



Metal nitrides, the Mars-van Krevelen mechanism and heterogeneously catalysed ammonia synthesis

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ABSTRACT

Whilst the Mars-van Krevelen mechanism is well established for metal oxide catalysed oxidation reactions, it has been much less studied in the case of nitrogen based reactions catalysed by metal nitrides. In this overview, some of the recent literature in relation to the possible operation of the Mars-van Krevelen mechanism for ammonia synthesis catalysed by metal nitrides is presented, along with some of the literature relating to the synthesis of ammonia via chemical looping approaches.

1. Introduction

Building upon prior work by Senisman and Nelson [1], Weiss et al. [2], Maxted [3] and Calderbank [4], in a landmark publication in 1954, Mars and van Krevelen provided a kinetic analysis of oxidation reactions conducted using vanadium pentoxide catalysts [5]. Whilst the kinetic expression derived in the work has been subject to subsequent criticism [6], the central tenet that in such oxidations the lattice oxygen is active is now widely accepted and has been demonstrated using, for example, isotopic labelling species. A generalised schematic of the mechanistic pathway is presented in Fig. 1 in which the oxidation of a substrate (S) is accomplished using the lattice oxide species of a catalytic material resulting in transient lattice vacancies which are subsequently replenished by an oxidant (in this case gas phase dioxygen). As had been recognised in the original publication [5], the initial oxidation step could be conducted in the absence of oxygen, e.g.

aromatic compound + oxidised catalyst → oxidation products + reduced catalyst

with regeneration of the catalytic material being conducted in a separate step.

reduced catalyst + oxygen → oxidised catalyst

The possibility of separating the overall reaction into different reaction steps is interesting in terms of process considerations. A partially oxidised substrate (SO in Fig. 1) could potentially be produced in the absence of gas-phase O₂, the presence of which, for example, may lead to

a loss of selectivity to the desired product through total oxidation. To this end, the application of a two-stage process for the production of maleic anhydride by the oxidation of n-butane has been investigated [7, 8]. In the large-scale fixed bed industrial process, which is catalysed by a vanadium phosphate based material, a very high ratio of air to n-butane is employed avoiding the flammability limits [9]. Exploration had been made of the application of a two-stage process such that the maleic anhydride product, which is susceptible to further oxidation, did not come into contact with the gas-phase oxidant in the presence of the catalyst. However, advances in terms of the application of such approach for industrial scale production of maleic anhydride have been limited by the attrition resistance of the oxygen carrier material which would have to be moved from the hydrocarbon reaction zone to the oxidant regeneration zone multiple times [7]. Nonetheless, the use of chemical looping in which the lattice oxide of a metal oxide based material (an oxygen carrier) is applied directly as a reactant to accomplish a conversion process with the reduced oxide being replenished (i.e. re-oxidised) in a separate step is an area of topical interest currently, see for example [10].

In terms of oxidation catalysis, from the schematic in Fig. 1, it can be imagined that reducible oxides would be effective catalysts with metal-oxygen bond strength being an important consideration [11], although non-reducible oxides able to accommodate electrons at vacancy sites would also exhibit activity. To this end, studies of isotopic oxygen exchange as exemplified in the work of Boreskov [12] and Winter [13] are of relevance, although with complex kinetic considerations in some instances [14], with the heterolytic isotopic exchange in which labelled

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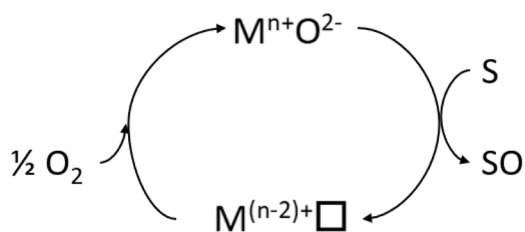


Fig. 1. A general schematic of the Mars-van Krevelen mechanism in which a metal oxide catalyst is involved in the oxidation of a substrate (S) using O_2 as the oxidant.

gas-phase oxygen (generally $^{18}O_2$) is scrambled with the lattice oxygen of a catalyst (such as a metal oxide in which the lattice oxygen is predominantly ^{16}O reflecting the natural isotopic abundance of oxygen) and homomolecular exchange (in which gas-phase $^{16}O_2/^{18}O_2$ mixtures are scrambled) proving informative.

Whilst the original postulation of the “Mars-van Krevelen mechanism” was based upon oxidation catalysis with metal oxides in which the lattice oxide was the active oxidant, leading to the transient formation of lattice vacancies at which the gas-phase oxidant is activated and the metal oxide catalyst regenerated to close the catalytic cycle, extensions have been made to sulfide, chloride and hydride based catalysts [11]. In the case of metal carbides, Mars-van Krevelen mechanisms have been reported to be operative for molybdenum carbide catalysed syn-gas related reactions such as, for example, partial oxidation of methane [15] and iron carbide catalysed carbon monoxide hydrogenation [16]. In a chemical looping like application, methane homologation (conversion to higher hydrocarbons) has been accomplished by the carbidation of metals using methane with the resultant metal carbides being reduced using hydrogen under different reaction conditions (lower reaction temperature for thermodynamic reasons see Fig. 2) [17]. Of relevance to the Mars-van Krevelen mechanism, an overview of the formation and control of surface vacancies for a wide range of catalytic materials including oxides, carbides, nitrides, sulfides and hydrides has been published recently [18]. It is also noteworthy that the formation of surface species, such as hydroxyls [19] and carbonates [20], which can undergo Mars-van Krevelen mechanisms have also been reported, see for example Fig. 3 [20].

