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The Role of Composition and Phase upon the Lattice Nitrogen Reactivity of Ternary Molybdenum Nitrides

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Abstract
The reactivity of the lattice nitrogen in the filled β-Mn structured Co$_2$Mo$_3$N and the η-carbide structured Co$_3$Mo$_3$N and Fe$_3$Mo$_3$N has been investigated under 3:1 H$_2$/Ar at temperatures up to 900 °C. The lattice nitrogen in Co$_3$Mo$_3$N was found to be reactive, as reported previously, whereas Co$_2$Mo$_3$N was shown to be stable up to 800 °C. Upon H$_2$/Ar treatment at 900 °C, the Co$_2$Mo$_3$N, Co$_3$Mo$_3$N and Fe$_3$Mo$_3$N phases decomposed. These results suggest that both metal composition and phase have an influence on the bulk lattice nitrogen reactivity of the ternary nitrides.

Keywords Ammonia · Cobalt · Iron · Molybdenum · Nitride

1 Introduction
Ammonia production is of high importance as it can be used as a precursor to form synthetic fertilisers. The industrial route for producing ammonia is via the Haber–Bosch process and this is stated to sustain around 40% of the world population [1]. However, when considering the entirety of the process, including the feedstream production, it accounts for 1–2% of the world energy demand [2]. One possible way to overcome this disadvantage is the development of a process that could operate under more moderate conditions and facilitate localised and sustainable production. However, this would require the development of a more active ammonia synthesis catalyst. The η-carbide structured Co$_3$Mo$_3$N has a high ammonia synthesis activity, especially when doped with a low percentage of Cs$^+$ and is reported to have a higher rate than the iron-based catalyst used in the Haber Bosch process [2]. One possible explanation for the high activity of this nitride has been proposed by a volcano relationship, where the combination of Co and Mo gives a material with an almost optimal nitrogen binding energy and results in a high turnover frequency for ammonia synthesis [3]. In this proposal, the lattice nitrogen is suggested to have no active role and CoMo is the active phase. The role of the lattice nitrogen is stated to be to ensure that the correct structural ordering occurs such that the (111) face containing both Co and Mo is exposed. One alternative explanation for the activity of Co$_3$Mo$_3$N is that it proceeds via a Mars-van Krevelen mechanism and hence, the lattice nitrogen is reactive. In this mechanim, the lattice nitrogen is directly hydrogenated to yield ammonia, generating a transient lattice vacancy, which is then replenished by gas-phase nitrogen. This proposed explanation has been supported by experimental work, where an investigation into the isostructural Co$_3$Mo$_3$C phase showed that the carbide required a higher temperature than Co$_3$Mo$_3$N before activity was exhibited and nitridation of the lattice carbon occurred during the reaction [4]. Furthermore, nitrogen isotopic exchange studies have shown that a substantial percentage of the lattice nitrogen in Co$_3$Mo$_3$N can be exchanged, depending on the pre-treatment conditions used [5]. In addition, computational modelling studies have suggested that an associative N$_2$ activation pathway on Co$_3$Mo$_3$N may occur at nitrogen lattice vacancies [6] and that there are significant lattice nitrogen vacancies for this nitride at temperatures relevant for ammonia synthesis [7]. This mechanism differs significantly from the widely proposed view of dinitrogen dissociation being the rate determining step in relation to promoted iron-based ammonia synthesis catalysts, although for that system Spencer has pointed out that under industrially relevant conditions ammonia synthesis cannot be described in terms of a single
rate determining step and that hydrogenation of adsorbed nitrogen species and ammonia desorption play a more significant role [8].

Related to the reactivity of lattice N, Co₃Mo₃N is also of interest due to its ability to lose half of its lattice nitrogen to form Co₃Mo₃N, where the remaining lattice nitrogen relocates from the 16c Wyckoff site to the 8a site [9, 10]. The original nitride can then be regenerated from Co₆Mo₆N under either N₂/H₂ or pure N₂ [9, 11]. Therefore, the lattice nitrogen in Co₂Mo₃N has been shown to be highly reactive, even at temperatures of 900 °C under 3:1 H₂/Ar [12]. Furthermore, the loss of lattice nitrogen from the η-carbide structured Ni₂Mo₃N, where the bulk lattice nitrogen has been shown to be unreactive, even at temperatures of 900 °C under 3:1 H₂/Ar [12].

