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# The role of preparation route upon the ambient pressure ammonia synthesis activity of $Ni_2Mo_3N$

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ABSTRACT

The preparation route has been shown to have a significant influence upon the catalytic behaviour of $Ni_2Mo_3N$ samples for ambient pressure ammonia synthesis. Materials prepared from a $NiMoO_4$ precursor necessarily contain a significant fraction of Ni impurity phase. Materials prepared from this precursor are relatively inactive for ammonia synthesis, whereas $Ni_2Mo_3N$ of much greater phase purity and catalytic activity can be prepared from precursors employing a modified Pechini method with the use of citrate gels. $Ni_2Mo_3N$ can be prepared by $N_2/H_2$ pre-treatment which represents a significant advantage over routes employing ammonolysis. Bulk lattice nitrogen appears to be relatively unreactive in $Ni_2Mo_3N$, although heterolytic nitrogen isotopic exchange studies indicate that a significant degree is exchangeable subject to pre-treatment conditions. The modified Pechini method based route has also been shown to be applicable to the preparation of $CoNiMo_3N$ of relatively high phase purity, thereby allowing access to the preparation of quaternary nitrides for catalytic screening.



## 1. Introduction

Metal nitrides have attracted interest as catalysts for a range of reactions [1–4]. Amongst such reactions, different binary and ternary systems have been studied for ammonia synthesis [5]. In recent years $Co_3Mo_3N$ based catalysts have been shown to exhibit promising activity with performance exceeding that of the iron-based Haber Bosch Process catalyst having been reported [6–10]. Given the importance of ammonia synthesis in terms of both the sustenance of the global population through the provision of a route to synthetic fertilisers and its energy intensive nature, any advance in this area could potentially be of high impact. To date, there have been few studies directed towards development of the understanding of the high activity of $Co_3Mo_3N$. In this area, a computational study undertaken by Norskov and co-workers in which activity is rationalised on the basis of a volcano relationship is of particular note [11]. In that study, calculated turnover frequencies are related to the enthalpy of adsorption of $N_2$ and the combination of Co, with a very low adsorption enthalpy, and Mo, with a high adsorption enthalpy, is shown to be close to that of Ru, an optimal system. An implicit suggestion of structure-sensitivity was made since it is the (1 1 1) surface plane where both Co and Mo are exposed that is proposed to be active. It is argued that the interstitial nitrogen plays no direct role in the reaction but rather provides the correct ordering such that the active surface plane is exhibited. To the authors' knowledge, despite the importance of $NH_3$ synthesis, no experimental studies documenting structure-sensitivity in this system have been reported. The related role of catalyst preparation method has not been widely studied systematically, although the role of ammonolysis in preparation of the active phase, as opposed to oxide precursor nitridation by $N_2/H_2$, seems to be significant [12]. Recent nitrogen isotopic exchange studies have shown the lattice nitrogen to be exchangeable, the extent of which is a strong function of sample pre-treatment, and based upon these studies the possibility of a nitrogen-based Mars-van Krevelen mechanism operating over $Co_3Mo_3N$ during ammonia synthesis has been raised [13].

Upon inspection of the volcano curve relationship reported by Norskov and co-workers [11], a superficial case could also be made for Ni-Mo catalysts exhibiting high activity for $NH_3$ synthesis, even possibly exceeding that of the Co-Mo system. Although lower than $Co_3Mo_3N$, $Ni_2Mo_3N$ has indeed been reported to possess relatively high activity in a number of studies [9,14], although in others a

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mixed phase of Ni and $Ni_2Mo_3N$ has proved to be significantly less active [12]. An additional advantage of the $Ni_2Mo_3N$ system is that it can potentially be prepared by nitridation of the oxide precursor using a $N_2/H_2$ reaction mixture, thus avoiding the potential issues of heat transfer and other problems documented for ammonolysis on the large scale [15]. In this study, we show the application of a sol–gel route for the preparation of $Ni_2Mo_3N$ possessing activity for ammonia synthesis at ambient pressure. The extension of this route to prepare a quaternary Co–Ni–Mo–N system is also reported. Accessible synthesis of quaternary nitrides opens the possibility for the further development of catalysts of enhanced activity; an exciting prospect in the area of ammonia synthesis where any reduction in severity of operating conditions could potentially yield massive environmental and economic benefit. A further consideration is that the reaction is favoured thermodynamically at lowered reaction temperature leading to the tantalising prospect of the "win-win" situation of enhanced reaction kinetics in a more thermodynamically favourable regime.

## 2. Experimental

Two routes to the preparation of $Ni_2Mo_3N$ based materials were applied. The first, which resulted in a material containing a significant Ni impurity content, involved nitridation of $NiMoO_4$ and the second, which resulted in a material with lower levels of impurity phases, involved nitridation of a mixed-phase precursor formed by an optimised modification of the Pechini method. $CoNiMo_3N$ was also prepared from a Pechini method derived precursor.

$NiMoO_4$ was prepared by dropwise addition of 400 mL of an aqueous 0.25 M solution of $Ni(NO_3)_2{\cdot}6H_2O$ (Sigma-Aldrich) to a 150 mL aqueous solution of $Na_2MoO_4{\cdot}2H_2O$. A green precipitate was obtained after vacuum filtration and the precipitate was washed twice with distilled water, once with ethanol and dried overnight at 150 °C. The powder was then calcined at 700 °C under a flow of nitrogen gas (5 mL $min^{-1}$).

