Rational design of metal nitride redox materials for solar-driven ammonia synthesis

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Fixed nitrogen is an essential chemical building block for plant and animal protein, which makes ammonia (NH₃) a central component of synthetic fertilizer for the global production of food and biofuels. A global project on artificial photosynthesis may foster the development of production technologies for renewable NH₃ fertilizer, hydrogen carrier and combustion fuel. This article presents an alternative path for the production of NH₃ from nitrogen, water and solar energy. The process is based on a thermochemical redox cycle driven by concentrated solar process heat at 700–1200 °C that yields NH₃ via the oxidation of a metal nitride with water. The metal nitride is recycled via solar-driven reduction of the oxidized redox material with nitrogen at atmospheric pressure. We employ electronic structure theory for the rational high-throughput design of novel metal nitride redox materials and to show how transition-metal doping controls the formation and consumption of nitrogen vacancies in metal nitrides. We confirm experimentally that iron doping of manganese nitride increases the concentration of nitrogen vacancies compared with no doping. The experiments are rationalized through the average energy of the dopant d-states, a descriptor for the theory-based design of advanced metal nitride redox materials to produce sustainable solar thermochemical ammonia.

1. Introduction

Renewable chemical fuels such as hydrocarbons, methanol, hydrogen and ammonia may be synthesized from CO₂, H₂O and N₂ by solar-driven photochemical [1,2], electrocatalytic [3,4] or thermochemical processes [5]. The latter approach uses the entire spectrum of concentrated solar energy as the source of high-temperature process heat, and as such provides a thermodynamically favourable path to solar fuels and materials production with high energy conversion efficiencies. A promising example is the production of syngas by thermochemically splitting CO₂ and H₂O via a metal oxide redox cycle [6] (and references therein).

Natural photosynthesis relies on structures—proteins—that are built with fixed nitrogen, such as ammonia (NH₃). Both sugar, a major product of natural photosynthesis, and protein are the central components of global food and biofuel production. In turn, synthetic ammonia is one of the major products of the chemical industry [7] that is mainly used as a fertilizer [8]. Additionally, NH₃ is an energy carrier formed via reduction of N₂, analogous to the products of photosynthesis, such as CO and hydrocarbon fuels via reduction of CO₂ and splitting of H₂O. Thus, NH₃ may find application as a hydrogen carrier [9,10] and as a fuel for alkaline fuel cells [11,12] and in internal combustion engines [13,14] (http://nh3fuelassociation.org/2013/06/20/the-amveh-an-ammonia-fueled-car-from-south-korea/). Currently, NH₃ is produced industrially from N₂ and H₂ via the catalytic Haber–Bosch process at up to 300 bar and 400–500 °C [7,15–18]. The overall process is characterized by the high energy consumption associated with the production of the reactants. Usually, H₂ is obtained by steam-reforming of natural gas, whereas N₂ is obtained by cryogenic separation.
from air. Both these processes require a major input of energy, either in the form of heat or electricity, and consequently cause a significant concomitant pollution derived from the combustion of fossil fuels for heat and electricity generation. The total energy requirement is in the range 28–166 GJ t⁻¹ NH₃ [7,15]. Furthermore, the severe process conditions require sophisticated high-pressure and high-temperature machinery that is operated in large-scale centralized plants producing typically 1000–3000 t NH₃ day⁻¹ [7,17].