The basis of the current study is to establish the potential role and structure/composition activity dependence of lattice nitrogen reactivity in terms of ternary metal nitrides. The analysis of the lattice nitrogen reactivity of nitrides through the comparison of their ammonia synthesis rates under Ar/H₂ would give an insight into the structure–activity and composition–activity relationships. Therefore, an investigation of the η-carbide structured Fe₃Mo₃N has been performed to provide a comparison with the isostructural Co₂Mo₃N. This information will give an insight into the role metal composition has on the lattice nitrogen reactivity and it is hoped that a more thorough understanding of this aspect may be applied to the further development of novel ammonia synthesis catalysts.

2 Experimental

2.1 Preparation of Fe₃Mo₃N

Iron molybdenum oxide was prepared by a similar procedure as detailed by Bem et al. [17]. 0.25 M aqueous solution of 37.1 mL of iron (II) chloride tetrahydrate (FeCl₂-4H₂O, Sigma Aldrich, ReagentPlus, 98%) was added dropwise to 0.66 M aqueous solution of 14 mL of sodium molybdate dihydrate (Na₂MoO₄·2H₂O, Hopkin and Williams, Analar, 99.0–102.0%). The solid product formed instantly upon the mixing of the two solutions. The mixture was left to stir for 1 h once all the FeCl₂·4H₂O aqueous solution was added. The solid was obtained by vacuum filtration and was washed twice with distilled water and once with ethanol. The oxide powder was dried overnight in an oven at 150 °C and was then calcined under 60 mL/min of nitrogen at 500 °C for 6 h. Finally, the oxide was cooled down to room temperature under nitrogen.

Fe₂Mo₃N was prepared by ammonolysis of the oxide precursor under 94 mL/min NH₃ gas (BOC 99.98%). 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 a final increase of 2.1 °C/min to 785 °C, then held at this temperature for 5 h before being cooled to room temperature. The system was flushed with nitrogen for 30 min and then the resultant material was passivated under a mixture of 2% O₂/Ar and N₂ for 1 h.

2.2 Preparation of Co₂Mo₃N

Cobalt molybdenum oxide was prepared by using a modified form of the Pechini method as described by Bion et al. [18]. The necessary amounts of ammonium molybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O, Fluka Analytical, puriss. p.a., ACS reagent, ≥ 99.0%) and cobalt (II) nitrate hexahydrate (Co(NO₃)₂·6H₂O, Alfa Aesar, ACS, 98.0–102.0%, crystalline) were added to a 10% aqueous solution of nitric acid to give a 2:3 ratio of Co:Mo. Citric acid monohydrate (C₆H₈O₇·H₂O, Sigma Aldrich, ACS reagent, ≥ 99.0%) was then added to the mixture. The mixture was stirred at room temperature, until the starting materials had been dissolved. Subsequently, the mixture was evaporated off at 70 °C, until a red coloured gel had formed. The gel was dried in an oven overnight at 120 °C and was then calcined in air at 500 °C for 2 h.

Co₂Mo₃N was prepared via nitridation of the mixed oxide precursor under 3:1 H₂/N₂ gas mixture at 700 °C for 3 h with a flow rate of 60 mL/min. A heating ramp rate of 10 °C/min was used to reach 700 °C.

2.3 Preparation of Co₃Mo₃N

Cobalt molybdenum oxide (CoMoO₄) was prepared by the reaction of the necessary amounts of ammonium molybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O, 99.98%, SigmaAldrich) with cobalt (II) nitrate hexahydrate (Co(NO₃)₂·6H₂O, > 98%, Sigma-Aldrich). The starting materials were dissolved separately in either 100 mL or 150 mL of deionised water, respectively. The solution of cobalt was then added dropwise to the molybdenum
solution. The resultant mixture was heated to 80 °C until a purple solid had formed, then vacuum filtered and the purple precipitate was washed twice with deionised water and once with ethanol. The oxide powder (CoMoO₄·nH₂O) was dried overnight in an oven at 150 °C and was then calcined in air at 600 °C for 3 h.

