



A comparison of the reactivity of lattice nitrogen in $\text{Co}_3\text{Mo}_3\text{N}$ and $\text{Ni}_2\text{Mo}_3\text{N}$ catalysts

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ABSTRACT

The influence of nitridding conditions upon the ammonia synthesis activities and structures of cobalt molybdenum and nickel molybdenum-based catalysts has been compared. Ammonolysis of cobalt molybdate is observed to produce a more active catalyst than H_2/N_2 pre-treatment. Post-reaction XRD analysis shows a pure $\text{Co}_3\text{Mo}_3\text{N}$ phase in the former case and a mixed phase, containing some $\text{Co}_3\text{Mo}_3\text{N}$, in the latter. Both ammonolysis and N_2/H_2 pretreatment of nickel molybdate lead to a mixture of $\text{Ni}_2\text{Mo}_3\text{N}$ and Ni, with the latter pretreatment leading to catalysts of higher activity. The reactivity of lattice nitrogen in η -6 carbide structure $\text{Co}_3\text{Mo}_3\text{N}$ and the β -Mn structure $\text{Ni}_2\text{Mo}_3\text{N}$ has been investigated. In both cases, lattice nitrogen is found to be reactive towards both H_2 and C_6H_6 and comparisons demonstrate $\text{Co}_3\text{Mo}_3\text{N}$ to be the more reactive. For $\text{Co}_3\text{Mo}_3\text{N}$, reaction with benzene yields $\text{Co}_3\text{Mo}_3\text{C}$ and graphite whereas a carbonitride and graphite is produced with $\text{Ni}_2\text{Mo}_3\text{N}$. In the case of reaction with H_2 , the nickel molybdenum system reacts to form $\text{Ni}_2\text{Mo}_3\text{N}_{1-x}$, whereas comparable conditions with $\text{Co}_3\text{Mo}_3\text{N}$ produce a novel $\text{Co}_6\text{Mo}_6\text{N}$ phase.

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1. Introduction

Spurred by the development of the ammonolysis procedure, in which high ammonia space velocities and controlled temperature ramp rates are applied to the preparation of high surface area nitrides typically from oxide precursors [1], there has been a resurgent effort in the catalytic activity of nitrides [2–4]. Catalytic attention has almost exclusively centred upon interstitial nitrides, and in particular molybdenum nitride, in which parallels between their catalytic behaviour and that for platinum group metals have been drawn. Amongst reactions studied to date have been ammonia synthesis [5,6], hydrazine decomposition [7,8], hydrodenitrogenation [2,4], NO reduction [9,10] and carbon monoxide hydrogenation [11]. Recently, Cs^+ doped $\text{Co}_3\text{Mo}_3\text{N}$ has attracted interest in terms of its ammonia synthesis activity where claims have been made that it displays higher efficacy than the commercial iron-based catalyst [12–17]. Jacobsen and co-workers [18] have explained the high activity of this system in terms of a volcano relationship in which the combination of Co (with too low a nitrogen binding energy) and Mo (with too high a binding energy) produces an alloy with an optimum nitrogen binding energy not too dissimilar to that for Ru. In this proposal, lattice nitrogen has been reported to be inactive and

its role has been ascribed to ensuring that the required ordering occurs resulting in the catalyst preferentially exposing the (111) surface termination plane in which both Co and Mo are present.

We have been interested in the possibility of applying metal nitrides as nitrogen transfer agents. It has been our aim to assess the reactivity of lattice nitrogen to determine if novel nitrogen transfer catalysis can be developed. This possibility has parallels in oxidation catalysis, where the well-known Mars-van Krevelen mechanism has been long established, and analogous processes have also been reported to occur in catalytic reactions involving sulfides [19] and carbides [20]. To this end, we have studied a series of binary and interstitial molybdenum nitrides in terms of the reactivity of their lattice nitrogen with hydrogen feedstreams in which comparisons can be drawn between ammonia synthesis rates in the presence and absence of co-fed gas-phase nitrogen. In the case of $\text{Co}_3\text{Mo}_3\text{N}$, which we have studied in greatest detail, we have demonstrated that at high temperature (i.e. 700 °C), it is possible to remove 50% of the lattice nitrogen, with that remaining relocating from the 16c to the 8a Wyckoff position, generating a novel η -12 carbide structure nitride, which was previously unknown [21]. This new phase has recently been confirmed in powder neutron diffraction studies. The original η -6 carbide structure $\text{Co}_3\text{Mo}_3\text{N}$ phase can be rapidly restored by switching the feedstream from Ar/H_2 to N_2/H_2 . In this way, it may prove possible to develop catalysts capable of directly transferring lattice nitrogen species from the lattice to an organic receptor molecule. To this end, it is interesting to note

