ORIGINAL PAPER

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

Angela Daisley[1] · Lucy Costley-Wood[1] · Justin S. J. Hargreaves[1]

Abstract

The reactivity of the lattice nitrogen in the filled β-Mn structured Co_2Mo_3N and the η-carbide structured Co_3Mo_3N and Fe_3Mo_3N has been investigated under 3:1 H_2/Ar at temperatures up to 900 °C. The lattice nitrogen in Co_3Mo_3N was found to be reactive, as reported previously, whereas Co_2Mo_3N was shown to be stable up to 800 °C. Upon H_2/Ar treatment at 900 °C, the Co_2Mo_3N, Co_3Mo_3N and Fe_3Mo_3N 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_3Mo_3N 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_3Mo_3N is that it proceeds via a Mars-van Krevelen mechanism and hence, the lattice nitrogen is reactive. In this mechanism, 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_3Mo_3C phase showed that the carbide required a higher temperature than Co_3Mo_3N 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_3Mo_3N 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_3Mo_3N 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

✉ Angela Daisley
angela.daisley@glasgow.ac.uk

Justin S. J. Hargreaves
Justin.Hargreaves@glasgow.ac.uk

1 School of Chemistry, Joseph Black Building, University of Glasgow, Glasgow G12 8QQ, UK

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, Co_3Mo_3N is also of interest due to its ability to lose half of its lattice nitrogen to form Co_6Mo_6N, 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 Co_6Mo_6N under either N_2/H_2 or pure N_2 [9, 11]. Therefore, the lattice nitrogen in Co_3Mo_3N has been shown to be highly reactive. This is not the case for the filled β-Mn structured Ni_2Mo_3N, where the bulk lattice nitrogen has been shown to be unreactive, even at temperatures of 900 °C under 3:1 H_2/Ar [12]. Furthermore, the loss of lattice nitrogen from the η-carbide structured Fe_3Mo_3N has been reported to be minimal under 3:1 H_2/Ar up to 800 °C [14, 15]. A comparison with the η-carbide structured Ni_3Mo_3N, which is isostructural with both Co_3Mo_3N and Fe_3Mo_3N, would be of further interest. However, this phase has not yet been successfully prepared even though, as documented elsewhere, there have been incorrect reports of its existence published in the literature [15]. Nitridation of a $NiMoO_4$ precursor, Ni_3Mo_3C or Ni_6Mo_6C instead yields a mixture of Ni metal and Ni_2Mo_3N [12, 13]. The filled β-Mn structured Co_2Mo_3N is a known phase and Adamski et al. have reduced a mixture containing both Co_2Mo_3N and Co_3Mo_3N phases under pure hydrogen at 700 °C. Co_3Mo_3N was observed to have transformed to Co_6Mo_6N, as would be expected for this phase [9, 10] and the lattice nitrogen in Co_2Mo_3N appeared to be less reactive under these conditions.

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/H_2 would give an insight into the structure–activity and composition-activity relationships. Therefore, an investigation of the η-carbide structured Fe_3Mo_3N has been performed to provide a comparison with the isostructural Co_3Mo_3N. 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 Fe_3Mo_3N

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 ($FeCl_2.4H_2O$,

Sigma Aldrich, ReagentPlus, 98%) was added dropwise to 0.66 M aqueous solution of 14 mL of sodium molybdate dihydrate ($Na_2MoO_4.2H_2O$, 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 $FeCl_2.4H_2O$ 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.

Fe_3Mo_3N was prepared by ammonolysis of the oxide precursor under 94 mL/min NH_3 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% O_2/Ar and N_2 for 1 h.

2.2 Preparation of Co_2Mo_3N

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 (($NH_4)_6Mo_7O_{24}.4H_2O$, Fluka Analytical, puriss. p.a., ACS reagent, $\geq$ 99.0%) and cobalt (II) nitrate hexahydrate ($Co(NO_3)_2.6H_2O$, 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 ($C_6H_8O_7.H_2O$, Sigma Aldrich, ACS reagent, $\geq$ 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.

Co_2Mo_3N was prepared via nitridation of the mixed oxide precursor under 3:1 H_2/N_2 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 Co_3Mo_3N

Cobalt molybdenum oxide ($CoMoO_4$) was prepared by the reaction of the necessary amounts of ammonium molybdate tetrahydrate (($NH_4)_6Mo_7O_{24}.4H_2O$, 99.98%, SigmaAldrich) with cobalt (II) nitrate hexahydrate ($Co(NO_3)_2.6H_2O$, > 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 ($CoMoO_4.nH_2O$) was dried overnight in an oven at 150 °C and was then calcined in air at 600 °C for 3 h.