To convert the nearly inert N₂ molecule into a reactive chemical, Haber’s early studies [19] examined the formation of NH₃ from H₂ and various metal nitrides. These studies were motivated by the temporary formation of NH₃ at low pressures from an iron nitride contamination of the catalyst that Ostwald used [20]. The NH₃ formation ceased quickly, because the spent iron nitride could not be regenerated with N₂ at low pressure and the work spurred the development of the Haber–Bosch process, in which NH₃ is formed at high pressure to shift the thermodynamic equilibrium [19]. Current metal nitrides for the production of complex nitrogen-containing molecules cannot be regenerated with 1 bar N₂ [21]. Examples are Ni₃N, Cu₃N, Zn₃N₂ and Ta₃N₅N₆, which liberate 30, 25, 23 and 13 mol% of their lattice nitrogen in the form of NH₃ when reacted with H₂ at 250, 250, 400 and 700 °C, respectively [22]. Certain metal nitrides have been studied as low-pressure NH₃ synthesis catalysts [23,24], and some ternary metal nitrides have been found to reversibly reduce N₂ at low pressure and to liberate the fixed nitrogen in the form of NH₃ in a second step, when reacted with H₂ [25–27]. A typical example of such a material is Co₃Mo₃N that yields Co₃Mo₃N and up to 8 mol% of its lattice nitrogen in the form of NH₃ when reacted for 60 min with H₂ at 400 °C [27]. To increase the NH₃ yield, current materials development focuses on increasing the amount of nitrogen stored in the metal nitride and on increasing the fraction of the lattice nitrogen that yields NH₃ [21].

This paper focuses on materials development for a solar-driven ammonia synthesis from N₂ and H₂O (instead of H₂) that—in contrast to the Haber–Bosch process—does not require fossil fuels, electricity or high-pressure operations [28–30]. In a first step, NH₃ is formed at 1 bar and below 200–500 °C via the oxidation of a solid metal nitride redox material with steam [31,32]. The oxidized redox material is subsequently regenerated in an endothermic step driven by concentrated solar process heat at up to 1200 °C with a stream of N₂ with or without a gaseous chemical reducing agent [28–30]. The reaction stoichiometry of this redox cycle is given in the electronic supplementary material. While this process has been demonstrated successfully with Al-based redox materials [33–35], the fixation of N₂ with Al₃O₃ requires a carbonaceous reducing agent and technically challenging temperatures above 1700 °C. [29,35,36]. Certain transition-metal redox materials such as Cr-based nitrides have been shown to circumvent the need for a solid reducing agent and allow one to regenerate the nitride below 1500 °C, but at the expense of lower extents of nitrogen fixation and ammonia evolution [28–30].

Only few metals accomplish the trade-off between thermodynamically stable formation of a metal nitride from N₂ that gives NH₃ upon hydrolysis [29,31,32] and formation of only intermediately stable metal oxides that can be recycled at moderate process conditions [28,29]. This is in analogy to the Sabatier principle in heterogeneous catalysis [37] that describes the ideal catalytic activity of a material as a function of an intermediately strong bond formed between the catalyst surface and key reaction intermediates [18,24]. As a starting point, we have chosen Mo and Mn as primary metals for the development of advanced metal nitride redox materials. However, while both metals exhibit promising characteristics, Mo binds nitrogen slightly too weakly leading to relatively low nitride and NH₃ yields [29,31] and Mn binds nitrogen somewhat too strongly leading to the formation of relatively stable metal oxides owing to the correlated stability of metal nitrides and metal oxides [38].

Here, we employ electronic structure computations to show how the bonding of nitrogen in the solid state can be controlled via doping with transition metals. Such novel theory-assisted design is analogous to the rational design of metal oxide redox materials [39–41], where reactivity is controlled by the oxygen vacancy formation energy [39,40]. To verify the concept, we experimentally demonstrate controlling nitrogen vacancy formation in manganese-based redox materials. Finally, we rationalize the trends in the Gibbs free energy of the nitrogen vacancy formation at the charge density distribution in the ternary metal nitrides and the d-band centre, a quantitative descriptor for the theory-based design of advanced metal nitride redox materials for sustainable solar-derived ammonia.