In the following, we summarise the literature relating to the possible occurrence, and application, of the Mars-van Krevelen mechanism in heterogeneously catalysed reactions employing metal nitride catalysts with ammonia synthesis being a particular area of interest. Related

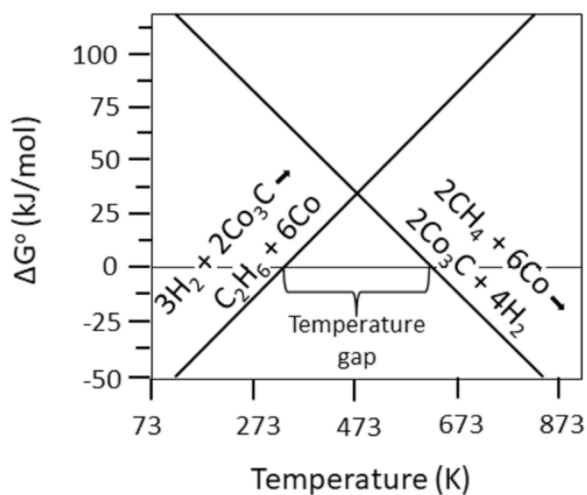


Fig. 2. The two-stage homologation of methane employing Co. (Figure adapted from reference [17] with permission).

chemical looping type approaches are also discussed, although strictly looping processes do not necessarily require the generation of bulk metal nitride phases and could be accomplished by the formation of surface bound nitrogen reactive species on, for example, metal surfaces.

2. The reactivity of lattice nitrogen in metal nitrides - catalysis

Early studies of ammonia synthesis identified metals which underwent nitridation under N_2 treatment as being of potential interest for ammonia synthesis when subsequently treated with H_2 [21], a process now known as chemical looping. Indeed, in 1905, Haber and van Oordt identified manganese as being of potential interest in this respect as shown in Fig. 4 [22]. Interest in the manganese nitride system continues to this day where lithium doping has been observed to enhance the reactivity of lattice nitrogen [23], leading to enhanced ammonia formation possibly via a reduction in the nitrogen vacancy formation energy [24]. The formation of ammonia from the manganese nitride and other nitride systems can be accomplished by hydrolysis using steam with the cycle being closed by the application of solar energy driven reduction of the oxidised material with nitrogen at atmospheric pressure with or without a gaseous chemical reducing agent [25]. Transition metal doping has been undertaken to modify the bonding of nitrogen in the nitride with iron doping reducing the nitrogen binding strength and enhancing the concentration of nitrogen vacancies [26]. In comparing different metal nitrides for ammonia production via hydrolysis, ionicity has been shown to be an important consideration [25]. In the case of hydrogenation of metal nitrides to yield ammonia, the presence of lattice hydrogen which has substituted some lattice nitrogen is proposed to be of importance [27] and it has recently been reported that for sodium promoted systems 100 kg of NH_3 per day could be produced using about 1200 kg of Mn in chemical looping with dinitrogen and dihydrogen and that there are further opportunities for improvement [28]. Another looping system reported in early studies is that of cerium nitride (CeN) [29] and, as discussed later, it is of interest to note that this is a component of the recently reported highly active Ni/CeN catalyst for which the favourable formation of nitrogen vacancies in CeN is argued to be of importance for the catalyst's good performance [30]. In investigating the kinetics of nitrogen evolution from an iron-nitrogen interstitial alloy, Goodeve and Jack showed that products other than ammonia can be produced by approaches involving metal nitrides which are related to chemical looping [31]. They reported that nitrogen was eliminated entirely as ammonia under hydrogen at temperatures from 250 °C to 450 °C and that at temperatures below 500 °C heating iron nitrides in the presence of carbon monoxide leads to isomorphous replacement of nearly three quarters of the lattice nitrogen by carbon with nitrogen being eliminated predominantly as dinitrogen and partly (25% or less) as cyanide [31].

The reactivity of lattice nitrogen, akin to the operation of the Mars-van Krevelen mechanism, in the catalytic synthesis of ammonia was reported in a number of studies by Sebba and co-workers [32–35]. In the case of a vanadium oxide-nitride solid state solution it was stated that lattice nitrogen was hydrogenated to form ammonia with the rate determining step being the adsorption of nitrogen into this state [32]. Discontinuous activity of samples in the temperature range 460–500 °C was ascribed to disordering of lattice species [33]. In the case of uranium nitride, an active ammonia synthesis catalyst, the proposal was made that weakly held nitrogen from sub-surface regions was active with diffusion of active atomic N to the surface which reacts rapidly with hydrogen to produce ammonia in the case of U_3N_2 [34,35]. For molybdenum nitride, Hillis et al. proposed the rate determining step of ammonia synthesis to be one of the steps in the conversion of adsorbed nitrogen to gas-phase ammonia rather than nitrogen adsorption [36], although contrary proposals were made by Aika and Ozaki [37]. In the work of Hillis et al. hydrogenation of bulk nitride to yield ammonia was observed, although it was stated to occur at a rate 50 times slower than the overall ammonia synthesis rate [36]. Again, concerning products