Co_3Mo_3N was prepared by nitridation of the oxide precursor under 3:1 H_2/N_2 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 H_2/N_2. For clarity, the nitride prepared at the different temperatures will be referred to as either CoMoN700, CoMoN800 and Co_3Mo_3N900.

2.4 Lattice Nitrogen Reactivity Testing

Approximately 0.3 g of material was tested at ambient pressure under 3:1 H_2/Ar (BOC, 99.98%) with a gas flow rate of 60 mL/min. The stability and possible lattice nitrogen reactivity of the prepared Co_2Mo_3N and Co_3Mo_3N material was investigated by testing the material under 3:1 H_2/Ar at 700 °C, 800 °C and 900 °C. Fe_3Mo_3N was also examined at 900 °C under 3:1 H_2/Ar for its lattice nitrogen reactivity. The decrease in conductivity of a 0.00108 M 200 mL solution of H_2SO_4, 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 N_2 and H_2.

2.5 Material Characterisation

Powder XRD patterns were obtained for the materials pre- and post-reaction by using a PANalytical X-Pert Pro Diffractometer (40 kV, 40 mA) with a monochromatised CuKα source (1.5418 Å). The data was collected in the range of 5–85° 2θ with a total scan time of 51 min and a step size of 0.02°. Phases were identified by comparison with the JCPDS database. CHN analysis was undertaken by combustion using an Exeter Analytical Inc CE-440 elemental analyser. SEM images were taken by using a Philips XL30 environmental scanning electron microscope. The samples were first covered with a film of gold/palladium to reduce charging. The microscope was also used to acquire Energy-Dispersive X-ray spectroscopy (EDX). The BET surface area of the pre-reaction Fe_3Mo_3N was measured using N_2 physisorption undertaken using a Quantachrome Quadrasorb evo Gas Sorption Surface Area and Pore Size Analyzer. Approximately 0.1 g of the

material was degassed at 110 °C overnight under vacuum before the measurement.

3 Results and Discussion

3.1 Lattice Nitrogen Reactivity of Fe_3Mo_3N

As the η-carbide structured Co_3Mo_3N and filled β-Mn structured Ni_2Mo_3N 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, Fe_3Mo_3N, has been investigated in this work. As this nitride has the same crystal structure type as Co_3Mo_3N 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 Fe_3Mo_3N is less reactive than in Co_3Mo_3N. Fe_3Mo_3N has been observed to be stable under 3:1 H_2/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 Fe_3Mo_3N [14]. A higher temperature has been investigated in the present study to investigate whether the bulk lattice nitrogen in the Fe_3Mo_3N phase is reactive but requires a higher temperature than that observed for Co_3Mo_3N. The Fe_3Mo_3N 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 Fe_3Mo_3N (2.98 wt%). However, NH_x species on the surface of the material, that
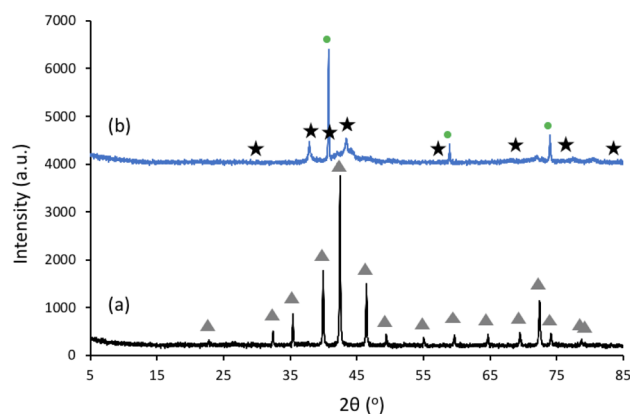
Fig. 1 XRD patterns of Fe_3Mo_3N: **a** pre-reaction and **b** post-reaction with 3:1 H_2/Ar at 900 °C. (▲) Fe_3Mo_3N (PDF ref.: 00–048-1408), (●) Mo (PDF ref.: 01–089-5023) and (★) ε-Fe_3N (PDF ref.: 01–073-2101)

Table 1 Nitrogen analysis pre- and post-reaction for Fe_3Mo_3N

Material	Nitrogen content (wt%)
Fe_3Mo_3N	4.27
Fe_3Mo_3N post H_2/Ar 900 °C	0.49

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 Fe_3Mo_3N consisted of rounded particles (Fig. 2). The material was observed to have a surface area of 13 m^2/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 Fe_3Mo_3N was examined by treating the nitride at 900 °C under 3:1 H_2/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 Co_3Mo_3N 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 N_2 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 Fe_3Mo_3N 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 Fe_3Mo_3N and was converted to ammonia was ca. 6%, with the rest of the nitrogen presumably being lost in the form of N_2. SEM analysis showed that the morphology was retained after the decomposition of the material compared to pre-reaction (Fig. 2).