This work is at the interface of fundamental physical science of redox materials and chemical engineering to store solar energy as ammonia. The ultimate vision of this work is a device that converts nitrogen from air, water and sunlight, at ambient pressure and without electricity, into ammonia and oxygen. Such a device would facilitate the production of NH₃ fuel, as an alternative to carbon-based fuels derived from solar-driven CO₂ and H₂O splitting. Ammonia fertilizer for food and biofuels could be produced without the infrastructure for supplying natural gas or coal and the know-how and technology for the high-pressure operations employed globally for the production of synthetic NH₃. A global project on artificial photosynthesis, as is contemplated in this themed issue [42,43], could raise the public profile of this field and may assist in funding the development of solar-driven NH₃ through governmental, private and corporate contributions. Although solar-derived NH₃ may be economically more attractive in certain geographically, economically or politically isolated regions than NH₃ from large-scale Haber–Bosch plants, accounting for ethical implications, such as diminished environmental impacts when avoiding the dependence on fossil fuel feedstock, may make solar-derived NH₃ economically competitive with NH₃ from Haber–Bosch plants. In this sense, solar-driven N₂ reduction is equivalent to solar-driven CO₂ reduction and H₂O splitting, the central reactions of ‘synthetic photosynthesis’ for an efficient production of solar fuel and food as well as acquisition of knowledge: ethically, they are common heritage of humanity and should not be fully owned by profit-focused private interests. The mild process conditions of solar-derived ammonia will allow implementation in parts of the world that may lack the infrastructure for a highly complex high-pressure catalytic process like the Haber–Bosch-based approach to ammonia. Ideally, global synthetic photosynthesis should be held on trust for humanity and its ecosystems and should be employed through a politically and economically neutral agency [43]. As verbalized at the Royal Society’s meeting discussing a global artificial photosynthesis project at Chicheley Hall in 2014: ‘Our goal is to work cooperatively and with
respect for basic ethical principles to produce the scientific breakthroughs that allow development and deployment of an affordable, equitably accessed, economically and environmentally sustainable, non-polluting global energy and food system that also contributes positively to our biosphere.

2. Material and methods

2.1. Thermochemical equilibrium calculations

To quantify the potential of binary transition-metal nitride redox materials for a solar-driven ammonia synthesis, the thermochemical equilibrium of the redox cycle was analysed for Mo- and Mn-based bulk metal nitrides at 1 bar and as a function of temperature from tabulated free energy data [38]. We note negative free energy differences mark exergonic reactions.

2.2. Electronic structure calculations

To quantify the effect of doping on the nitrogen vacancy formation energetics in transition-metal nitrides, cubic γ-Mo2N and hexagonal ζ-Mn2N were modelled via density functional theory, performed with the grid-based projector-augmented wave (GPAW) code [44,45]. Exchange-correlation interactions were treated by the revised Perdew–Burke–Ernzerhof (RPBE) functional of Hammer et al. [46] and atomic configurations were handled in the atomic simulation environment (ASE) [47] (both ASE and GPAW are open-source code available from the Department of Physics at the Technical University of Denmark and are available at https://wiki.fysik.dtu.dk/ase/ and https://wiki.fysik.dtu.dk/gpaw/). Mo2N and Mn2N were modelled with four and eight metal atoms, respectively, and the stoichiometric amount of nitrogen occupying half of the octahedral interstitial sites. The bulk structures had periodic boundary conditions in all directions and were modelled with a k-point sampling of \( 4 \times 4 \times 4 \). The corresponding D\(_0\) for Mo\(_2\)N and D\(_0\) for Mn\(_2\)N ternary metal nitride models were created via replacing one of the parent metal atoms in each model with a dopant, D = Sc, Ti, V, Cr, Mo, Mn, Fe, Co, Ni, Cu or Zn, where all compositions containing Mn, Fe, Co, or Ni were modelled with spin-polarized calculations. The free energy of forming nitrogen vacancies in the bulk was determined as the difference in the total electronic energy of the metal nitride with nitrogen vacancies (50% and 25% relative to the stoichiometric composition of Mo2N and Mn2N, respectively) and the stoichiometric metal nitride plus the chemical potential of N\(_2\) in the gas phase. The value was converted to free energy at 25°C and 1 bar using standard statistical mechanical equations evaluated through ASE. The partial charge density was determined for all metal nitride models via Bader decomposition [48]. Computational details are given in the electronic supplementary material.