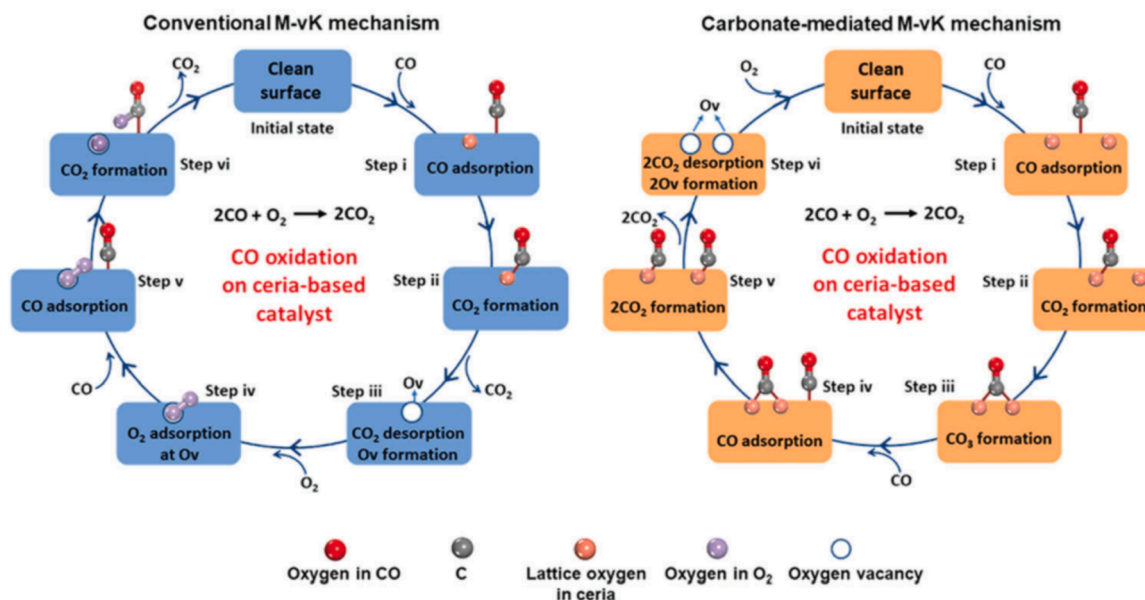


Fig. 3. Conventional versus carbonate mediated Mars-van Krevelen mechanisms for carbon monoxide oxidation catalysed by cobalt doped ceria. (Figure reproduced from reference [20] with permission).

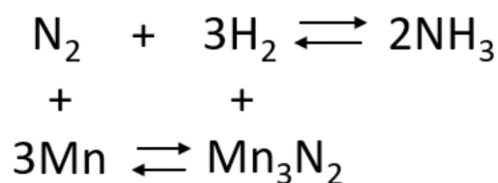


Fig. 4. The two-stage production of ammonia from manganese. (Figure adapted from reference [22]).

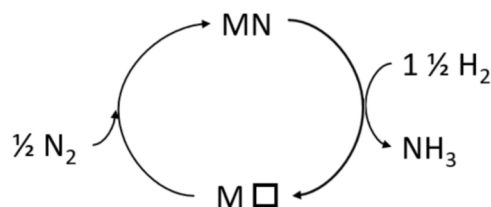


Fig. 5. General schematic for metal nitride catalysed ammonia synthesis.

other than ammonia, it is interesting to note that double Mars-van Krevelen mechanism involving both lattice nitrogen and lattice oxygen is reported to occur for the ammoxidation of propane to yield acrylonitrile when catalysed by amorphous vanadium aluminium oxynitride [38].

The discovery of the high activity of some ternary nitrides attracted interest, with that of $\text{Co}_3\text{Mo}_3\text{N}$, particularly when promoted by Cs^+ , being of note [39–44]. The activity of this system has been rationalised on the basis of a combination of Co and Mo, being expressed in the (111) surface plane, leading to an averaging of nitrogen binding strength being close to optimal for ammonia synthesis [45]. The presence of lattice N in the system was argued to assist with the crystallographic ordering such that the active (111) surface plane was expressed [45]. The obvious implication of structure-sensitivity being operational for this system has been little explored, although this may be a result of the sensitivity of the system to air and moisture (carefully controlled passivation to preserve bulk structure is recommended for many nitrides prior to discharge from reactor systems [46]). However, the phase has been successfully dispersed on a CeO_2 support leading to more efficient utilisation of Co and Mo [47]. An alternative consideration for the activity of $\text{Co}_3\text{Mo}_3\text{N}$ is the possible occurrence of a Mars-van Krevelen mechanism where, rather than being inert, the lattice nitrogen is an active species, as outlined in the general schematic presented in Fig. 5. Since the promoted system may prove challenging in terms of phase stability, the unpromoted $\text{Co}_3\text{Mo}_3\text{N}$ system along with a number of other binary and ternary nitrides ($\beta\text{-Mo}_2\text{N}_{0.78}$, $\gamma\text{-Mo}_2\text{N}$, $\delta\text{-MoN}$, $\text{Ni}_2\text{Mo}_3\text{N}$ and $\text{Fe}_3\text{Mo}_3\text{N}$) were tested for this possibility using their ability to produce ammonia in the absence of the gas-phase nitrogen source by feeding a 3:1 H_2 :Ar mixture (representing a comparison with the 3:1 H_2 : N_2 catalytic ammonia synthesis mixture applied in many studies) [48]. In temperature