Co₃Mo₃N was prepared by nitridation of the oxide precursor under 3:1 H₂/N₂ gas mixture (BOC, 99.98%) at either 700 °C, 800 °C or 900 °C for 4 h with a flow rate of 60 mL/min. A heating ramp rate of 10 °C/min was used. The resultant nitride was cooled to ambient temperature under 3:1 H₂/N₂. For clarity, the nitride prepared at the different temperatures will be referred to as either CoMoN700, CoMoN800 and Co₃Mo₃N900.

2.4 Lattice Nitrogen Reactivity Testing

Approximately 0.3 g of material was tested at ambient pressure under 3:1 H₂/Ar (BOC, 99.98%) with a gas flow rate of 60 mL/min. The stability and possible lattice nitrogen reactivity of the prepared Co₂Mo₃N and Co₃Mo₃N material was investigated by testing the material under 3:1 H₂/Ar at 700 °C, 800 °C and 900 °C. Fe₃Mo₃N was also examined at 900 °C under 3:1 H₂/Ar for its lattice nitrogen reactivity. The decrease in conductivity of a 0.00108 M 200 mL solution of H₂SO₄, which the exit stream of gas flowed through, was used to determine the production of ammonia. At such high reaction temperatures (700–900 °C), ammonia is thermodynamically unstable with respect to decomposition into N₂ and H₂.

3 Results and Discussion

3.1 Lattice Nitrogen Reactivity of Fe₃Mo₃N

As the η-carbide structured Co₃Mo₃N and filled β-Mn structured Ni₂Mo₃N have been shown to have different lattice nitrogen reactivities, it would be of interest to investigate whether the phase or metal composition has the larger impact on the reactivity. This could lead to the development and design of active nitrides for ammonia synthesis. Therefore, the lattice nitrogen reactivity of another η-carbide structured nitride, Fe₃Mo₃N, has been investigated in this work. As this nitride has the same crystal structure type as Co₃Mo₃N but a different metal composition, it may prove possible to gain an insight into the role of the metal composition-activity relationship. It has previously been reported that the lattice nitrogen of Fe₃Mo₃N is less reactive than in Co₃Mo₃N. Fe₃Mo₃N has been observed to be stable under 3:1 H₂/Ar up to 800 °C, with a minimal loss of lattice nitrogen [13, 14]. Furthermore, neutron diffraction analysis revealed that bulk nitrogen was not lost from Fe₃Mo₃N [14]. A higher temperature has been investigated in the present study to investigate whether the bulk lattice nitrogen in the Fe₃Mo₃N phase is reactive but requires a higher temperature than that observed for Co₃Mo₃N. The Fe₃Mo₃N appeared from XRD to be phase pure when prepared from ammonolysis of an iron molybdenum oxide precursor as evidenced in Fig. 1a. The nitrogen analysis (Table 1) showed that the nitride had a considerably higher nitrogen content than the calculated stoichiometric value for Fe₃Mo₃N (2.98 wt%). However, NH₃ species on the surface of the material, that

![Fig. 1 XRD patterns of Fe₃Mo₃N: a pre-reaction and b post-reaction with 3:1 H₂/Ar at 900 °C. (▲) Fe₃Mo₃N (PDF ref.: 00–048–1408), (●) Mo (PDF ref.: 01–089–5023) and (★) ε-Fe₃N (PDF ref.: 01–073–2101)](image-url)
are a result of the preparation method, could account for this difference in values as could the presence of an amorphous N containing component. Representative SEM images show that Fe₃Mo₃N consisted of rounded particles (Fig. 2). The material was observed to have a surface area of 13 m²/g, which is comparable with those reported in the literature for this nitride [19, 20]. However, as the nitride was passivated prior to exposure to air, as is standard for nitride materials, the BET surface area will possibly not be representative of the area under the testing conditions. As expected, passivation of nitrides changes surface composition [21] and can lead to changes in surface area [22].