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that Mori and co-workers have developed homogeneous titanium containing systems which they have shown capable of incorporating active nitrogen species, generated from gas-phase N_2 at low temperature, into a variety of organic molecules [23–27]. In terms of heterogeneous systems, Segal and Sebba have previously described the high efficacy of lattice nitrogen within uranium nitride during ammonia synthesis [28,29]. More recently in a TAP reactor study, Olea et al. [30] have proposed the occurrence of a double Mars-van Krevelen mechanism involving the transfer of both lattice oxygen and nitrogen during propane ammoxidation over VAION catalysts. In addition, based on the dramatic onset of ammonia decomposition activity associated with the β - to β' -phase transition of zirconium oxynitride, Soerijanto et al. [31] suggested a mechanism in which part of the product nitrogen originates from the lattice in a catalytic cycle wherein it is subsequently replenished from gas-phase NH_3 .

In this study, a comparison between the η -6 carbide structure Co_3Mo_3N and Ni_2Mo_3N , which possesses the β -Mn structure [32], has been made. We have investigated the role of preparation on ammonia synthesis efficacy, i.e. ammonolysis versus treatment with N_2/H_2 , since the latter would be preferable in terms of large-scale application [33]. Comparison of the reactivity of lattice nitrogen species in the two systems has been made in terms of the ammonia synthesis activities with a Ar/H_2 feed and also the reactivity with C_6H_6 at high temperature.

2. Experimental

$CoMoO_4 \cdot nH_2O$ precursor was prepared by adding aqueous solutions of $Co(NO_3)_2 \cdot 6H_2O$ (Sigma–Aldrich, 98+%) to $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (Alfa Aesar, JM 81–83% as MoO_3) and heating the mixed solution to approximately $80^\circ C$. A purple precipitate was obtained after vacuum filtration and the precipitate was washed twice with distilled water, once with ethanol and then dried overnight at $150^\circ C$. The powder was calcined in air at $500^\circ C$. When nitrided by ammonolysis, approximately 1 g of material was placed in a vertical quartz reactor into which a 94 ml min^{-1} NH_3 (BOC, 99.98%) was introduced. The furnace was programmed to heat the material in three stages. The temperature was increased from ambient to $357^\circ C$ at a rate of $5.6^\circ C\text{ min}^{-1}$ and then to $447^\circ C$ at $0.5^\circ C\text{ min}^{-1}$, then to $785^\circ C$ at $2.1^\circ C\text{ min}^{-1}$ 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 of the material to air, the material was passivated overnight using a mixture containing $<0.1\%$ O_2 .

$NiMoO_4$ was prepared by dropwise addition of 400 ml (0.25 M) of an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ (Sigma–Aldrich), to a 150 ml solution of $Na_2MoO_4 \cdot (H_2O)_2$. A green precipitate was obtained after vacuum filtration and the precipitate was washed twice with distilled water, once with ethanol and dried overnight at $150^\circ C$. The powder was then calcined at $700^\circ C$ for 6 h under a flow of nitrogen gas (5 ml min^{-1}). Where appropriate, the nickel molybdate was nitrided under a flow of NH_3 , as described above for Co_3Mo_3N .

Reaction studies were performed using 0.4 g of material placed in a silica reactor tube and held centrally between two silica wool plugs within the heated zone of a tube furnace. All materials were pre-treated at $700^\circ C$ with 60 ml min^{-1} of $1/3\text{ }N_2/H_2$ (BOC, H_2 99.998%, N_2 99.995%) for 2 h. Ammonia synthesis experiments were then performed at $400^\circ C$ using this gas mixture, following cooling under the reactant 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 by determined from the rate of change of conductivity with respect to time. H_2/Ar reactions

Table 1

Ammonia synthesis activities of ternary nitrides prepared by ammonolysis and mixed oxides exposed to the reaction mixture (60 ml min^{-1} $1/3\text{ }N_2/H_2$, 0.4 g catalyst)

Catalyst	Surface area ($\text{m}^2\text{ g}^{-1}$)	NH_3 synthesis rate ($\mu\text{mol h}^{-1}\text{ g}^{-1}$)
Co_3Mo_3N	18	165
Ni_2Mo_3N	1	27
$CoMoO_4 \cdot nH_2O$	13	135
$NiMoO_4$	3	46

were performed using a $1/3\text{ }Ar/H_2$ mixture (BOC, H_2 99.998%, Ar 99.99%) following the $700^\circ C$ pre-treatment and subsequent cooling to $400^\circ C$ under H_2/N_2 .