programmed experiments, ammonia production was observed for most systems with $\text{Co}_3\text{Mo}_3\text{N}$ proving to be particularly interesting. In this system, upon increasing the temperature up to 700 °C, 50% of the lattice nitrogen could be lost (with an overall conversion of ca 10% lattice N to NH_3 , the rest which was being lost forming N_2) with the remaining lattice nitrogen being retained in the sample (now of stoichiometry $\text{Co}_6\text{Mo}_6\text{N}$), despite all the lattice N being initially in the same crystallographic environment [49]. However, the local environment of the retained N clearly must have changed as this N was not lost from the system. Powder XRD demonstrated a reduction in lattice parameter, as would be expected for the loss of lattice species, with the original cubic F_{d3m} space group being maintained. Due to the fact that XRD is sensitive to electron density and the electron density associated with the lattice N is very small in the $\text{Co}_3\text{Mo}_3\text{N}$ system, accordingly, powder neutron diffraction was applied to the system to address this question of the change in nature of the residual lattice N. It was discovered that $\text{Co}_3\text{Mo}_3\text{N}$ and $\text{Co}_6\text{Mo}_6\text{N}$ existed as line phases (i.e. there were no intermediate stoichiometric forms lying between them) and that the lattice nitrogen had moved from the slightly distorted octahedral (Mo_6N) 16c Wyckoff site in $\text{Co}_3\text{Mo}_3\text{N}$ (possessing the so-called η -6 carbide structure) to the non-distorted octahedral (Mo_6N) 8a Wyckoff site in $\text{Co}_6\text{Mo}_6\text{N}$ (possessing the so-called η -12 carbide structure) [50]. These phase structures are analogous to the corresponding Co-Mo carbides [51]. Upon treatment with a 3:1 H_2 : N_2 mixture at 400 °C (a typical reaction temperature for ammonia synthesis) rapid regeneration of $\text{Co}_3\text{Mo}_3\text{N}$ from $\text{Co}_6\text{Mo}_6\text{N}$ was observed [50] – a transformation which can also be achieved by using N_2 alone albeit at the much higher temperature of 700 °C [52] (and thereby opening the opportunity to a cyclic chemical looping route to ammonia synthesis albeit with a low gravimetric N content and fairly low lattice conversion efficiency to NH_3). As

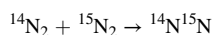
a further test of the role/reactivity of lattice N for ammonia synthesis, the catalytic performance of the corresponding $\text{Co}_3\text{Mo}_3\text{C}$ and $\text{Co}_6\text{Mo}_6\text{C}$ systems was evaluated with a topotactic synthesis method – involving controlled carbidation of a $\text{Co}_3\text{Mo}_3\text{N}$ precursor phase with CH_4/H_2 – so as not to introduce artefacts resulting from any change in morphology being employed [53]. In this study, a higher reaction temperature was required to induce catalytic performance in $\text{Co}_3\text{Mo}_3\text{C}$ when employing a 3:1 $\text{H}_2:\text{N}_2$ reaction mixture and such performance was only observed after a lag-period after which lattice N occupying the 16c Wyckoff site was observed – over the extended course of the reaction, the replacement of C in the 16c site by N progressively occurred with the performance remaining steady state. Whether the presence of lattice N in the 16c site results in ammonia synthesis activity or whether it is as a result of it, remains an open question. Interestingly, under the same conditions, lattice C in the 8a site remains completely stable – and no lattice N is introduced into the system – upon extended reaction which contrasts markedly with the observations made for the isostructural $\text{Co}_6\text{Mo}_6\text{N}$ phase.

As for the case of metal oxide catalysts, isotopic exchange has a significant role to play in developing fundamental understanding of the reactivity of N species in nitride catalysts. Two general approaches to isotopic exchange can be applied:

heterolytic exchange involving exchange of labelled gas-phase nitrogen ($^{15}\text{N}_2$) with the lattice nitrogen of the system (predominantly ^{14}N in accordance with expected isotopic abundance);.



and homomolecular exchange involving the isotopic exchange occurring between gas-phase $^{14}\text{N}_2$ and $^{15}\text{N}_2$;