Nitridation of $NiMoO_4$ was undertaken by two routes (a) ammonolysis and (b) in situ by $N_2/H_2$ using the standard pre-treatment conditions applied prior to the start of ammonia synthesis testing. Ammonolysis of this precursor was undertaken by subjecting ca 1 g of precursor held in a vertical quartz reactor to treatment with 94 mL $min^{-1}$ $NH_3$ (BOC, 99.98%). The Carbolite MTF 12/25/250 furnace was programmed to heat in three stages – (i) from ambient to 357 °C at a programmed ramp rate of 5.6 °C $min^{-1}$, (ii) from 357 to 447 °C at a programmed rate of 2.1 °C $min^{-1}$ and finally (iii) from 447 to 785 °C at a programmed rate of 2.1 °C $min^{-1}$ at which point it was held for 5 h. The nitrided material was cooled in flowing ammonia to ambient temperature, then nitrogen was flushed through the system at 100 mL $min^{-1}$. To prevent bulk oxidation on exposure to air, the material was passivated overnight using a mixture containing <0.1% $O_2$. In situ nitridation was performed in the microreactor when the oxide precursor was loaded and subjected to the standard catalyst pre-treatment method as detailed below. All samples prepared from $NiMoO_4$ are denoted as Ni + $Ni_2Mo_3N$ throughout the article, whereas sol–gel derived materials are denoted by the formula of the pure nitride (i.e. $Ni_2Mo_3N$ or $CoNiMo_3N$ as appropriate).

Oxide precursors were also prepared by a modified version of the Pechini method. In a typical synthesis $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (20.00 g) and stoichiometric amounts of $M(NO_3)_2{\cdot}6H_2O$ (M = Ni or Co) were dissolved in 8–10% aqueous $HNO_3$ (600 mL) at room temperature, followed by citric acid monohydrate (79.35 g) and the mixture stirred to obtain a clear solution. The beaker containing the solution was placed in a sand bath at 70 °C and evaporated with stirring to a volume of ~100 mL (about 15 h) by which time a transparent green (for the Ni–Mo system) or wine-red (for the Co-Ni-Mo system) coloured solution with a gel-like consistency had formed. Approximately 5 $cm^3$ portions of this gel were calcined in air at 500 °C (heating rate 60 °C $min^{-1}$) for 2 h to obtain greyish foams that were ground thoroughly before ammonolysis or in situ treatment in the catalyst microreactor.

The following method was applied for ammonolysis of the Pechini method derived precursor. 3.0 g of oxide precursor was placed in a 20 mL high alumina combustion boat. The boat was placed inside a quartz furnace tube, which was purged thoroughly with dry $NH_3$ gas for 15 min and then heated at 5 °C $min^{-1}$ to the target temperature (600 or 700 °C) and maintained for times as described in the text (6 or 12 h), before cooling at 10 °C $min^{-1}$. A high $NH_3$ flow rate was maintained throughout the process. The ceramic yield of the nitride products was 72% relative to the oxide precursors [the calculated yield for $Ni_2Mo_3O_{11}$ (581.20 AMU) → $Ni_2Mo_3N$ (419.21 AMU) = 72%].

Reaction studies were performed using 0.4 g of material placed in a silica reactor tube and held vertically between two silica wool plugs in the heated zone of a tube furnace. All materials were pre-treated at 700 °C with 60 mL $min^{-1}$ of 1/3 $N_2/H_2$ (BOC, $H_2$ 99.998%, $N_2$ 99.995%) for 2 h. Ammonia synthesis experiments were then performed at 400 °C using this gas mixture. The vent gas from the reactor was flowed through 200 mL of a 0.00108 M sulfuric acid solution and the rate of ammonia formation was calculated from the rate of change of conductivity of the solution. The reaction with the $H_2$/Ar mixture was performed using a 1/3 Ar/$H_2$ mixture (BOC, $H_2$ 99.998%, Ar min. 99.99%) following the 700 °C pre-treatment and subsequent cooling to 400 °C under $H_2/N_2$.

$^{15}N_2$ isotopic exchange measurements were performed using an apparatus which was previously applied for oxygen isotopic exchange studies and which is detailed elsewhere [16]. A U-form reactor was placed in a closed recycle system which was connected on one side to a mass spectrometer (Pfeiffer Vacuum, QMS 200) for monitoring the gas phase composition and on the other side by a vacuum pump. The recycling pump placed in the system removes limitations due to gas-phase diffusion. Two heterolytic exchange [$^{15}N_{2(g)} + {}^{14}N_{(s)} \rightarrow {}^{14}N^{15}N_{(g)} + {}^{15}N_{(s)}$] experiments were undertaken on 200 mg of $Ni_2Mo_3N$ as described below. For both, the sample was additionally subjected to a 1/3 $N_2/H_2$ (80 mL $min^{-1}$) activation step at 700 °C for 1 h with a ramp of 10 °C $min^{-1}$ prior to applying a $N_2$ purge (20 mL $min^{-1}$) at 700 °C.

(i) In the first experiment, temperature programmed nitrogen isotopic exchange (TPNIE) was undertaken. Following the purging step, the sample was cooled to 400 °C and the system was again purged using secondary vacuum. Following this, 55 mbar of $^{15}N_2$ (98%+ purity, supplied by Cambridge Isotope Laboratories, Inc.) was charged into the recycle system at 400 °C over 15 min and the temperature was increased with a ramp rate of 2 °C $min^{-1}$ up to 700 °C.