2.3. \( \text{N}_2 \) reduction

The effect of doping Mo- and Mn-based redox materials with Cr and Fe on the stability of the metal nitrides formed by Mo and Mn, respectively, was studied by reacting approximately 0.75–2.00 g Cr, Mn, Fe, Mo or equimolar Mo/Fe and Mn/Fe metal powder mixtures with \( \text{N}_2 \). The metal powder was placed into a quartz boat and heated with a tube furnace (HTF55347C furnace, CC58434C temperature controller, Lindberg/Blue) for 0.5, 5, 10, 30 and 120 min (all samples) and 60, 90 and 240 min (samples containing Mn) at 750°C in 1.86 L\(_{\text{STP}}\) \( \text{N}_2 \) min\(^{-1}\) (all samples) and 1.86 L\(_{\text{STP}}\) \( \text{N}_2 \) min\(^{-1}\) diluted with 0.47 L\(_{\text{STP}}\) \( \text{H}_2 \) min\(^{-1}\) (samples containing Mo or Cr). All metals (99.8% pure Cr, 99.9% Mn, 99.9% Fe and 99.95% Mo, from Noah Technologies, minor impurity levels are specified in electronic supplementary material) were 325 mesh and had comparable average particle diameters and specific BET surface areas, as shown in the electronic supplementary material. All gases were of UHP zero grade (Linweld). This article discusses the data for the \( \text{N}_2 \) reduction with Mn, Fe and Mn/Fe, whereas the data for Mo, Cr and Mo/Cr are given in the electronic supplementary material.

2.4. Solid-state analysis

The composition of the solids was quantified via powder X-ray diffraction using a MiniFlex II diffractometer (5–80° 29 range, Cu-target X-ray tube, 30 kV/15 mA output, diffracted beam monochromator, Rigaku). Scanning electron microscopy (SEM) was used (S-3500N scanning electron microscope, Hitachi, 20 kV) to determine the average particle diameter and energy-dispersive X-ray spectroscopy (Nova NanoSEM 430, FEI Company, 5–15 kV, beam deceleration, high stability Schottky field emission gun, and Oxford X-Max Large Area Analytical silicon drift detector) was used to map the distribution of metal dopant and nitrogen at the surface. All reactants and products were weighed (AE260 DeltaRange balance, Mettler) and the specific BET surface area was analysed by NanoScale Inc., Manhattan, KS.

3. Results and discussion

3.1. Controlling the nitrogen vacancy formation in transition-metal nitrides

To drive a two-step ammonia synthesis with concentrated solar energy and to facilitate the use of water as hydrogen source for the \( \text{NH}_3 \) evolution, this section outlines the process conditions of a solar– thermochemical ammonia synthesis with metal nitride redox materials. We start our analysis with thermochemical equilibrium calculations for Mn\(_2\)N\(_2\) and Mo\(_2\)N, metal nitrides that facilitate the trade-off between high \( \text{NH}_3 \) yields on one side and high \( \text{N}_2 \) reduction yields on the other side. Thereafter, we establish a rationale for how to further improve this trade-off via doping metal nitrides with transition metals.