The lattice nitrogen in Fe_3Mo_3N was much more reactive at 900 °C than for the filled β-Mn structured Ni_2Mo_3N, which was shown to be stable at this temperature [12]. Therefore, this possibly suggests that metal composition has a major impact on the activity.

3.2 Lattice Nitrogen Reactivity of Co_2Mo_3N

The ability of the Co_3Mo_3N phase to lose bulk lattice nitrogen at 700 °C under H_2/Ar [24], contrasted with Fe_3Mo_3N 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 Co_2Mo_3N phase, which has the same metal composition but different crystal structure type. Comparing the lattice nitrogen reactivity of Co_2Mo_3N with the η-carbide structured Co_3Mo_3N might provide an insight into the crystal structure–activity relationship. To investigate this potential relationship, attempts were made to prepare the pure phase Co_2Mo_3N. The modified Pechini method was chosen for the synthesis process as it has previously been used to synthesis pure phase filled β-Mn structured Ni_2Mo_3N [18]. The filled β-Mn structured Co_2Mo_3N was prepared via nitridation of the oxide precursor at 700 °C for three hours under 3:1 H_2/N_2. 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 Co_2Mo_3N, Co_3Mo_3N and β-$Mo_2N_{0.78}$ 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 Co_2Mo_3N is 3.34 wt%). The SEM images of the mixed Co_2Mo_3N show that the material had a porous and smooth surface (Fig. 4a). Although the material