(ii) In the second experiment, the sample was subjected to isothermal nitrogen isotopic exchange (INIE). In this case, the system was directly purged using secondary vacuum at 700 °C and the same amount (55 mbar) of $^{15}N_2$ was introduced in the system and the exchange performed for 1 h.

The masses 28, 29, 30 $m/z$ were monitored as a function of time to follow the exchange. The $m/z$ values of 2, 17 and 18 were also recorded to determine if H atoms remained at the surface of the nitride, thus yielding $NH_3$ or $H_2$ in the gas phase after decomposition. The absence of $NO_x$ and $O_2$ was confirmed by monitoring the corresponding $m/z$ values. The calculations undertaken for the determinations of the atomic fraction of $^{15}N$ in the gas-phase ($\alpha_g$)

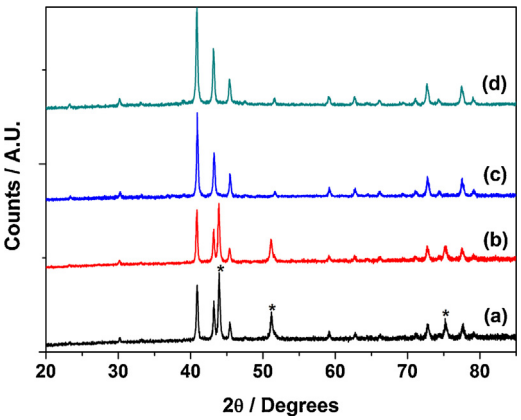


**Fig. 1.** Powder X-ray diffraction patterns of $Ni_2Mo_3N$ materials. (a) Ni + $Ni_2Mo_3N$ prepared via ammonolysis, (b) Ni + $Ni_2Mo_3N$ prepared via the $N_2/H_2$ mixture, (c) $Ni_2Mo_3N$ prepared via ammonolysis, (d) $Ni_2Mo_3N$ prepared via the $N_2/H_2$ mixture. Reflections marked by * correspond to the Ni impurity phase.

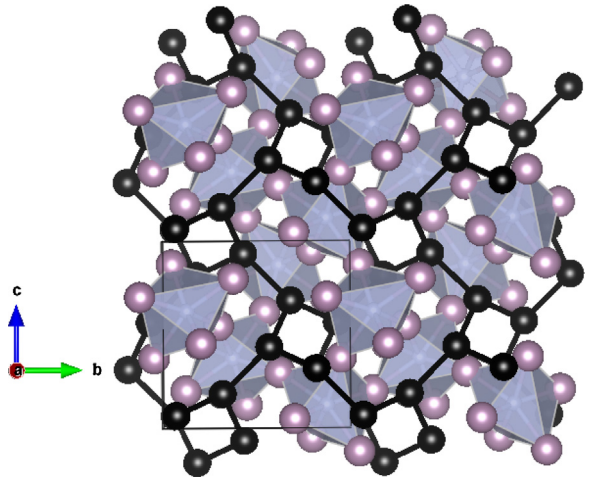


**Fig. 2.** View of the crystal structure of $CoNiMo_3N$ along [1 0 0], showing the distorted, corner-sharing $Mo_6N$ octahedra and the Ni-Ni bonding framework. $CoNiMo_3N$ is isostructural.

and of the number of atoms exchanged ($N_e$) have been described in previous publications [16,17]. Typically:

$$\alpha_g = \frac{P_{30} + \frac{1}{2}P_{29}}{P_{30} + P_{29} + P_{28}}$$

where $P_{30}$, $P_{29}$, $P_{28}$ are the partial pressures of $^{15}N_2$, $^{14}N^{15}N$ and $^{14}N_2$, respectively;

$$N_e = N_g(1 - \alpha_g)$$

where $N_g$ is the number of $^{15}N$ atoms in gas-phase at the beginning of the reaction.

The materials were characterised by a range of techniques as follows. Most powder XRD patterns were recorded with a Siemens D5000 diffractometer using Cu $K_{\alpha 1}$ radiation. Samples were prepared by compaction into sample holders and measurements were undertaken in the 5–85° 2$\theta$ range with a step size of 0.02° using a counting rate of 1 s per step. Data presented in Fig. 3 were obtained using a Bruker D2 PHASER. Powder neutron diffraction data were collected with the GEM diffractometer at the ISIS source. Rietveld refinements used the GSAS/EXPGUI package [18]. Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis were obtained with a JEOL JSM 6500F. Samples were prepared by dispersion of dry powders onto carbon coated stubs. Surface areas of the degassed samples were evaluated by application of the BET method to $N_2$ physisorption isotherms determined with the use of Micromeritics Gemini surface area analyser. N analyses were undertaken by combustion using an Exeter Analytical CE-440 elemental analyser (the error on the experimental analyses is 0.3 wt%). N analyses of as synthesised and post-reaction samples are shown in Table 1 and generally demonstrate a close agreement to the values expected on the basis of stoichiometric considerations confirming the formation, and stability, of the nitrides. Carbon analyses were simultaneously conducted upon all samples and no carbon was found.