Figure 1a shows the thermodynamic equilibrium for the oxidation of Mn\(_2\)N\(_2\) with water at 1 bar yielding MnO, \( \text{NH}_3 \) and the balance \( \text{H}_2 \). As indicated with the shaded area, the reaction is exergonic—that is thermodynamically favouring the formation of the reaction products—over the entire examined temperature range. We note that forming \( \text{NH}_3 \) at elevated temperatures and 1 bar requires the need to quickly remove \( \text{NH}_3 \) from the reactor to thereby avoid its decomposition into \( \text{N}_2 \) and \( \text{H}_2 \) above 180°C at thermodynamic equilibrium [19,29]. The oxygen can be abstracted from the formed MnO in a second step above 1230°C (below the melting point of Mn) using by-produced \( \text{H}_2 \) as reducing agent and ensuring that the partial pressure of water, p\( \text{H}_2\text{O} \), is below 1.5 \times 10\(^{-4}\) bar. This endothermic reaction can be driven with concentrated solar radiation and stores the chemical potential in the redox material that is employed for the subsequent reduction of \( \text{N}_2 \) at 1 bar yielding Mn\(_2\)N\(_2\) below 1060°C. Figure 1b shows that the composition of the metal nitride allows one to alter these reaction conditions: with Mo\(_2\)N the \( \text{NH}_3 \) evolution and the \( \text{N}_2 \) reduction are both limited at 1 bar to temperatures below 640°C and 700°C, respectively. However, the reduction of the formed MoO\(_2\) can be achieved more facilely with CO as reducing agent (e.g. from gasified biomass) at above 730°C and below 4.0 \times 10\(^{-3}\) bar p\( \text{CO}_2 \). We note the ideal temperature
for the reduction of MoO$_2$ with CO depends also on the vapour pressure of the molybdenum oxides that are formed during the NH$_3$ evolution and the tendency for undesirable carbon deposition in the reactor.

The ideal metal nitride composition would confer thermochemical properties to the redox material for a solar-driven NH$_3$ synthesis that lie between those of Mn$_5$N$_2$ and Mo$_2$N. Ideally, the metal nitride should be slightly more stable than Mo$_2$N—to fix more nitrogen above 700°C—whereas the metal oxide should be less stable than MnO—to avoid the need for temperatures above 1200°C and the means to establish low partial pressures of H$_2$O or CO$_2$, respectively. Similar to the possibility to control the adsorption energy of adsorbates at surfaces by altering the surface composition [18,24,37], doping bulk metal nitrides with transition metals may diminish or augment the formation of the metal nitride [49]. However, no rationale exists yet that describes how to compose metal nitrides to control the stability of the lattice nitrogen.

To establish trends in the effect of doping transition-metal nitrides on the bonding of the lattice nitrogen, we compute the free energy of the nitrogen vacancy formation across 22 metal nitride compositions. We hypothesize that negative free energies of the nitrogen vacancy formation correlate with metal nitride compositions that spontaneously liberate lattice nitrogen (in the form of NH$_3$ if a hydrogen source such as H$_2$ or H$_2$O is present) and that less readily form lattice nitrogen from N$_2$, and vice versa. Figure 2 plots the free energy of the nitrogen vacancy formation in Mn$_2$N bulk (i.e. the ζ-phase manganese nitride with a broad stoichiometry that includes Mn$_3$N$_2$ and Mn$_4$N$_{2.58}$) [50] doped with a transition metal versus the number of d-electrons in the ground state of the dopant. Figure 2 shows that all tested dopants decrease the stability of the lattice nitrogen, relative to the value for undoped Mn$_2$N, which is shown with a solid line. As a general trend, a high occupancy of the dopant d-states correlates with a high unstability of the lattice nitrogen. In other words, filling the metal d-states of the metal nitride decreases the bonding strength of the lattice nitrogen. We note Zn$_{0.25}$Mn$_{1.75}$N shows the largest deviation from this trend, which is discussed in §3.3. Figure 3 shows the equivalent analysis for Mo$_2$N. The steeper slope of the linear correlation for Mo$_2$N, i.e. $-0.162$ eV for Mo$_2$N versus $-0.072$ eV for Mn$_2$N, suggests that the stability of the lattice nitrogen in doped Mo$_2$N is significantly more sensitive to the occupancy of the d-states than the stability of the lattice nitrogen in doped Mn$_2$N. In summary, the formation and consumption of nitrogen vacancies in transition-metal nitrides can be controlled with the occupancy of the metal d-states. Aiming at the design of metal nitride redox materials, we suggest the relatively strong bonding of nitrogen in Mn$_2$N may be diminished via doping with metals such as Fe, whereas the relatively weak binding of nitrogen in Mo$_2$N may be augmented via doping with metals such as Cr.