The reactivity of the lattice nitrogen in Fe₃Mo₃N was examined by treating the nitride at 900 °C under 3:1 H₂/Ar at ambient pressure for 7 h. If the material operated via a Mars-van Krevelen mechanism for ammonia synthesis, a reduction in the nitrogen content might occur and additionally, there may be a transformation of the structure as was observed for the Co₃Mo₃N counterpart. The conductivity profile (Online Resource Fig. S1) implies that only a minimal amount of ammonia was produced under these conditions. A total of 35 μmol of ammonia was produced over the 7 h of the reaction. However, it must be noted that ammonia is thermodynamically unstable at this temperature and will decompose [23] and, therefore, the loss of lattice nitrogen in the final form of N₂ will be more favourable. The post-reaction XRD pattern shows that the nitride had decomposed to Mo metal and an iron nitride phase under these reaction conditions (Fig. 1b). It appears that trace amounts of Fe₃Mo₃N were still present in the material as reflections were observed at 42° and 72° 2θ. The nitrogen analysis confirms the loss of lattice nitrogen from this material as there was a significant decrease post-reaction (Table 1). The percentage of the overall nitrogen that was removed from Fe₃Mo₃N and was converted to ammonia was ca. 6%, with the rest of the nitrogen presumably being lost in the form of N₂. SEM analysis showed that the morphology was retained after the decomposition of the material compared to pre-reaction (Fig. 2). The lattice nitrogen in Fe₃Mo₃N was much more reactive at 900 °C than for the filled β-Mn structured Ni₂Mo₃N, which was shown to be stable at this temperature [12]. Therefore, this possibly suggests that metal composition has a major impact on the activity.

### Table 1 Nitrogen analysis pre- and post-reaction for Fe₃Mo₃N

| Material      | Nitrogen content (wt%) |
|---------------|------------------------|
| Fe₃Mo₃N      | 4.27                   |
| Fe₃Mo₃N post H₂/Ar 900 °C | 0.49                   |

3.2 Lattice Nitrogen Reactivity of Co₂Mo₃N

The ability of the Co₃Mo₃N phase to lose bulk lattice nitrogen at 700 °C under H₂/Ar [24], contrasted with Fe₃Mo₃N as discussed above, suggests that this is possibly due to the CoMo composition. Therefore, it was of interest to examine the filled β-Mn structured Co₂Mo₃N phase, which has the same metal composition but different crystal structure type. Comparing the lattice nitrogen reactivity of Co₂Mo₃N with the η-carbide structured Co₃Mo₃N might provide an insight into the crystal structure–activity relationship. To investigate this potential relationship, attempts were made to prepare the pure phase Co₂Mo₃N. The modified Pechini method was chosen for the synthesis process as it has previously been used to synthesis pure phase filled β-Mn structured Ni₂Mo₃N [18]. The filled β-Mn structured Co₂Mo₃N was prepared via nitridation of the oxide precursor at 700 °C for three hours under 3:1 H₂/N₂. This was found to be the optimum preparation temperature and duration to give the highest amount of the desired nitride. The preparation of the pure phase nitride was unsuccessful, with instead a mixture of Co₂Mo₃N, Co₃Mo₃N and β-Mo₂N₀.₇₈ being formed (Fig. 3). This material contained 3.82 wt% nitrogen from elemental analysis as presented in Table 2 (the expected stoichiometric nitrogen content of Co₂Mo₃N is 3.34 wt%). The SEM images of the mixed Co₂Mo₃N show that the material had a porous and smooth surface (Fig. 4a). Although the material

![Fig. 2](image-url) Representative SEM images of Fe₃Mo₃N: a pre-reaction and b post H₂/Ar reaction at 900 °C.
was shown to contain the Co$_3$Mo$_3$N phase, the expected needle morphology for this phase was not observed.