Fig. 2 Representative SEM images of Fe_3Mo_3N: **a** pre-reaction and **b** post H_2/Ar reaction at 900 °C
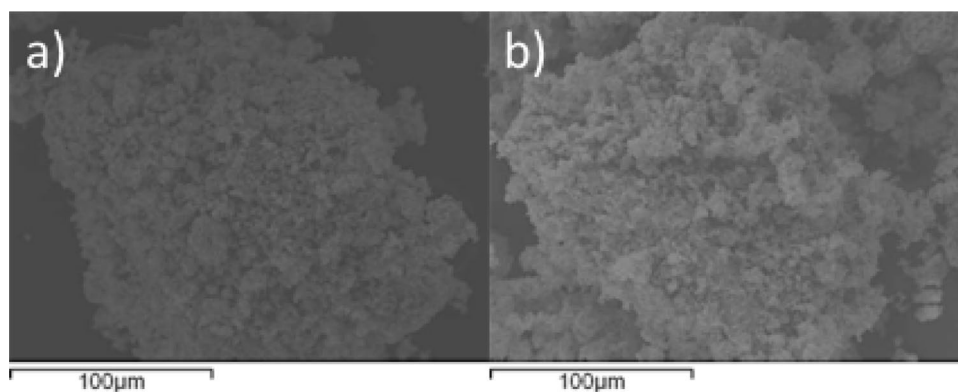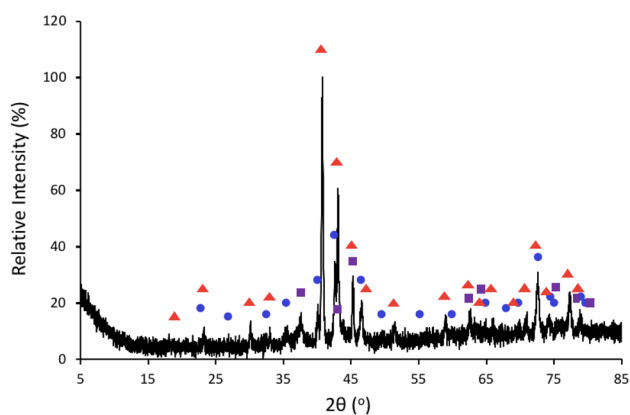
Fig. 3 XRD pattern of prepared Co_2Mo_3N. (▲) Co_2Mo_3N (PDF ref.: 01–072-6570), (●) Co_3Mo_3N (PDF ref.: 01–089-7953) and (■) β-$Mo_2N_{0.78}$ (PDF ref.: 03–065-6236)
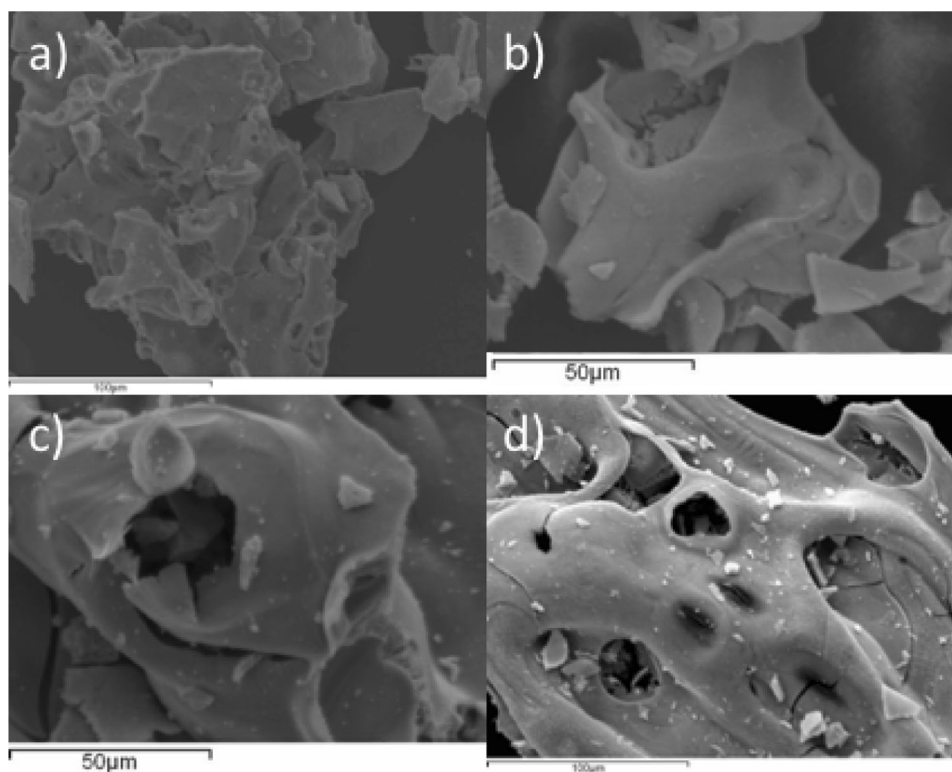
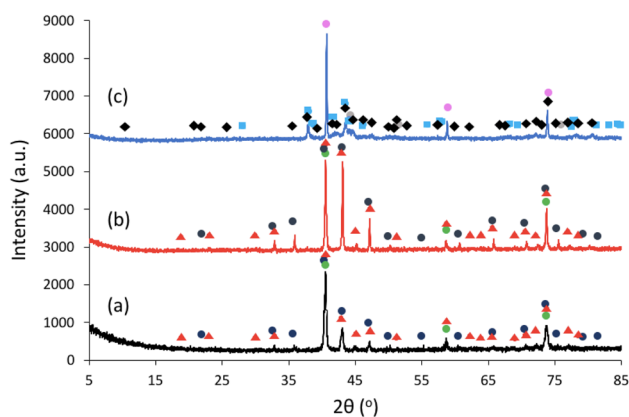**Table 2** Nitrogen analysis pre- and post-reaction for the prepared "Co_2Mo_3N" samples

Material	Nitrogen content (wt%)
"Co_2Mo_3N"	3.82
"Co_2Mo_3N" post H_2/Ar 700 °C	2.07
"Co_2Mo_3N" post H_2/Ar 800 °C	0.72
"Co_2Mo_3N" post H_2/Ar 900 °C	0.48

Fig. 4 Representative SEM images of the prepared Co_2Mo_3N: **a** pre-reaction, **b** post H_2/Ar reaction at 700 °C, **c** post H_2/Ar reaction at 800 °C and **d** post H_2/Ar reaction at 900 °C

was shown to contain the Co_3Mo_3N phase, the expected needle morphology for this phase was not observed.

