fe$_3$Mo$_3$C.

Figure 225: Depth profile for $^{92}$MoN from Fe$_3$Mo$_3$C.
Figure 226: Depth profiles for MoO$_3^-$ (red) and CN$^-$ (green) from Fe$_3$Mo$_3$C.

Figure 227: Depth profiles for FeMoO$_4^-$ (green), $^{92}$MoC$^-$ (grey), $^{94}$MoC (blue) and $^{92}$MoMoN (pink) from Fe$_3$Mo$_3$C.
ToF-SIMS Data for Fe₃Mo₃C Post-Reaction with 3:1 H₂/N₂ at 400°C for 4 Hours and 500°C for 32 Hours

Figure 228: ToF-SIMS analysis from 100 – 120 m/z for Fe₃Mo₃C post-reaction with 3:1 H₂/N₂ at 400°C for 4 hours and 500°C for 32 hours.

Figure 229: Depth profile for ^{92}MoN from Fe₃Mo₃C post-reaction with 3:1 H₂/N₂ at 400°C for 4 hours and 500°C for 32 hours.
Figure 230: Depth profiles for MoO$_3^-$ (red) and CN$^-$ (green) from Fe$_3$Mo$_3$C post-reaction with 3:1 H$_2$/N$_2$ at 400°C for 4 hours and 500°C for 32 hours.

Figure 231: Depth profiles for FeMoO$_4^-$ (green), $^{92}$MoC$^-$ (grey), $^{94}$MoC (blue), $^{92}$MoMoN (pink) and Mo$_2$N (purple) from Fe$_3$Mo$_3$C post-reaction with 3:1 H$_2$/N$_2$ at 400°C for 4 hours and 500°C for 32 hours.
ToF-SIMS Data for Fe₃Mo₃C Post-Reaction with 3:1 H₂/N₂ at 500°C for 8 Hours

Figure 232: ToF-SIMS analysis from 100 – 120 m/z for Fe₃Mo₃C post-reaction with 3:1 H₂/N₂ at 500°C for 8 hours.

Figure 233: Depth profile for ^92MoN from Fe₃Mo₃C post-reaction with 3:1 H₂/N₂ at 500°C for 8 hours.
Figure 234: Depth profiles for MoO\(^{3-}\) (red) and CN\(^{-}\) (green) from Fe\(_3\)Mo\(_3\)C post-reaction with 3:1 H\(_2\)/N\(_2\) at 500\(^\circ\)C for 8 hours.

Figure 235: Depth profiles for FeMoO\(_4\) (green), \(^{92}\)MoC\(^{-}\) (grey), \(^{94}\)MoC (dark blue) and \(^{92}\)MoMoN (light blue) from Fe\(_3\)Mo\(_3\)C post-reaction with 3:1 H\(_2\)/N\(_2\) at 500\(^\circ\)C for 8 hours.