In order to investigate the lattice nitrogen reactivity of the mixed phase Co$_2$Mo$_3$N and Co$_3$Mo$_3$N, the material was reduced at 700 °C, 800 °C or 900 °C under 3:1 H$_2$/Ar at ambient pressure for 7 h. The conductivity profile data under 3:1 H$_2$/Ar at 700 °C for the mixed Co$_2$Mo$_3$N and Co$_3$Mo$_3$N material is provided (Online Resource Fig. S2). A total of 37 μmol of ammonia was formed over the 7 h of reaction. The conductivity profiles for the 800 °C and 900 °C reactions (Online Resource Figure S2) show that the rates were non-steady state and the production of ammonia was minimal. The total amount of ammonia formed was 32 μmol and 22 μmol over the 7 h at 800 °C and 900 °C, respectively. These results agree with the limited stability of ammonia under these conditions and therefore, it would be expected that most of the lattice nitrogen would be lost in the final form of N$_2$. The Co$_3$Mo$_3$N reflections were shown to have shifted to higher 2θ angles post 700 °C reaction (Fig. 5a), suggesting that there was a decrease in the lattice nitrogen content of this phase, which is to be expected when it transforms to the Co$_6$Mo$_6$N phase [13]. Due to the degree of overlap between the reflections of Co$_2$Mo$_3$N and Co$_3$Mo$_3$N this is somewhat difficult to observe. However, this was most clearly noticed when comparing the pre- and post-reaction reflection at approximately 35.5° 2θ, where there is no overlap of reflections. The shift of Co$_3$Mo$_3$N reflections to higher

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**Table 2** Nitrogen analysis pre- and post-reaction for the prepared “Co$_2$Mo$_3$N” samples

| Material                        | Nitrogen content (wt%) |
|---------------------------------|------------------------|
| “Co$_2$Mo$_3$N”                 | 3.82                   |
| “Co$_2$Mo$_3$N” post H$_2$/Ar 700 °C | 2.07                   |
| “Co$_3$Mo$_3$N” post H$_2$/Ar 800 °C | 0.72                   |
| “Co$_3$Mo$_3$N” post H$_2$/Ar 900 °C | 0.48                   |

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**Fig. 3** XRD pattern of prepared Co$_2$Mo$_3$N. (▲) Co$_2$Mo$_3$N (PDF ref.: 01–072-6570), (●) Co$_3$Mo$_3$N (PDF ref.: 01–089-7953) and (■) β-Mo$_2$N$_{0.78}$ (PDF ref.: 03–065-6236)
structure. When Co$_2$Mo$_4$N transforms into Co$_2$Mo$_2$N, the residual lattice nitrogen relocates from the 16c site to the 8a site, an apparently less reactive site from which it is not lost. The XRD pattern of the “Co$_2$Mo$_2$N” material post 900 °C reaction shows it has decomposed to α-Co, Co$_{0.08}$Mo$_{0.92}$ and either a cobalt nitride phase or a cobalt molybdenum alloy (Fig. 5c). Fe$_3$Mo$_3$N was shown to have a similar decomposition as Co$_2$Mo$_2$N and Co$_3$Mo$_3$N under these conditions. This is again in contrast to the filled β-Mn structured Ni$_2$Mo$_3$N, which was stable at 900 °C [12]. As expected, the nitrogen analysis showed that the nitrogen content decreased significantly post H$_2$/Ar reaction for all three temperatures compared to pre-reaction as seen in Table 2. As the post 700 °C reaction material consisted of Co$_2$Mo$_3$N, Co$_3$Mo$_3$N and Mo, the stoichiometric percentage in this material is expected to be 1.92 wt% nitrogen, if it is assumed that the phases have a 1:1:1 ratio. The obtained value of 2.07 wt% agrees quite well with this value. For the post 800 °C reaction material, based upon the XRD pattern, it would be expected that the loss of nitrogen from this material is predominantly from the Co$_3$Mo$_3$N and β-Mo$_2$N$_{0.78}$ phases. The significant loss of nitrogen from the post 900 °C material agrees with the observed decomposition during the reaction. The percentage of the overall nitrogen that was removed from the material and was converted to ammonia was ca. 25%, 24% and 13% for the 700 °C, 800 °C and 900 °C reactions, respectively. The SEM images in Fig. 4 show that the morphology for all three post H$_2$/Ar reaction materials were similar to the pre-reaction material. Therefore, the decomposition of the material during the 900 °C reaction did not have a major effect on the morphology. However, the material appeared to be more porous following 900 °C reaction. Other materials have been reported to have a porous nature post-reaction when they decomposed under 3:1 H$_2$/Ar [25].