### 3.2. N$_2$ reduction with Fe-doped Mn

To test the predicted weakening of the nitrogen bonding in manganese nitride when doping with late transition metals, this section evaluates trends in the formation of manganese
nitrides and iron nitrides from manganese, iron, an equimolar mixture of both metals and N₂ at 1 bar and 750 °C. Figure 4 shows the formation of Mn₄N and Mn₆N₂.58 (which is equivalent to Mn₅N₂ and Mn₂N discussed in §3.1) [50] as a function of time. Mn fixes N₂ quickly, yielding about 85 mol% Mn₄N after 30 min. Thereafter, the yield of Mn₄N decreases, whereas the yield of the additional Mn₆N₂.58 phase increases to 85 mol% Mn₆N₂.58 after 240 min, indicating that the nitride with increased nitrogen content is formed via nitridation of the nitride with lower nitrogen content. We note the formation of these two manganese nitride phases is as predicted by the Mn–N phase diagram [51], whereas the γ and ζ phases with higher nitrogen content [50] are unstable at 750 °C [51]. Furthermore, the transformation of the ε phase via nitridation into the ζ phase is expected [51] and analogous to the formation of related interstitial nitrides, such as CrN.

Figure 4. Kinetics of N₂ reduction: reaction yield in mol% of the indicated metal nitride formed relative to a stoichiometric conversion of Mn at 750 °C with (a) Mn and (b) Fe-doped Mn forming Mn₄N (light orange symbols) and Mn₆N₂.58 (dark blue symbols). Error propagation within a 95% CI (error bars) yields in average ± 17.81%. Solid lines are kinetic models limited by solid-state diffusion that are fitted to the data at 5–30 min for Mn₄N and 60–240 min for Mn₆N₂.58. (Online version in colour.)

from CrN [28]. Details of the crystal phases and physical characteristics of the redox materials are given in the electronic supplementary material, table S1. In the presence of Fe, as
shown with figure 4h, the quick formation of Mn$_3$N levels after 30 min at approximately 64 mol% and the subsequent formation of Mn$_6$N$_{2.58}$ reaches only 29 mol% after 240 min. That is, Mn fixes about 0.24–0.28 mol nitrogen per mol Mn after 60–240 min in the presence of Fe, which is about 66–74% of 0.32–0.40 mol nitrogen fixed per mol Mn in the absence of Fe. This indicates that Fe destabilizes the lattice nitrogen in manganese nitrides. Assessing whether or not the dopant affects the diffusion kinetics of the nitrogen vacancies as well requires further studies.

While Fe appears to destabilize the bond that is formed between Mn and the lattice nitrogen, Mn stabilizes the formation of iron nitrides that are thermodynamically unstable in the absence of Mn, as shown in figure 5. As expected [38], Fe does not reduce N$_2$ at 1 bar and 750°C. However, in the presence of Mn, some nitrogen appears to intercalate into the Fe lattice yielding up to 54 mol% of a cubic FeN$_{0.0324}$ phase after 240 min. In conclusion, iron appears to diminish the formation of manganese nitrides—as predicted with figure 2—whereas manganese augments the formation of iron nitrides—in agreement with the lower occupancy of the d-states in Mn versus Fe, as discussed in §3.1.