## 3. Results and discussion

The powder X-ray diffraction patterns and the surface areas and nitrogen contents of the two materials prepared by ammonolysis and $N_2/H_2$ pre-treatment of the $NiMoO_4$ precursor are presented in Fig. 1 and Table 1, respectively. As is evident from Fig. 1a and b, the powder X-ray diffraction patterns of both the $Ni_2Mo_3N$ samples comprise a Ni metal phase in addition to $Ni_2Mo_3N$. This has been observed within other studies [12,19] and is unsurprising in view of stoichiometric considerations (Ni/Mo ratio) [20]. Unlike the analogous Co and Mo ternary systems which exhibit stoichiometries of $Co_3Mo_3N$ and $Fe_3Mo_3N$, respectively, and which possess the η-6 carbide structure, the filled β-Mn structured $Ni_2Mo_3N$ phase is favoured in the Ni-Mo-N system (although this has been a source of confusion [20]). The crystallography of filled β-Mn structured nitrides has been discussed in detail elsewhere [21,22]. Fig. 2 presents a view of the crystal structure along the [1 0 0] direction in which the salient features of distorted corner sharing $Mo_6N$ octahedra and the Ni–Ni bonding framework are evident. In terms of nitrogen local environment, there is a strong degree of similarity with the $Co_3Mo_3N$ and $Fe_3Mo_3N$ counterparts which may be of interest in view of the suggestion of the possible occurrence of a N based Mars-van Krevelen mechanism associated with the high ammonia synthesis activity of $Co_3Mo_3N$. Ambient pressure ammonia synthesis testing has been undertaken with both the samples which have been found, consistent with previous observations [12], to exhibit very low activities (in this case being <15 μmol $g^{-1}$ $h^{-1}$.) Accordingly, in view of literature indicating $Ni_2Mo_3N$ materials to be active catalysts, and the observation that it seems possible to form this phase by direct application of $N_2/H_2$ which would be of greater interest than ammonolysis for large scale application, the role of preparation method has been investigated in more detail. To this end, a sol–gel route based upon the Pechini method [23] has been applied and optimised according to the method described in the Experimental section. The oxide precursor produced by this method was shown to be a mixture of $NiMoO_4$ and $MoO_3$ from powder X-ray diffraction (as presented in the Supplementary information section – Fig. S1.) Initial ammonolysis experiments undertaken at 600 °C yielded a mixture of resultant phases including $Ni_{0.2}Mo_{0.8}N$, $MoO_2$ and Ni (data not shown). Accordingly, ammonolysis of the precursor at 700 °C was undertaken for 12 h and was found to yield crystalline $Ni_2Mo_3N$ as shown in the powder diffraction pattern presented in Fig. 1c, although a trace impurity as indicated by a very small broad reflection apparent at ca. 37.5° 2$\theta$ was apparent. The 200 reflection of the β-manganese structure coincides with this broad region of the pattern and must be distinguished from the secondary phase. Following exclusion of this broad feature, which could not be definitively identified, single phase Rietveld refinement on the data was undertaken and was found to converge rapidly to a filled β-Mn structure with space group $P4_132$. The fitted X-ray diffraction pattern is presented in Fig. 3 and the extracted structural parameters are presented in Table 2. The crystallite size extracted from the GSAS refinement profile coefficients was 43 nm. When using much

**Table 1**
Summary of the materials investigated, their physicochemical characteristics and their ammonia synthesis activity.

| Sample | Surface area ($m^2\ g^{-1}$) | Stoichiometric nitrogen content (wt%) | Pre-reaction nitrogen content (wt%) | Post-reaction nitrogen content (wt%) | Ammonia synthesis rate[b] ($\mu mol\ h^{-1}\ g^{-1}$) |
|---|---|---|---|---|---|
| $Ni + Ni_2Mo_3N$ ($NH_3$)[a] | 6.5 | 2.93 | 3.35 | 3.32 | <15 |
| $Ni + Ni_2Mo_3N$ ($N_2/H_2$)[a] | 10.5 | 2.93 | – | 1.38 | <15 |
| $Ni_2Mo_3N$ ($NH_3$)[a] | 8.7 | 3.34 | 3.72 | 3.34 | 383 ± 22 |
| $Ni_2Mo_3N$ ($N_2/H_2$)[a] | 9.4 | 3.34 | – | 3.13 | 395 ± 6 |
| $CoNiMo_3N$ ($NH_3$)[a] | 8.0 | 3.34 | 3.74 | 3.26 | 160 ± 10 |

[a] Gas used for nitridation.
[b] Steady state rates obtained at 400 °C and ambient pressure using 60 mL $min^{-1}$ of the 1/3 $N_2/H_2$ feed.

**Table 2**
Refined structural parameters of $Ni_2Mo_3N$[a], lattice parameters $a = b = c = 6.63047(8)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 291.496(11)$ Å$^3$.

| Atom | Wyckoff symbol | $x$ | $y$ | $z$ | $U_{iso} \times 100$ (Å)$^2$ | Occupancy |
|---|---|---|---|---|---|---|
| Ni | 8c | 0.06696(5) | 0.06696(5) | 0.06696(5) | 3.44(3) | 1.000 |
| Mo | 12d | 0.20188(3) | 0.45188(3) | 1/8 | 3.644(19) | 1.000 |
| N | 4a | 3/8 | 3/8 | 3/8 | 2.5 | 1.000 |

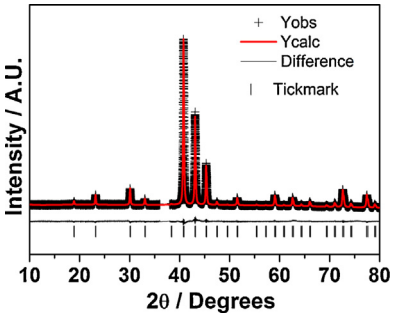


**Fig. 3.** Fit to the powder XRD pattern for $Ni_2Mo_3N$, where crosses mark the data points, the red line the fit, the black line the difference and tick marks the allowed reflection positions in $P4_132$. WRp = 3.44%, Rp = 2.67%. The range 2.37–2.48 Å was excluded due to the presence of a broad low-intense peak.