Reactions with C_6H_6 were performed by bubbling 60 ml min^{-1} of $1/3\text{ }N_2/H_2$ through a C_6H_6 (Sigma AnalR) saturator. This yielded a feedstream containing ca. 12% benzene by volume.

Powder diffraction analyses were performed using a Siemens D5000 instrument operating with $Cu\text{ K}\alpha$ radiation. A 2θ range between 5° and 85° was scanned using a counting rate of 1 s per step with a step size of 0.02° . Samples were prepared by compaction into a Si sample holder.

CHN analysis was performed using an Exeter Analytical CE-440 elemental analyser.

BET surface areas were determined from nitrogen physisorption isotherms measured at liquid nitrogen temperature using a Micromeritics Gemini instrument.

3. Results and discussion

As discussed by Wise and Markel [33], it is preferable to apply N_2/H_2 mixtures rather than NH_3 for nitridation on the large scale. Accordingly, we have compared the use of NH_3 and N_2/H_2 as nitriding agent for both Co_3Mo_3N and Ni_2Mo_3N . For nitridation with N_2/H_2 , the oxide precursors were subjected to treatment with the stoichiometric $1/3$ ammonia synthesis mixture at $700^\circ C$ for 2 h prior to reaction, as were the passivated materials prepared by ammonolysis. The steady state rates for ammonia synthesis at $400^\circ C$ are shown in Table 1. In all cases, the same mass of material (0.4 g) has been loaded into the reactor and the rates are normalised to this mass. It can be seen that the cobalt molybdenum containing catalyst is more active when nitrided with NH_3 , although that producing using N_2/H_2 , a far simpler technique, is almost as active. In the case of the nickel molybdenum catalyst, a more active catalyst is generated with N_2/H_2 . Fig. 1 presents the powder diffraction pattern for the Co_3Mo_3N phase prepared by ammonolysis. Prior to reaction, it can be seen that the passivated catalyst contains

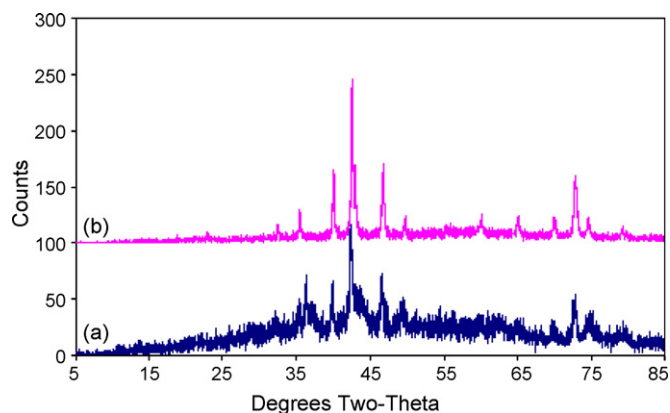


Fig. 1. Powder X-ray diffraction patterns of (a) pre-reaction and (b) post-reaction Co_3Mo_3N prepared by ammonolysis.

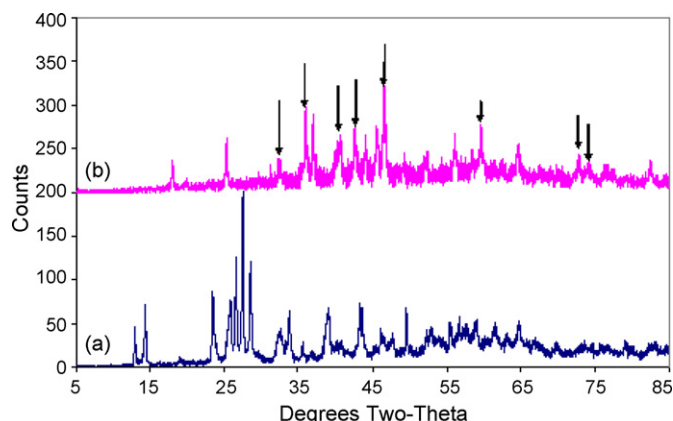


Fig. 2. Powder X-ray diffraction patterns of cobalt molybdenum oxide (a) prior to and (b) after ammonia synthesis. The arrows indicate the positions of major $\text{Co}_3\text{Mo}_3\text{N}$ reflections.