### 3.3 Co$_3$Mo$_3$N Prepared by Nitridation with N$_2$/H$_2$

The η-carbide structured Co$_3$Mo$_3$N is traditionally prepared in a pure form by temperature programmed ammonolysis of a CoMoO$_4$ precursor [13, 24, 26]. However, the formation of nitrides via temperature programmed ammonolysis has several disadvantages, including reduction in efficiency in the process due to large amounts of heat transfer and problems arising due to using ammonia at a large scale [27]. Therefore, although the bulk lattice nitrogen in Ni$_2$Mo$_3$N appears to be relatively unreactive, this nitride has an advantage in that it is able to be prepared under N$_2$/H$_2$ at 700 °C [18]. Co$_3$Mo$_3$N appears to be uniquely active with regards to its lattice nitrogen reactivity which could have interesting applications as a nitrogen transfer material. It would therefore be of interest to prepare Co$_3$Mo$_3$N under N$_2$/H$_2$. In this work, attempts were made to prepare Co$_3$Mo$_3$N directly by nitridation of the oxide with N$_2$/H$_2$ at 700 °C, 800 °C or 900 °C.
The direct \( \text{N}_2/\text{H}_2 \) nitridation process at 700 \(^\circ\text{C} \) resulted in a mixed phased material of \( \text{Co}_2\text{Mo}_3\text{N} \) with minor amounts of \( \text{Co}_3\text{Mo}_3\text{N} \) and \( \beta\)-\( \text{Mo}_2\text{N}_{0.78} \) as can be observed in Fig. 6(a). As stoichiometric amounts of cobalt and molybdenum were used in the preparation, it appears that there is unidentified \( \text{Co} \) present in the material. Cobalt metal may be present but undetected due to peak overlap at 44° 2θ, as previously suggested by Adamski et al. [16]. The preparation at 800 °C results in a mixture of \( \text{Co}_3\text{Mo}_3\text{N} \) and \( \text{Co}_2\text{Mo}_3\text{N} \), with \( \text{Co}_2\text{Mo}_3\text{N} \) being the majority phase (Fig. 6b). A small reflection at 44° 2θ is observed, suggesting that the excess cobalt is present in its elemental form. Preparation at the highest temperature of 900 °C produces the pure phase highly crystalline \( \text{Co}_3\text{Mo}_3\text{N} \) (Fig. 6c). Adamski et al. have proposed that the oxide precursor is first transformed to \( \text{Co}_2\text{Mo}_3\text{N} \) and a molybdenum nitride phase, before forming the \( \text{Co}_3\text{Mo}_3\text{N} \) phase [28]. Therefore, this may be an explanation for why the pure phased \( \text{Co}_2\text{Mo}_3\text{N} \) is only formed at high temperatures under \( \text{N}_2/\text{H}_2 \). This result shows promise for forming \( \text{Co}_3\text{Mo}_3\text{N} \) under nitridation conditions. It appears that there is a significant difference in morphology between the cobalt molybdenum nitrides as observed in Fig. 7. The material prepared at 700 °C (CoMoN700) consists of small solid particles. The morphology of the material prepared at 900 °C (CoMoN900) was similar to the expected needle structure for \( \text{Co}_3\text{Mo}_3\text{N} \) that is observed when it is prepared under ammonolysis [4, 29]. The nitrogen analysis (Table 3) mainly agrees with the assignment for the nitrides prepared at the different temperatures. CoMoN700 has the highest nitrogen content. The nitrogen content of the material prepared at 800 °C (CoMoN800) is below that expected for stoichiometric \( \text{Co}_3\text{Mo}_3\text{N} \) and the material was found from XRD to comprise \( \text{Co}_2\text{Mo}_3\text{N} \), \( \text{Co}_3\text{Mo}_3\text{N} \) and \( \text{Co} \). The nitrogen content of \( \text{Co}_3\text{Mo}_3\text{N} \) is in very close agreement with the expected stoichiometric nitrogen weight percentage for \( \text{Co}_3\text{Mo}_3\text{N} \) (2.93 wt%), further confirming the successful synthesis of the pure phase \( \text{Co}_3\text{Mo}_3\text{N} \).