longer counting times, some potential evidence for an extremely minor additional γ-$Mo_2N$ phase was observed (as can be seen in Fig. S2 in the Supplementary information section), although this is present in very low proportion. SEM investigation of the sample was undertaken and a representative micrograph is presented in Fig. 4, where it is evident that the sample comprises well-formed grains, consistent with the relatively narrow reflections widths evident in its powder diffraction pattern. EDX showed an atomic ratio Mo:Ni of 62:38, within experimental error of the expected ratio (60:40 for $Ni_2Mo_3N$). Upon testing the material for ambient pressure ammonia synthesis at 400 °C, a dramatic enhancement of activity is evident over the samples prepared from the $NiMoO_4$ precursor. Furthermore, in an experiment extending beyond 30 h testing time where no deactivation was evident, the rate was shown to correspond to steady state. In order to assess the validity of nitridation by $N_2/H_2$ rather than $NH_3$ which, as discussed earlier, would be preferable for large scale synthesis the oxide precursor was loaded into the reactor and nitrided in situ by applying a 2 h pre-treatment at 700 °C under a 1/3 $N_2/H_2$ mixture. As reported in Table 1, the resultant material was again found to exhibit significant activity being similar to that for the sample prepared by ammonolysis. Inspection of the post-reaction powder X-ray diffraction pattern, as presented in Fig. 1d, indicated the $Ni_2Mo_3N$ phase to have been formed although this time the trace impurity reflection at ca. 37.5° 2$\theta$ was no longer evident. Taken together, these results demonstrate the role of preparation in generating an active catalyst providing an accessible route to an active nitride without an initial ammonolysis step. Whilst being completely reproducible, the origin of the poisoned activity in the materials generated from the $NiMoO_4$ precursor is not clear. An obvious difference is, of course, the presence of the significant Ni impurity phase and one possibility could be its segregation to the surface of the $Ni_2Mo_3N$ blocking reactant access to active sites. However, as of yet, there is no definite evidence for this proposal, and investigations upon the origin of the difference in activity for these samples, which will include detailed microstructural studies, are currently ongoing.

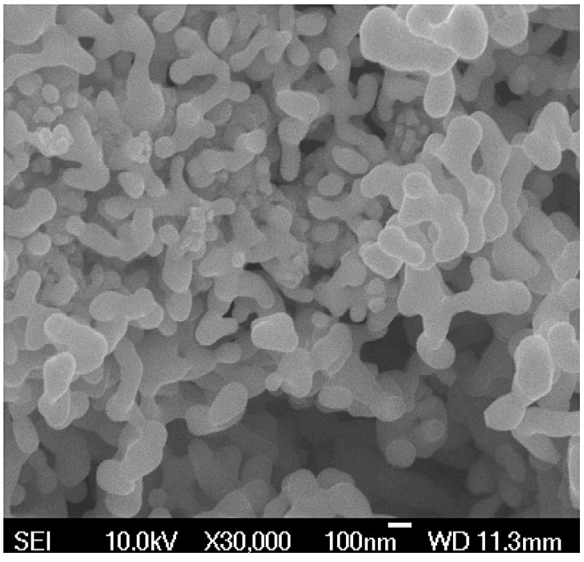


**Fig. 4.** SEM image of $Ni_2Mo_3N$ prepared by ammonolysis of a Pechini method synthesised precursor for 12 h at 700 °C.

In order to gain more insight into the nature of the reactivity of the lattice nitrogen within the ternary nitride systems prepared from the precursor arising from the Pechini method based route, temperature-programmed studies of its reactivity with an $Ar/H_2$ mixture in which the partial pressure of $H_2$ is equivalent to that in the ammonia synthesis gas mixture were undertaken. This measurement is undertaken to determine the activity for ammonia formation directly from lattice N in the absence of a gas-phase nitrogen source. The measurement is taken as a sequence of temperature programmed reactions within the 400–700 °C range and $NH_3$ formation is evidenced by the decline in conductivity of a standard $H_2SO_4$ solution through which the reactor effluent is bubbled. Similar investigations have previously been reported for both $Co_3Mo_3N$ and $Ni + Ni_2Mo_3N$ materials [12]. In the case of $Co_3Mo_3N$, the loss of 50% of the lattice N, predominantly in the form of $N_2$, has observed up to 700 °C with the $Co_6Mo_6N$ phase being formed [24,25]. $Co_3Mo_3N$ and $Co_6Mo_6N$ are found to be two line phases

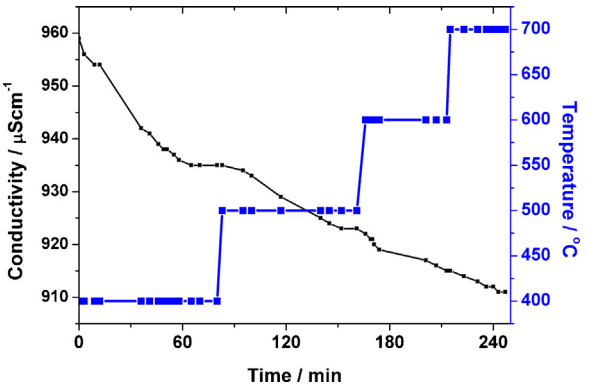


**Fig. 5.** Conductivity profile showing the evolution of $NH_3$ during temperature programmed reaction of $Ni_2Mo_3N$ (prepared by ammonolysis of a Pechini method synthesised precursor for 12 h at 700 °C) with the $Ar/H_2$ mixture.