an amorphous component. However, the post-reaction pattern is representative of a much more crystalline $\text{Co}_3\text{Mo}_3\text{N}$ phase. In the case of the sample treated with N_2/H_2 , the pre-reaction sample is a relatively complex mixture, as can be seen in Fig. 2. This is found to partially match the diffraction pattern for $\text{CoMoO}_4 \cdot n\text{H}_2\text{O}$ [34] and $\alpha\text{-CoMoO}_4$ [35] reported in the literature, although some expected reflections are absent. After reaction, it can be seen that there are some reflections, as marked, which correspond to those which would be expected for $\text{Co}_3\text{Mo}_3\text{N}$, although these are not well developed. However, there are a number of additional reflections which correspond to some of those evident in the pre-reaction sample. Post-reaction CHN data, as given in Table 2, confirm that the nitrogen content is close to that expected for stoichiometric $\text{Co}_3\text{Mo}_3\text{N}$ in the sample prepared by ammonolysis, whereas it is only about 50% of that in the case of the sample subjected to N_2/H_2 . During nitridation of MoO_3 with N_2/H_2 , Wise and Markel [33] have proposed that intermediate Mo metal forms which is generated via MoO_2 . An unidentified molybdenum oxide, hydroxide or hydrate is reportedly often also observed. Powder diffraction patterns are presented for nickel molybdenum systems in Figs. 3 and 4. The exact assignment of the $\text{Ni}_2\text{Mo}_3\text{N}$ phase has been controversial in the literature, with some authors assigning the phase as $\text{Ni}_3\text{Mo}_3\text{N}$ [36,37]. However, as can be seen in Fig. 3, the well defined $\text{Ni}_2\text{Mo}_3\text{N}$ pattern evident after reaction is accompanied by reflections indicative of the presence of Ni, as described by others, which lends weight to the assignment of mixed Ni–Mo phase with a Ni:Mo ratio <1. Again, as for the Co–Mo case, the reaction and/or pre-treatment environment has modified the phase present and it can be seen that a “clean” $\text{Ni}_2\text{Mo}_3\text{N}$ phase in association with Ni is generated. In the pre-reaction sample, nickel nitride and a different mixed nickel molybdenum nitride are also present, as indicated. Others have also reported the presence of Ni_3N and $\text{Ni}_{0.2}\text{Mo}_{0.8}\text{N}$ phases in the synthesis of nickel molybdenum nitride [37]. However, upon reaction under our conditions, these additional phases appear to be lost. In

Table 2

Post-reaction nitrogen analysis following 5.5 h reaction with 60 ml min^{-1} 1/3 N_2/H_2 at 400 °C (0.4 g catalyst)

Sample	Stoichiometric nitrogen content (wt%)	Post N_2/H_2 , 400 °C reaction nitrogen (wt%)
$\text{Co}_3\text{Mo}_3\text{N}$	2.92	2.80
$\text{Ni}_2\text{Mo}_3\text{N}$	2.93 ^a	2.57
$\text{CoMoO}_4 \cdot n\text{H}_2\text{O}$	Nil	1.51
NiMoO_4	Nil	2.31

^a Calculated on the basis of the occurrence of a 1:1 $\text{Ni}_2\text{Mo}_3\text{N}:\text{Ni}$ mixture.

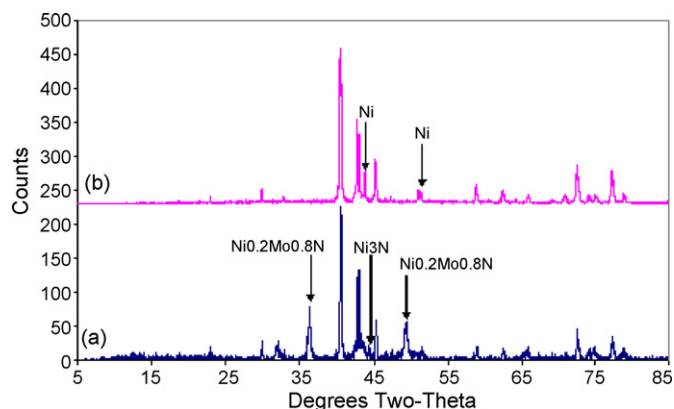


Fig. 3. Powder X-ray diffraction patterns of (a) pre-reaction and (b) post-reaction $\text{Ni}_2\text{Mo}_3\text{N}$ prepared by ammonolysis.