It can be imagined that the former process would be a suitable probe of lattice nitrogen reactivity, with the latter being the probe of the ability of the system to activate, dissociate, recombine and desorb N_2 (although the results could be masked by accompanying heterolytic exchange with the atomic fraction of the two isotopes being quantified to take account of this). Studies of heterolytic $^{15}\text{N}_2$ exchange with $\text{Co}_3\text{Mo}_3\text{N}$ demonstrate that, when treated appropriately, 40% of the lattice nitrogen is exchanged within 40 min at 600 °C [54]. The observation of this exchange, occurring in the absence of hydrogen, demonstrates the dynamic and reactive nature of lattice N. Fig. 6 [54] presents the exchange profile for the $\text{Co}_3\text{Mo}_3\text{N}$ system and Fig. 7 [54] that for the $\text{Co}_6\text{Mo}_6\text{N}$ system. Further support for the possible role of a Mars-van Krevelen mechanism is provided by computational modelling studies undertaken on model (111) $\text{Co}_3\text{Mo}_3\text{N}$ surfaces in which significant concentrations of surface 3-fold and 5-fold hollow N vacancies are predicted at temperatures corresponding to those applied for ammonia synthesis. The interaction of N_2 with the 3- and 5- fold vacancies was modelled with elongation of the N-N bond occurring as electron density increases in the π^* anti-bonding orbitals, (the ultimate result being N-N bond dissociation) [55]. Interestingly, although quantification was not made, the reduction in pressure evident in Figs. 6 and 7 might correspond to replenishment of vacancies in pre-treated $\text{Co}_3\text{Mo}_3\text{N}$ and (partial) regeneration of $\text{Co}_3\text{Mo}_3\text{N}$ respectively.

Comparison between $\text{Co}_3\text{Mo}_3\text{N}$ and other, related, ternary nitrides shows it to exhibit a number of unique features. The isostructural $\text{Fe}_3\text{Mo}_3\text{N}$ [48] and also $\text{Ni}_2\text{Mo}_3\text{N}$ [48] (which possesses the filled β -Mn structure and which has frequently been misidentified as $\text{Ni}_3\text{Mo}_3\text{N}$ within the literature [56]) and $\text{Co}_2\text{Mo}_3\text{N}$ [57,58] (which also possesses the filled β -Mn structure) do not exhibit the degree of bulk lattice N reduction observed for $\text{Co}_3\text{Mo}_3\text{N}$. In the case of $\text{Fe}_3\text{Mo}_3\text{N}$, attempts to reduce the nitrogen content at higher reduction temperature lead to a collapse of the structure [58] and attempts to prepare the quaternary $(\text{Co},\text{Fe})_3\text{Mo}_3\text{N}$ nitride containing equivalent Co and Fe content resulted in a biphasic mixture of iron rich and cobalt rich quaternary nitrides

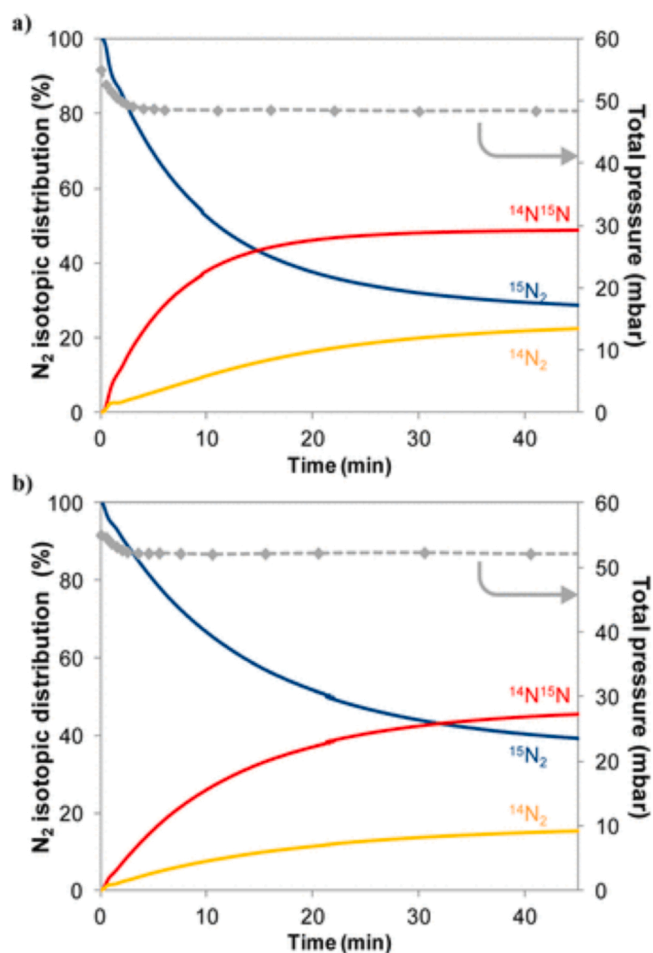


Fig. 6. Heterolytic isotopic exchange of $^{15}\text{N}_2$ at 600 °C with $\text{Co}_3\text{Mo}_3\text{N}$ pre-treated with 3:1 $\text{H}_2:\text{N}_2$ followed by (a) a N_2 purge for 30 min or (b) an Ar purge and subsequent N_2 purge for 30 min. (Figure reproduced from reference [54]).