In order to investigate the lattice nitrogen reactivity of the mixed phase Co_2Mo_3N and Co_3Mo_3N, 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_2Mo_3N and Co_3Mo_3N 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_3Mo_3N 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_6Mo_6N phase [13]. Due to the degree of overlap between the reflections of Co_6Mo_6N and Co_2Mo_3N 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_3Mo_3N reflections to higher

Fig. 5 XRD patterns of mixed Co_2Mo_3N and Co_3Mo_3N: **a** post-reaction 3:1 H_2/Ar at 700 °C **b** post-reaction 3:1 H_2/Ar at 800 °C **c** post-reaction 3:1 H_2/Ar at 900 °C (▲) Co_2Mo_3N (PDF ref.: 01–072-6570), (●) Co_6Mo_6N (data from [29]), (●) Mo (PDF ref.: 01–071-4645), (●) $Co_{0.08}Mo_{0.92}$ (PDF ref.: 01–071-7326), (●) α-Co (PDF ref.: 01–089-4307), (■) Co_2N (PDF ref.: 01–074-8393) and (◆) Co_7Mo_6 (PDF ref.: 00–029-0489)

2θ values was also observed post 800 °C reaction (Fig. 5b). The lattice nitrogen in Co_2Mo_3N appears to be unreactive at 700 °C and 800 °C under H_2/Ar as there was no shift in the peak positions for this phase compared to pre-reaction (Fig. 5a, b) as clearly seen by the peak at approximately 45° 2θ. These results agree with the previously published work of Adamski et al. who noticed that under pure hydrogen at 700 °C Co_3Mo_3N transitioned to Co_6Mo_6N, while Co_2Mo_3N remained stable [16]. β-$Mo_2N_{0.78}$ was believed to have been reduced to molybdenum metal during the reaction at both 700 °C and 800 °C (Fig. 5a, b). As there are not any unique reflections for Mo, the presence of this phase cannot be completely established. However, it has been previously reported that molybdenum nitride is reduced to Mo under 3:1 H_2/Ar at 700 °C [14] and therefore, it would be expected to occur.

The lack of reactivity of the lattice nitrogen in the filled β-Mn structured Co_2Mo_3N under H_2/Ar up to a temperature of 800 °C has also been observed for the isostructural Ni_2Mo_3N and, as discussed above, η-carbide structured Fe_3Mo_3N [12, 14]. Although Fe_3Mo_3N and Co_3Mo_3N have the same crystal structure type, the lattice nitrogen reactivity is different between these two nitrides under H_2/Ar at 700 °C and 800 °C, suggesting that metal composition is more important than the structure type. However, Co_3Mo_3N and Co_2Mo_3N, have different stabilities suggesting that the phase also has an impact. Therefore, there appears to be a complex relationship between metal composition and phase which controls the lattice nitrogen reactivity of the ternary nitrides. In both the filled β-Mn structure and η-carbide structure, the local nitrogen environment is similar with the lattice nitrogen being coordinated to six Mo species in each

structure. When Co_3Mo_3N transforms into Co_6Mo_6N, 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_2Mo_3N" 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_3Mo_3N was shown to have a similar decomposition as Co_2Mo_3N and Co_3Mo_3N under these conditions. This is again in contrast to the filled β-Mn structured Ni_2Mo_3N, 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_2Mo_3N, Co_6Mo_6N 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_3Mo_3N and β-$Mo_2N_{0.78}$ 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_3Mo_3N Prepared by Nitridation with N_2/H_2

The η-carbide structured Co_3Mo_3N 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_2Mo_3N 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_3Mo_3N 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_3Mo_3N under N_2/H_2. In this work, attempts were made to prepare Co_3Mo_3N directly by nitridation of the oxide with N_2/H_2 at 700 °C, 800 °C or 900 °C.

The direct N_2/H_2 nitridation process at 700 °C resulted in a mixed phased material of Co_2Mo_3N with minor amounts of Co_3Mo_3N and β-$Mo_2N_{0.78}$ 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 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 Co_3Mo_3N and Co_2Mo_3N, with Co_3Mo_3N 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 Co_3Mo_3N (Fig. 6c). Adamski et al. have proposed that the oxide precursor is first transformed to Co_2Mo_3N and a molybdenum nitride phase, before forming the Co_3Mo_3N phase [28]. Therefore, this may be an explanation for why the pure phased Co_3Mo_3N is only formed at high temperatures under N_2/H_2. This result shows promise for forming Co_3Mo_3N 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 (Co_3Mo_3N900) was similar to the expected needle structure for Co_3Mo_3N 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 Co_3Mo_3N and the material was found from XRD to comprise Co_2Mo_3N, Co_3Mo_3N and Co. The nitrogen content of Co_3Mo_3N900 is in very close agreement with the expected stoichiometric nitrogen weight percentage for Co_3Mo_3N (2.93 wt%), further confirming the successful synthesis of the pure phase Co_3Mo_3N.