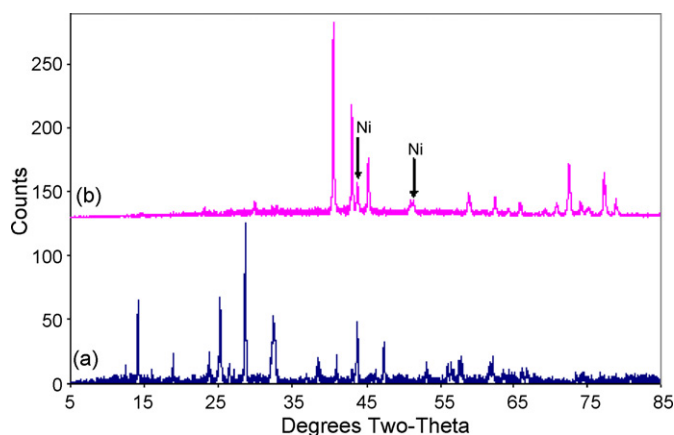


Fig. 4. Powder X-ray diffraction patterns of nickel molybdenum oxide (a) prior to and (b) after ammonia synthesis.

the case of N_2/H_2 treatment of the oxide, the pre-reaction XRD pattern matches that published for $\alpha\text{-NiMoO}_4$ [38] well. Upon reaction, it can be seen that a very crystalline $\text{Ni}_2\text{Mo}_3\text{N}$ phase in association with Ni is generated. Post-reaction BET surface area analysis indicates that this sample has a higher surface area than its counterpart generated from NH_3 . This is a likely explanation for the differences in their activity.

In view of the main focus our research, which is an investigation of the reactivity of lattice nitrogen species, we have measured the rates of ammonia synthesis with a 1/3 Ar/H_2 feed. Table 3 presents data relating to the $\text{Co}_3\text{Mo}_3\text{N}$ and $\text{Ni}_2\text{Mo}_3\text{N} + \text{Ni}$ samples prepared by ammonolysis. The data relates to 7 h runs at temperatures up to 700 °C over the time periods shown. The data for 400 °C has been broken down into two different time intervals, since there are two distinct phases of activity. Overall, it can be seen that ammonia evolution occurs from the samples and that the $\text{Co}_3\text{Mo}_3\text{N}$ sample is much more active than its Ni–Mo based counterpart. The absence

Table 3

Ammonia synthesis rates in the absence of gas-phase N_2 using a 1/3 Ar/H_2 feed (60 ml min^{-1} , 0.4 g of catalyst, time refers to total time on stream)

Reaction temperature/time	$\text{Co}_3\text{Mo}_3\text{N}$ NH_3 synthesis rate ($\mu\text{mol h}^{-1} \text{g}^{-1}$)	$\text{Ni}_2\text{Mo}_3\text{N}$ NH_3 synthesis rate ($\mu\text{mol h}^{-1} \text{g}^{-1}$)
400 °C (0–0.5 h)	98	11
400 °C (1–4 h)	12	1
500 °C (4–5 h)	0	9
600 °C (5–6 h)	16	7
700 °C (6.5–7.5 h)	12	0

Table 4

Ammonia synthesis rate as a function of temperature for $\text{Co}_3\text{Mo}_3\text{N}$ with 1/3 N_2/H_2 (60 ml min^{-1} , 0.4 g of catalyst, time refers to total time on stream)

Reaction temperature/time	NH_3 synthesis rate ($\mu\text{mol h}^{-1} \text{g}^{-1}$)
400 °C (0–0.5 h)	189
400 °C (0.5–4 h)	158
500 °C (4–5 h)	369
600 °C (5–6 h)	173
700 °C (6.5–7 h)	83

Table 5

Post- H_2/Ar reaction nitrogen analysis data (conditions as for those given in Table 4)

Sample	Stoichiometric nitrogen content (wt%)	Post H_2/Ar 700 °C reaction nitrogen (wt%)
$\text{Co}_3\text{Mo}_3\text{N}$	2.92	1.50
$\text{Ni}_2\text{Mo}_3\text{N}$	2.93 ^a	2.33