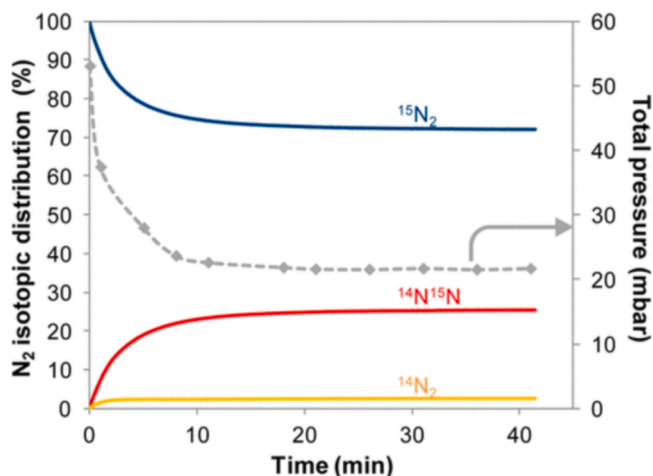


Fig. 7. Heterolytic isotopic exchange of $^{15}\text{N}_2$ at 600 °C with $\text{Co}_6\text{Mo}_6\text{N}$ pre-treated with 3:1 $\text{H}_2:\text{Ar}$ followed by an Ar purge. (Figure reproduced from reference [54]).

with the iron rich system behaving like $\text{Fe}_3\text{Mo}_3\text{N}$ and the cobalt rich one behaving like $\text{Co}_3\text{Mo}_3\text{N}$ [59]. Whilst, as stated above, $\text{Ni}_2\text{Mo}_3\text{N}$ and $\text{Co}_2\text{Mo}_3\text{N}$ also do not show bulk lattice N loss, the possibility of a surface-based Mars-van Krevelen mechanism has been proposed for

$\text{Ni}_2\text{Mo}_3\text{N}$ [60], and it is perhaps not surprising that CoNiMo_3N also possesses stable bulk lattice N [61]. It is clear that the relationship between lattice N reactivity and composition-structure is a complex one and the development of a greater understanding in this area could guide the discovery of new catalysts operating via N based Mars-van Krevelen reactions as well as new N chemical looping systems. $(\text{Cu,Ni})_2\text{Mo}_3\text{N}$ and $(\text{Fe,Ni})_2\text{Mo}_3\text{N}$ were observed to be active catalysts for ammonia synthesis with differences in performance potentially relating to differences in surface area [62].

In the ternary and quaternary systems discussed above, local environment around the lattice N species (Mo_6N) is similar despite the exhibited differences in lattice nitrogen reactivity and it could be considered that differences could arise in relation to the activation of hydrogen. In considering the potential importance of the Mars-van Krevelen mechanism for nitride catalysed ammonia synthesis and also the requirement for efficient and effective hydrogen activation, Hosono and co-workers have recently reported a series of bifunctional metal and nitride catalysts that are highly active for ammonia synthesis. These have included Ni/LaN for which the Ni component – not generally associated with effective ammonia synthesis, but very well established for hydrogenation – was of importance for H_2 activation, with N_2 activation being accomplished on nitrogen vacancies associated with LaN [63]. Calculations have demonstrated that the vacancy formation energy for LaN is low. Related to this, the same group have demonstrated the utility of LaNi_5 to make core shell nanostructures comprising Ni-LaN which are effective catalysts for ammonia synthesis [64]. In a very recent modelling study based upon nitrogen vacancy formation energy and the nitrogen adsorption energy as descriptors, Zhiu et al. proposed CeN, LaN, VN and NbN as promising candidates in ammonia synthesis [65]. Combined experimental and modelling studies had been previously reported by Hosono and co-workers applying rare earth nitrides (CeN, YN and LaN) as catalysts/supports and CeN and Ni/CeN were determined to be of particular interest, with H_2 and N_2 activation occurring at Ni and nitrogen vacancy sites respectively for Ni/CeN and such vacancy sites activating both reactions for CeN alone [30]. For Co/CeN, the low work function for N vacancies within CeN was argued to lead to electron donation facilitating the efficient cleavage of N_2 over Co in a dissociative NH_3 synthesis pathway occurring alongside an associative one as shown in the schematic presented in Fig. 8 [66]. In the case of $\text{Co}_3\text{Mo}_3\text{N}$, following on from a DFT based study in which the initial activation of both N_2 and H_2 occurred on (111) surfaces [67], the possible occurrence of associative and dissociative pathways has been modelled with the former (as schematically outlined in Fig. 9 [68]) being the more favourable from an energetic point of view [69]. It is interesting to note that the potential occurrence of an associative

pathway is consistent with the observation that $\text{Co}_3\text{Mo}_3\text{N}$ is inactive for homomolecular isotopic exchange at 400°C [54], a temperature at which it is active for catalytic ammonia synthesis. The development of novel catalysts operative via associative pathways is an interesting and exciting challenge as it provides a link to enzymatic nitrogen fixation and may be a key to the identification of catalysts active at lower reaction temperatures where ammonia synthesis is thermodynamically more favourable.

3. The reactivity of lattice nitrogen in nitrides – reactions and chemical looping

In addition to having implications for catalysis, reactive nitrogen in metal nitrides can be used to accomplish reactions and chemical looping (although in relation to looping, there is no strict requirement for application of a metal nitride, as the surface bound reactive nitrogen on, for example, a metal could be applied, e.g. [70]). Related to the concept of looping is the application of nitrogen permeable membrane reactors operating at ambient pressure comprising N_2 on one side and H_2 on the other. In this regard, interesting results for the sustainable synthesis of ammonia have recently been reported for a Nb_4N_5 reactor system [71].