with no evidence of materials of intermediate stoichiometry being formed [26]. Furthermore, the observation that $Co_3Mo_3N$ can be regenerated by $N_2$ treatment of $Co_6Mo_6N$ [26], albeit at higher temperatures than those necessary for a $N_2/H_2$ mixture, indicates the possible application of the material as a two-stage ammonia synthesis reactant. In the case of Ni + $Ni_2Mo_3N$, the lattice N was found to be much less reactive and no corresponding phase transition was found for the nitride component [12]. Given that the purer phase $Ni_2Mo_3N$ materials reported in this study have much greater activity for ammonia synthesis than the Ni containing systems, it was of interest to further investigate their reactivity with the $Ar/H_2$ mixture – if a link could be established between reactivity of lattice N under $H_2$ and ammonia synthesis, mechanistic insight could be provided. Additionally, the generation of $NH_3$ under the $Ar/H_2$ mixture could also provide access to the utilisation of $Ni_2Mo_3N$ as a two-stage ammonia synthesis reagent providing regeneration of the N depleted system from $N_2$ was accessible. As shown in Fig. 5, the production of ammonia from treatment of phase purer $Ni_2Mo_3N$ is minimal (representing 143 μmol $g^{-1}$ over the entire temperature range shown) and overall the contribution of the random scatter on the points can become more significant. As indicated in Fig. S2 in the Supplementary information section, the powder X-ray diffraction pattern of the post-reaction sample shows minimal changes, further confirming that the bulk lattice N in the $Ni_2Mo_3N$ ternary system is essentially unreactive under the conditions tested. X-ray diffraction patterns taken at much longer counting times of samples before and after reaction with the $Ar/H_2$ mixture show no lattice shifts, although the minor impurities evident in the pre-reaction sample are lost upon reaction. Since both $Ni_2Mo_3N$ prepared via the Pechini method based route and $Co_3Mo_3N$ are both active ammonia synthesis catalysts which behave very differently upon $Ar/H_2$ treatment, this also has the implication that no direct simple link can be discerned between catalytic activity and bulk lattice nitrogen reactivity despite the crystallographic similarity of the lattice N being associated with $Mo_6N$ octahedra in both materials. Hence, bulk reduction of the samples under $Ar/H_2$ cannot be used as an indirect probe of ammonia synthesis activity. However, reactivity of lattice N within $Ni_2Mo_3N$ has been observed under some circumstances. For example, topotactic replacement of lattice nitrogen by carbon to yield nickel molybdenum carbonitrides using a $CH_4/H_2/Ar$ gas mixture at 650 °C has been reported [27]. To investigate the reactivity of the lattice N in greater detail, and to discern its possible implication in ammonia synthesis, preliminary heterolytic isotopic exchange studies were undertaken. The results are presented in Fig. 6 and Table 3. From the data, it can be seen that there is a degree of lattice exchange evident. However, this was found to be strongly dependent upon sample pre-treatment and was only

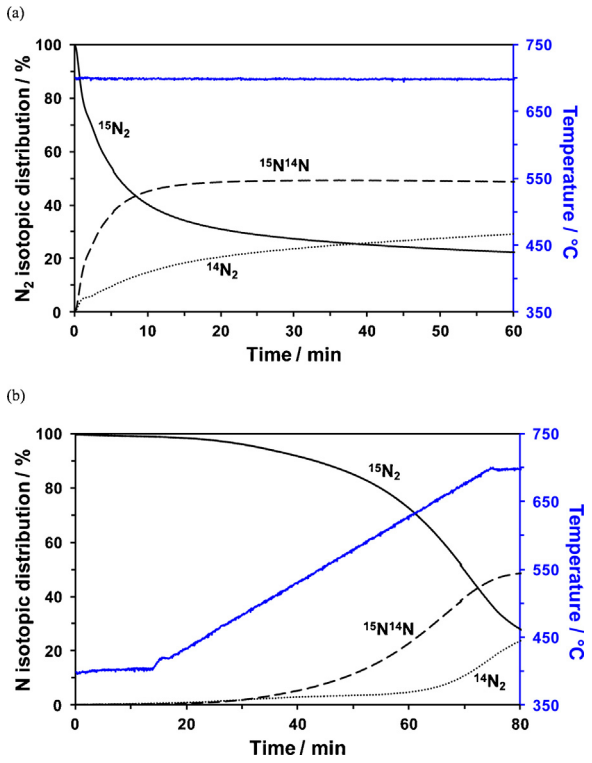


**Fig. 6.** Heterolytic $^{15}N_2$ exchange patterns over $Ni_2Mo_3N$ (a) held isothermally at 700 °C and (b) during temperature programmed studies from 400 to 700 °C with a ramp rate of 2 °C $min^{-1}$.