^a Calculated on the basis of the occurrence of a 1:1 $\text{Ni}_2\text{Mo}_3\text{N}:\text{Ni}$ mixture.

of NH_3 formation at 500 °C in the case of $\text{Co}_3\text{Mo}_3\text{N}$ suggests that an active pool of nitrogen has been exhausted by this temperature and that beyond this temperature an additional active pool is accessed. The results for NH_3 synthesis using a 3/1 H_2/N_2 mixture under comparable conditions are presented in Table 4 for $\text{Co}_3\text{Mo}_3\text{N}$ and from this it can be seen that the rate of ammonia synthesis from H_2/Ar is much lower than that from H_2/N_2 for this system, although it is still significant. Beyond the initial 30 min on stream, the catalytic activity was stable for each temperature studied in Table 4. The depletion of nitrogen from both systems under the Ar/H_2 treatment regime is evident from the N analysis data presented in Table 5. One possible pathway for the generation of NH_3 in the absence of co-fed N_2 is the hydrogenation of surface bound NH_x residues. However, lattice shifts evident in post-reaction powder diffraction patterns confirm the loss of N species indicating that there is, at least, a significant contribution of lattice N to the NH_3 formed. As described elsewhere and discussed in the introduction, these shifts are noteworthy in the case of $\text{Co}_3\text{Mo}_3\text{N}$ where a new phase, the η -12 $\text{Co}_6\text{Mo}_6\text{N}$ phase, is generated [21,22]. In the case of $\text{Ni}_2\text{Mo}_3\text{N}$, shown in Fig. 5 for a selected region of the pattern, smaller shifts are evident as would be expected in relation to the data presented in Table 3 which indicates that overall much less lattice N is removed from this system.

The carburisation of γ - Mo_2N is an acknowledged route to the synthesis of the face centred cubic based α - MoC_{1-x} carbide [39], which can otherwise be difficult to obtain. Such a reaction, which is generally conducted at elevated temperature (i.e. ca 700 °C) using

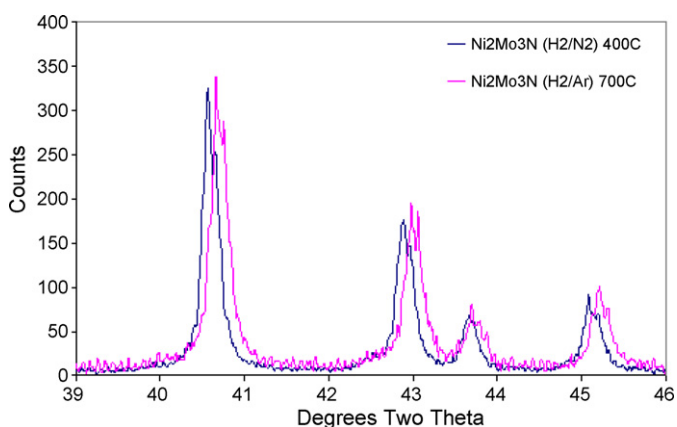


Fig. 5. Overlaid powder X-ray diffraction patterns showing the lattice shift indicative of the depletion of lattice nitrogen in the $\text{Ni}_2\text{Mo}_3\text{N}$ system evident upon reaction with Ar/H_2 .

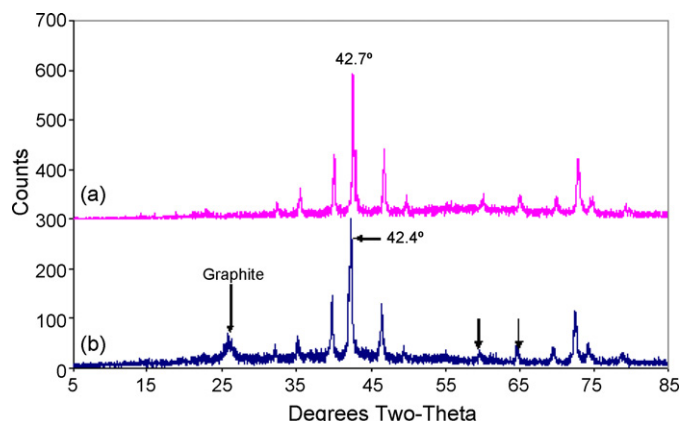


Fig. 6. Powder X-ray diffraction patterns of $\text{Co}_3\text{Mo}_3\text{N}$ (a) before and (b) after reaction with C_6H_6 .