Although relatively few, there are a number of examples of nitrides being applied as sources of ammonia in reactions. For example, Ley and co-workers have applied Mg_3N_2 as a convenient source of ammonia in the preparation of pyrroles [72], primary amides [73] and dihydropyridines [74] wherein NH_3 is generated in-situ via hydrolysis and extreme caution should be exercised when applying this approach as there is a documented explosion risk [75]. The work of Pfromm and co-workers in relation to the development of solar powered nitrogen looping systems for ammonia synthesis has been discussed above. Cyclic ammonia production utilising hydrogen as the reductant has been reported in an investigation of TiFe_2 and $\text{Ru}/\text{Al}_2\text{O}_3/\text{TiFe}_2$ Laves phases [76] with the latter composition being active when nitriding using N_2 alone whereas the former is not. Ammonia production by reduction of nitrides including Cu_3N [77], Ni_3N [77], Re_3N [78], Zn_3N_2 [77] and Ta_3N_5 [77] has been reported although, for chemical looping application, their regeneration using dinitrogen has yet to be achieved and approaches such as those documented for the Laves phase above, in terms of adding an additional component to facilitate N_2 activation, have not hitherto been explored to the authors' knowledge. In the case of Ta_3N_5 , it seems that ammonia is formed from an X-ray amorphous component of the sample. Doping with low levels of cobalt dopant was shown to enhance ammonia production [79] which may be associated with enhanced hydrogen dissociation [80]. Anti-perovskite nitrides, which offer the possibility of tuning the lattice N reactivity through

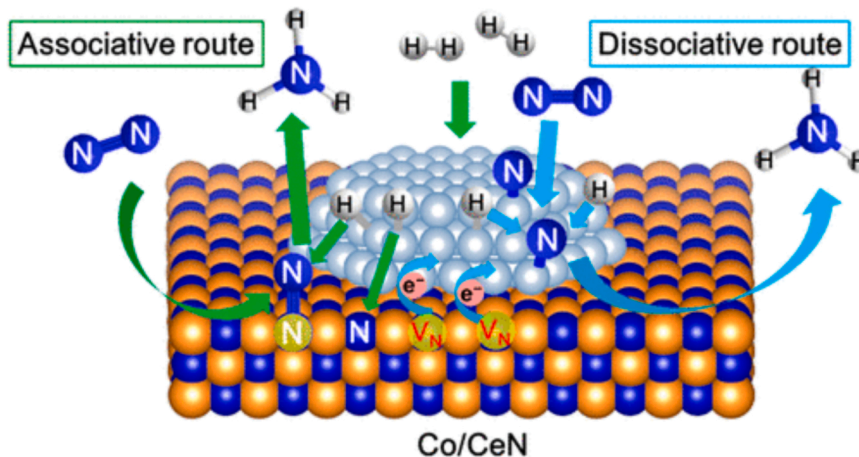


Fig. 8. Schematic of the proposed dual associative and dissociative mechanistic pathways over Co/CeN. (Figure reproduced with permission from reference [66]).

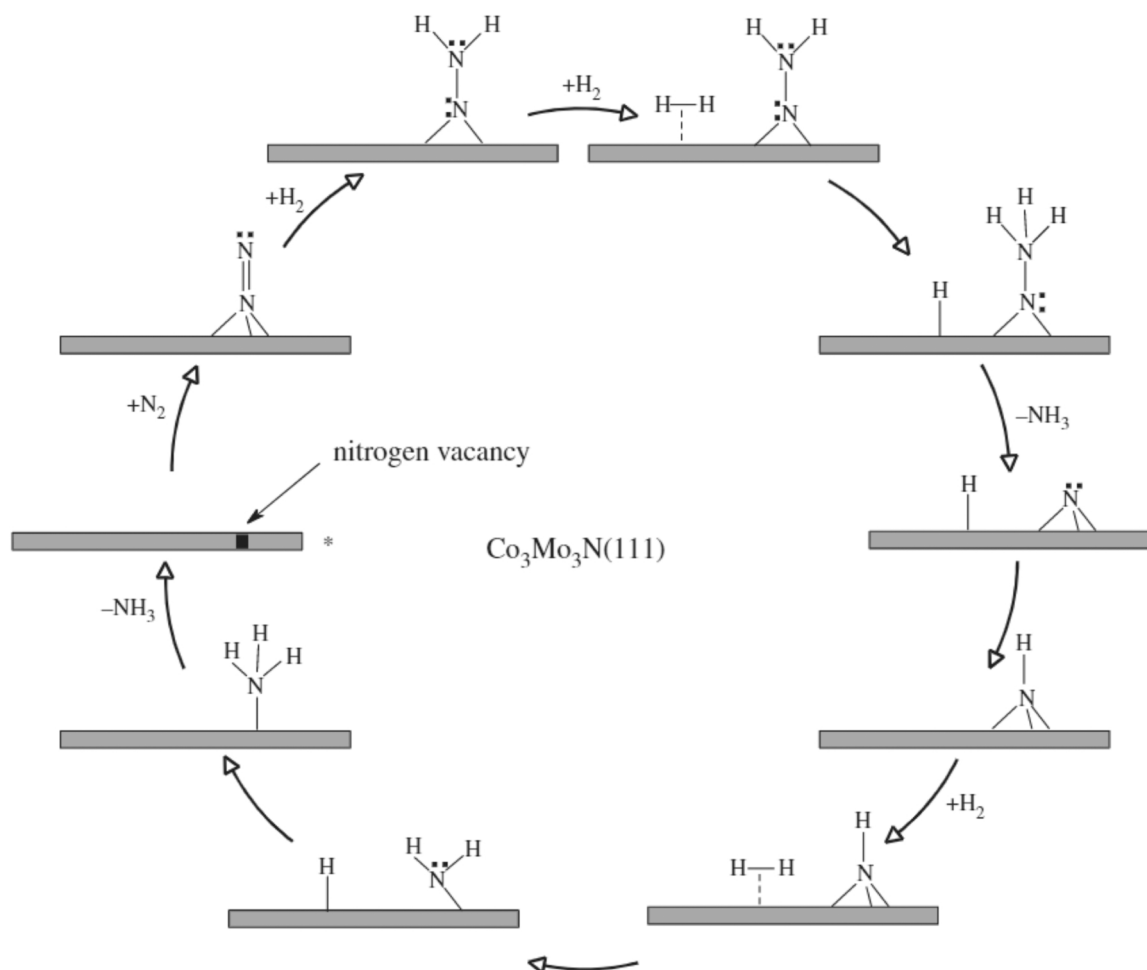
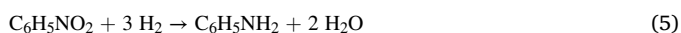
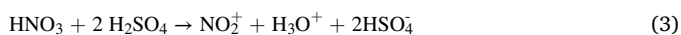