observed in samples which were purged with $N_2$ prior to vacuum degassing and subsequent exchange. Such conditions do not correspond to those applied for the measurements undertaken with the $Ar/H_2$ mixture detailed above. Very interestingly, no exchange activity was found in samples which were either vacuum degassed immediately after $N_2/H_2$ pre-treatment or which were subject to a $N_2$ purge at 600 °C immediately prior to exchange measurement. In the case of samples pre-treated with $N_2$ at 700 °C, the temperature of degassing (400 °C versus 700 °C) did not exert an influence over the exchange activity. In previous work on $Co_3Mo_3N$ for which the potential role of adsorbed N atoms can be discounted, a pronounced effect of pre-treatment conditions upon exchange behaviour has been documented and this has tentatively been ascribed to the $N_2$ pre-treatment step creating or preserving preferential sites for the limiting step of $^{15}N_2$ dissociation [13]. It is probable that a

**Table 3**
$^{15}N_2$ heterolytic isotopic exchange over $Ni_2Mo_3N$ prepared by ammonolysis of the Pechini method precursor.

| Pre-treatment conditions | $N_2/H_2$ 700 °C/$N_2$ 700 °C/evacuation at 700 °C | $N_2/H_2$ 700 °C/$N_2$ 700 °C/evacuation at 400 °C |
|---|---|---|
| Mass of sample/mg | 200 | 200 |
| Temperature of exchange/°C | 700 | 400–700 at a ramp rate of 2 °C per minute |
| $N_e$ at 30 min/$10^{20}$ atoms $g^{-1}$ | 4.05 | 4.13[b] |
| $\alpha_{g30min}$ (%) | 52 | 51[b] |
| %Exchange ($N_e/N_{total}$)[a] | 28.2 | 28.7[b] |
| $N_e$ at 60 min/$10^{20}$ atoms $g^{-1}$ | 4.49 | – |
| $\alpha_{g60min}$ (%) | 46 | – |
| %Exchange ($N_e/N_{total}$)[a] | 31.2 | – |

Data correspond to activity determined using 55 mbar of $^{15}N_2$.

[a] $N_{total}$ corresponds to the total number of $N$ atoms in the sample (= $14.37 \times 10^{20}$ $g^{-1}$).

[b] Values when 700 °C is reached.

similar situation prevails in the $Ni_2Mo_3N$ system. This is the subject of further ongoing investigation where the contrast of behaviour between the $Ni_2Mo_3N$ systems active for ammonia synthesis with the much less active Ni + $Ni_2Mo_3N$ could prove most informative. As for the $Co_3Mo_3N$ system, the observation of lattice N exchange for $Ni_2Mo_3N$ does open up the possibility of a Mars-van Krevelen mechanism being operative for ammonia synthesis. Whilst exchange is only evident from ca 480 °C in this study, it has to be borne in mind that the presence of the $H_2$ component in the ammonia synthesis reactant mixture may be important for the generation of lacunary sites capable of activation of $N_2$ at the reaction temperature of 400 °C. Whilst the studies undertaken with the $Ar/H_2$ mixture presented above indicate that this may only occur to a limited extent, the presence of very few such sites could be significant if their turnover frequency was high. Further studies to elucidate these aspects, which will include isotopic tracing of $NH_3$ synthesis, are in progress.

The modified Pechini synthesis route adopted in this study has been extended towards the preparation of quaternary nitrides. Such nitrides seem to have been little studied in the literature as catalysts and the possibility of controlled introduction of additional elements into the lattice opens up a whole new range of materials to be explored for ammonia synthesis. Initial targeting has been directed towards the preparation of $CoNiMo_3N$. As evident in the powder X-ray diffraction patterns presented in Fig. S1 in the Supplementary information section, the precursor oxide was found to comprise a mixture of $NiMoO_4$, $CoMoO_4$ and $MoO_3$. Upon ammonolysis, $CoNiMo_3N$ (space group $P4_132$) was formed as evidenced in the powder neutron diffraction pattern presented in Fig. 7b. Rietveld refinement yielded the structural parameters presented in Table 3. The crystallite size from a fit to the XRD data was 39 nm, similar to that observed in $Ni_2Mo_3N$. The model in space group $P4_132$ started with the literature structure for $Ni_2Mo_3N$ [20,21] with an equal distribution of Ni and Co occupancies on the Ni site (Wyckoff symbol 8c). The structure of $Ni_2Mo_3N$ consists of a network of highly distorted, corner-sharing $NMo_6$ octahedra with Ni atoms occupying sites bound to Mo and other Ni atoms (as for the structure shown in Fig. 2). All Ni-Ni distances in the Ni sublattice highlighted in Fig. 2 are 2.4611(5) Å and overall the Ni atoms are 12-coordinate, with a further 9 Ni–Mo bonds with lengths between 2.7163(15) and 2.8130(3) Å. The Ni and Co occupancies were fixed at the known stoichiometry (confirmed by EDX analysis where Mo:Ni:Co = 62:19:19, within experimental error of $CoNiMo_3N$). The structural parameters of $Ni_2Mo_3N$ and $CoNiMo_3N$, including refined unit cell volume, bond distances and bond angles, are very similar as expected from the similar sizes of Ni and Co. The previous report of $CoNiMo_3N$ by refinement of XRD data gave only a lattice parameter of $a$ = 6.643 Å for this phase [21], which is very slightly larger than that found here (Table 4). Whilst, as expected, the predominant phase was found to be $CoNiMo_3N$, a minor rock salt-structured impurity was also evident, as was also found in Pechini method derived $Ni_2Mo_3N$ as detailed above. This secondary phase was more prominent in the powder neutron diffraction data from $CoNiMo_3N$, where it was modelled as a rock salt-type phase (NiO or some mixed metal oxide/nitride phase) with a resultant improvement in the fitting quality. The phase fraction of this second phase corresponded to about 8 wt%.