### 4 Conclusions

The bulk lattice nitrogen reactivity of the \( \eta \)-carbide structured \( \text{Fe}_3\text{Mo}_3\text{N} \) and \( \text{Co}_3\text{Mo}_3\text{N} \) and filled \( \beta \)-Mn structured \( \text{Co}_2\text{Mo}_3\text{N} \) has been investigated by testing the materials under \( \text{Ar}/\text{H}_2 \). The metal composition-activity relationship was examined by comparison of the isostructural \( \text{Fe}_3\text{Mo}_3\text{N} \) and \( \text{Co}_3\text{Mo}_3\text{N} \). \( \text{Fe}_3\text{Mo}_3\text{N} \) was shown to decompose to Mo and an iron nitride phase under 3:1 \( \text{H}_2/\text{Ar} \) at 900 °C. In the literature, the bulk lattice nitrogen of \( \text{Fe}_3\text{Mo}_3\text{N} \) has been reported to be unreactive up to a temperature of 800 °C [13,

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**Table 3** Nitrogen analysis for the prepared \( \text{Co}_3\text{Mo}_3\text{N} \) samples at different temperatures

| Material          | Nitrogen content (wt%) |
|-------------------|------------------------|
| CoMoN700          | 3.99                   |
| CoMoN800          | 2.58                   |
| \( \text{Co}_3\text{Mo}_3\text{N} \) | 2.88                   |

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Therefore, it appears that the Fe$_3$Mo$_3$N phase has a different reactivity to Co$_3$Mo$_3$N, even at high temperatures, possibly suggesting that metal composition is the dominant influence on the bulk lattice nitrogen reactivity. Additionally, with this in mind, an investigation of the filled β-Mn structured Co$_2$Mo$_3$N and the η-carbide structured Co$_3$Mo$_3$N has also been performed to provide an insight into a possible structure–activity relationship. The filled β-Mn structured Co$_2$Mo$_3$N could not be synthesised in the pure form, with instead the material being a mixture of Co$_2$Mo$_3$N and Co$_3$Mo$_3$N. The mixed phase Co$_2$Mo$_3$N and Co$_3$Mo$_3$N were examined for their lattice nitrogen reactivities between 700 °C and 900 °C under 3:1 H$_2$/Ar. At 700 °C and 800 °C, the filled β-Mn structured Co$_2$Mo$_3$N was shown to be stable and η-carbide structured Co$_3$Mo$_3$N was observed to be more reactive by losing the majority of its lattice nitrogen. When reacted at 900 °C, the material decomposed to its metal constituents and the majority of the lattice nitrogen was removed, as was observed for Fe$_3$Mo$_3$N. It has previously been observed that the filled β-Mn structured Ni$_2$Mo$_3$N was stable at this temperature [12]. Overall, the lattice nitrogen reactivity of the ternary nitrides has been found to be complex. Additionally, pure phase η-carbide structured Co$_3$Mo$_3$N with needle morphology was synthesised under 3:1 H$_2$/N$_2$ at 900 °C.

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Data Availability The data generated in this work are available on reasonable request to the corresponding authors.

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