CH_4 as the carbon source, is an obvious demonstration of the reactivity of lattice nitrogen species. We have followed this reaction and have evidenced some ammonia production (accounting for ca. 10% of the lost nitrogen.) Elsewhere, others have shown that carburisation of $\text{Co}_3\text{Mo}_3\text{N}$ with CH_4 is an effective route for the generation of $\text{Co}_3\text{Mo}_3\text{C}$ [40,41]. Accordingly, we have made comparisons of the carburisation of $\text{Co}_3\text{Mo}_3\text{N}$ and $\text{Ni}_2\text{Mo}_3\text{N} + \text{Ni}$ systems, using C_6H_6 as carburisation agent in a 1/3 N_2/H_2 mixture as carrier under the same temperature programming regime applied for the Ar/H_2 mixtures, to ascertain the relative reactivity of the N sublattice with a carbon source. Caution must be adopted in this and similar procedures, since cyanides could be possible products of reaction. Liquid phase reaction products were trapped using an ice bath and analysis showed only the presence of unreacted benzene. However, the phases of the nitrides were dramatically altered by such treatment. In the case of post-reaction XRD analysis of $\text{Co}_3\text{Mo}_3\text{N}$, shown in Fig. 6, lattice parameter shifts were again evident, although in this instance an increase in lattice parameter was observed whereas Ar/H_2 decreased it. The shifts shown exactly correspond to those reported by Bussell and co-workers in the transformation of $\text{Co}_3\text{Mo}_3\text{N}$ to $\text{Co}_3\text{Mo}_3\text{C}$ [41]. Furthermore, a broad reflection at ca $26^\circ 2\theta$ is evident which is indicative of the formation of graphite [42]. If the width of this reflection is assumed to be solely due to Scherrer broadening effects, and the interlayer spacing of graphite is taken to be 3.35 Å, then this suggests that ca. 65 layers of graphite are laid down. The complete removal of nitrogen from this system is confirmed by the data presented in Table 6, which shows that the amount of carbon deposited is significant (and far in excess of that corresponding to the formation of $\text{Co}_3\text{Mo}_3\text{C}$ which would be 2.52 wt%). In the case of $\text{Ni}_2\text{Mo}_3\text{N} + \text{Ni}$, minor lattice parameter shifts are evident and post-reaction analysis indicates that there is still some residual N in the system, which indicates the possible formation of a carbonitride phase with associated graphite formation. Taken together, the carbidation results for both phases confirm the observation made in the Ar/H_2 experiments, that the lattice nitrogen in the η -6 carbide structured $\text{Co}_3\text{Mo}_3\text{N}$ ternary nitride is more reactive than that in the β -Mn phase $\text{Ni}_2\text{Mo}_3\text{N}$ ternary phase,

Table 6

CHN data following reaction of ternary nitride systems with 12% C_6H_6 and 60 ml min^{-1} 1/3 N_2/H_2 (0.4 g material, applying the temperature programmed regime shown in Table 4.)

Sample	Observed N content (wt.%)	Observed C content (wt.%)	Observed H content (wt.%)
$\text{Co}_3\text{Mo}_3\text{N}$	Nil	28.96	Nil
$\text{Ni}_2\text{Mo}_3\text{N}$	1.00	25.54	Nil

although caution should be exercised in this comparison since the BET surface area of the former is approximately twenty times that of the latter.

4. Conclusions

Unlike binary molybdenum nitrides and nickel molybdenum nitride, controlled temperature ammonolysis is observed to generate cobalt molybdenum nitride catalysts with greater activity than those generated by treatment with the stoichiometric N_2/H_2 ammonia synthesis gas mixture. In the instance of N_2/H_2 treatment, a mixed phase containing some Co_3Mo_3N is produced, whereas pure phase Co_3Mo_3N is produced by ammonolysis. In the case of the nickel molybdenum ternary systems, a pure phase mixture of Ni_2Mo_3N and Ni is produced by either method and the ammonia synthesis activity of samples prepared by N_2/H_2 is slightly higher. The reactivity of lattice nitrogen is evident in both systems by temperature-programmed reaction with Ar/H_2 and also with C_6H_6 . In both circumstances, Co_3Mo_3N is found to be more reactive than Ni_2Mo_3N . In the former case Co_6Mo_6N and Co_3Mo_3C are produced respectively, whereas in the latter case lattice nitrogen is lost to a much lesser extent yielding $Ni_2Mo_3N_{1-x}$ and a carbonitride phase.

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