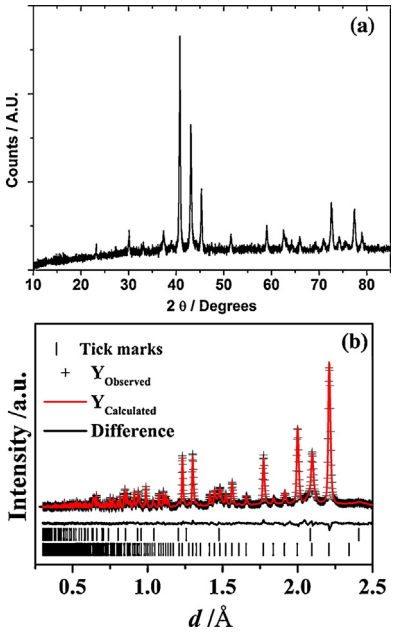


**Fig. 7.** (a) Powder XRD pattern of $CoNiMo_3N$ sample synthesised by ammonolysis at 700 °C for 12 h, and (b) fit to the PND (GEM bank 5) pattern of $NiCoMo_3N$, where crosses mark the data points, the red line the fit, the black line the difference and bottom set of tick marks the allowed reflection positions in $P4_132$. The top set of tick marks are the allowed positions of reflections for the rock salt-type impurity phase ($Fm$–$3m$). WRp = 2.44%, Rp = 2.12%, reduced $\chi^2$ =1.758. Refined weight fractions of phases 1 and 2 are 0.93 and 0.07, respectively.

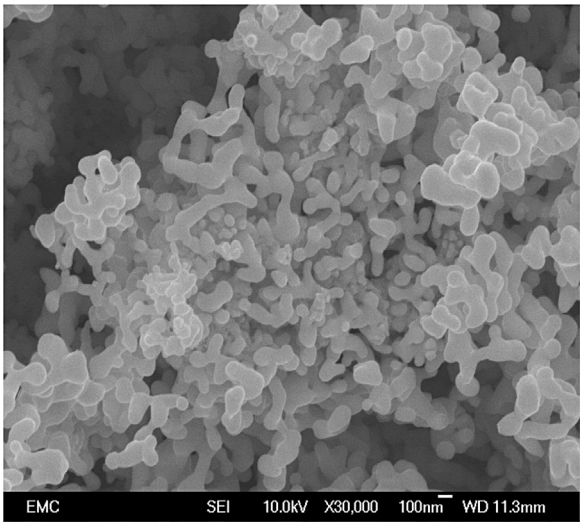


**Fig. 8.** SEM image of $CoNiMo_3N$ synthesised by ammonolysis at 700 °C for 12 h.

SEM analysis of $CoNiMo_3N$, Fig. 8, showed the sample to consist of well-formed grains. The characteristics and ammonia synthesis activity of the sample are reported in Table 1 where it can be seen that it is active for ammonia synthesis, albeit exhibiting a lower rate than those reported for the corresponding $Ni_2Mo_3N$ samples

**Table 4**
Refined structural parameters of $CoNiMo_3N$[a], lattice parameters $a = b = c = 6.62323(19)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 290.542(14)$ Å$^3$.

| Atom | Wyckoff symbol | $x$ | $y$ | $z$ | $U_{iso} \times 100$ (Å)$^2$ | Occupancy |
|---|---|---|---|---|---|---|
| Ni | 8c | 0.06782(13) | 0.06782(13) | 0.06782(13) | 0.264(21) | 0.5 |
| Co | 8c | 0.06782(13) | 0.06782(13) | 0.06782(13) | 0.264(21) | 0.5 |
| Mo | 12d | 0.20136(11) | 0.45136(11) | 1/8 | 0.330(17) | 1 |
| N | 4a | 3/8 | 3/8 | 3/8 | 0.454(22) | 1 |

prepared via precursors synthesised by the Pechini method. Whilst these results may indicate the inclusion of Co to lower activity, current studies aimed at developing a fuller understanding of the system are investigating $Co_xNi_{2-x}Mo_3N$ materials with a range of composition.

## 4. Conclusions

This study has shown that synthesis routes based upon the Pechini method are useful for preparing $Ni_2Mo_3N$ materials which are active catalysts for ambient pressure ammonia synthesis. Despite mixed oxide precursors comprising $NiMoO_4$ and $MoO_3$ being formed, this method is effective for the preparation of relatively pure phase $Ni_2Mo_3N$ samples. Nitridation can be achieved via both ammonolysis and $N_2/H_2$ pre-treatment, with the latter being of importance for larger scale synthesis where heat transfer and other issues may prove problematic for ammonolysis. Overall, the reactivity of bulk lattice nitrogen as evidenced by temperature programmed reaction with an $Ar/H_2$ mixture is limited. Isotopic exchange studies show that the lattice nitrogen is exchangeable within the system, although this behaviour is very strong function of pre-treatment with activity only being observed when a stage applying $N_2$ at 700 °C is included. This observation hints at the possible occurrence of a Mars-van Krevelen mechanism being operative for ammonia synthesis, although further studies to elucidate this are necessary. It has also been shown that the preparation method can be adapted to the synthesis of a high quality $CoNiMo_3N$ phase, thereby opening up access to a host of quaternary nitride systems for screening in terms of their ammonia synthesis activity.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2014.10.030.

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