4 Conclusions

The bulk lattice nitrogen reactivity of the η-carbide structured Fe_3Mo_3N and Co_3Mo_3N and filled β-Mn structured Co_2Mo_3N has been investigated by testing the materials under Ar/H_2. The metal composition-activity relationship was examined by comparison of the isostructural Fe_3Mo_3N and Co_3Mo_3N. Fe_3Mo_3N was shown to decompose to Mo and an iron nitride phase under 3:1 H_2/Ar at 900 °C. In the literature, the bulk lattice nitrogen of Fe_3Mo_3N has been reported to be unreactive up to a temperature of 800 °C [13,
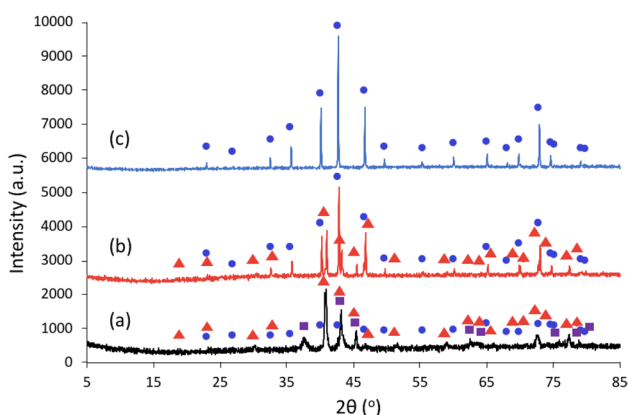

Fig. 6 XRD pattern of prepared Co_3Mo_3N: **a** CoMoN700 **b** CoMoN800 **c** Co_3Mo_3N900. (●) Co_3Mo_3N (PDF ref.: 01–089-7953), (▲) Co_2Mo_3N (PDF ref.: 01–072-6570) and (■) β-$Mo_2N_{0.78}$ (PDF ref.: 03–065-6236)

Table 3 Nitrogen analysis for the prepared Co_3Mo_3N samples at different temperatures

Material	Nitrogen content (wt%)
CoMoN700	3.99
CoMoN800	2.58
Co_3Mo_3N900	2.88

Fig. 7 Representative SEM images of prepared Co_3Mo_3N: **a** CoMoN700 and **b** Co_3Mo_3N900
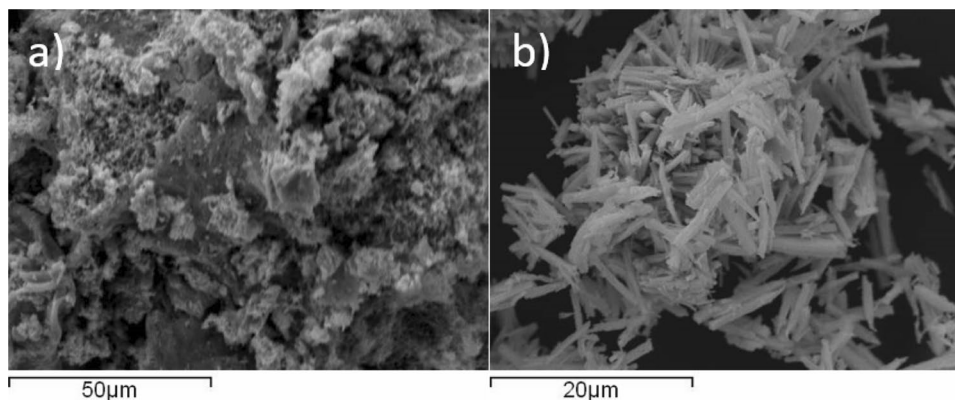
14]. Therefore, it appears that the Fe_3Mo_3N phase has a different reactivity to Co_3Mo_3N, even at high temperatures, possibly suggesting that metal composition is the dominant influence on the bulk lattice nitrogen reactivity. Additionally, with this in mind, an investigation of the filled β-Mn structured Co_2Mo_3N and the η-carbide structured Co_3Mo_3N has also been performed to provide an insight into a possible structure–activity relationship. The filled β-Mn structured Co_2Mo_3N could not be synthesised in the pure form, with instead the material being a mixture of Co_2Mo_3N and Co_3Mo_3N. The mixed phase Co_2Mo_3N and Co_3Mo_3N 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_2Mo_3N was shown to be stable and η-carbide structured Co_3Mo_3N 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_3Mo_3N. It has previously been observed that the filled β-Mn structured Ni_2Mo_3N 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_3Mo_3N with needle morphology was synthesised under 3:1 H_2/N_2 at 900 °C.

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