Fig. 9. Proposed associative ammonia synthesis pathway in operation on the (111) surface of $\text{Co}_3\text{Mo}_3\text{N}$. (Figure adapted from reference [68]).

controlled modification of composition, are of potential interest for both nitrogen looping and catalytic applications with their well-defined structure facilitating computational modelling possibly leading to the identification of new catalytic materials. To this end, Co_3ZnN , Ni_3ZnN , Co_3InN and Ni_3InN have been investigated [81]. They are ineffective as catalysts but decompose to yield ammonia under reaction conditions indicating their potential interest in looping, although regeneration using N_2 has not been accomplished despite the topotactic nature of lattice N loss being evident for the Ni containing systems.

There continues to be great interest in the development of systems able to incorporate N_2 directly into organic target molecules since this may avoid the application of NH_3 , or its derivatives, prepared by the highly energy-intensive Haber Bosch Process for such a purpose [82]. Perhaps the application of metal nitrides comprising reactive nitrogen have a role to play here. This consideration is exemplified by the production of aniline, a large scale industrial product, which could be viewed as follows in terms of a nitrogen cycle:



for which 1. represents the energy intense and large carbon footprint

Haber Bosch Process, 2. is the high temperature Ostwald Process, 3. involves a corrosive mixture and 4. and 5. present inherent selectivity challenges with the overall scheme involving indirect water production reduction schemes involving O and H_2 . The possible application of a metal nitride looping system as outlined in Fig. 10 is of interest. A number of further instances of this general approach can be envisaged.

4. Conclusion

The potential occurrence of the Mars-van Krevelen mechanistic pathway is of interest for the development of novel ammonia synthesis catalysts which potentially by-pass the limitations imposed by scaling considerations leading to the development of more sustainable and smaller scale processes. Metal nitrides have potential for sustainable ammonia production by chemical looping which is an area of current interest although with a history which pre-dates the introduction of the

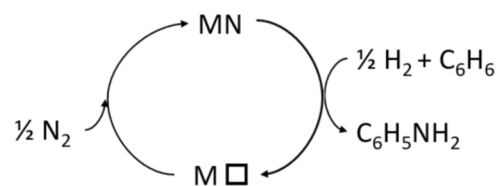


Fig. 10. Schematic of possible metal nitride mediated chemical looping route to aniline by $\text{H}_2/\text{C}_6\text{H}_6$ treatment. N_2 regeneration of the system would be operated as a separate step.

Haber Bosch Process. Chemical looping approaches are also of interest for the potential development of new routes to the incorporation of N into organic target molecules, by-passing the use of ammonia and employing N₂. It is clear that whilst comparatively few studies have been based upon metal nitride heterogeneous catalysts to date, particularly in relation to Mars-van Krevelen mechanisms, this is arguably an area that is gaining attention, as are analogous studies based upon metal hydrides where similar hydrogen based mechanistic pathways may be operative, e.g. [83]. Interestingly, for BaCeO_{3-x}N_yH_z and Ru/LaN/ZrH₂, a dual nitrogen and hydrogen Mars-van Krevelen mechanism has been reported [84,85]. The research area of metal nitrides has an exciting future, where there is a great opportunity for further studies. The development of enhanced understanding on the relationship between composition and structure-activity has a role to play in the design of new nitride-based catalysts and chemical looping systems of enhanced performance.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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