We note while the preparation and cycling of ternary metal nitrides [25–27] or nanocomposites would provide the possibility to quantify the effect of the dopant on the bond energy of the lattice nitrogen, the discussed data for metal powders and metal powder mixtures confirm the trends in the stability of transition-metal nitrides predicted via electronic structure theory. To visualize the morphology of the metal nitrides employed in this work, figure 6 shows SEM images of cubic Mn$_3$N (up to 84.6 mol%), mostly cubic Mo and tetragonal Mo$_2$N (up to 21.1 mol%) and a powder mixture of mostly trigonal Cr$_3$N, cubic Mo and some cubic CrN and tetragonal Mo$_2$N. Details are given in the electronic supplementary material. The X-ray emission map of the metal powder mixture shows that the parent metal, Mo, and the metal dopant, Cr, are closely located in some regions. We suggest that these are the domains where the bonding of the lattice nitrogen is affected by both metals, whereas in other domains of the metal mixture, the bonding of nitrogen is dominated by the presence of one metal only. We note while Cr increases the fraction of nitrogen fixed by Mo, as shown in the electronic supplementary material, figure S2, the amount of nitrogen fixed by Mo is still below that fixed by Cr, as shown in figure 6c by the inhomogeneous distribution of nitrogen mostly located with Cr. The Cr dopant appears to support the nitridation of Mo with N$_2$ into Mo$_2$N, presumably owing to reduction of molybdenum oxides at the surface (discussed in the electronic supplementary material) and owing to stronger binding of the lattice nitrogen (such as discussed above for the formation of iron nitrides).

From a practical perspective, an optimized metal nitride redox material should provide a high specific surface area for the formation and consumption of nitrogen vacancies, either via a porous structure [52], similar to the structure of advanced metal oxide redox materials [53], or in the form of a porous particle bed [54]. As a starting point, we have computed the apparent nitrogen diffusion constants at 750°C (see details in the electronic supplementary material) with 7.77 × 10^{-9} cm$^2$ s$^{-1}$ for the formation of Mn$_6$N$_{2.58}$ and 3.07 × 10^{-11} cm$^2$ s$^{-1}$ for the formation of Mo$_2$N. These values compare well with those reported previously, i.e. 3.07 × 10^{-9} cm$^2$ s$^{-1}$ for the Cr-manganese nitride phase at 890°C [55] and 5 × 10^{-10} to 3 × 10^{-14} cm$^2$ s$^{-1}$ for Mo$_2$N at 600–750°C [56,57]. Comparing these values for a presumably interstitial nitrogen diffusion process [56] with the diffusion constants for nitrogen vacancy diffusion in good anion conductors, such as 2 × 10^{-11} cm$^2$ s$^{-1}$ at 700°C in nitrogen-doped yttria-stabilized zirconia [58], indicates that transition-metal nitrides are promising materials for the fixation of N$_2$. Owing to the higher fraction of fixed nitrogen per metal and the higher diffusion constant, manganese nitrides might be ideal starting materials for the development of advanced metal nitride redox materials for a solar-driven low-pressure ammonia synthesis.

### 3.3. Electronic structure descriptors

To understand how doping controls the formation and consumption of nitrogen vacancies in transition-metal nitrides, this section discusses trends in the electronic structure of doped Mn$_3$N and doped Mo$_2$N. We find that the stability of the lattice nitrogen in these materials can be predicted with the average energy of the metal d-states of the dopant and the quantity and geometry of partially localized electronic charge. Employing these trends for the computational screening [3,59] of advanced metal nitride redox materials is outlined.

Figure 7a decomposes the electronic interaction of the metal dopant, as an example for doped Mo$_2$N, into the metal-projected s-, p- and d-orbitals. Figure 7 identifies continuous filling of the d-states and emptying of s- and p-states when moving the dopant from the left to the right in the periodic table. These trends correlate with a decreasing stability of the lattice nitrogen, as shown in figure 7b,c. Figure 7b employs...
the d-band centre—that is the central moment of the dopant d-band—as a descriptor for the electronic structure trends in transition-metal-doped metal nitrides. This metric has been used successfully for describing adsorption energy trends at transition-metal surfaces which, in turn, has revolutionized the high-throughput screening of advanced catalysts [60]. As a general trend, the positive slope of the correlation shown with figure 7b identifies the anti-bonding character of the dopant d-states, whereas the negative slope of the two correlations shown with figure 7c identifies the bonding contribution of the dopant s- and p-states to the bonding of the lattice nitrogen. However, while the d-band centre yields a linear correlation with predictive value, the correlation of the p- and, in particular, the s-band centre is rather qualitative. Essentially, only the values for the Zn dopant deviate from the d-band centre correlation owing to the stable configuration of the completely filled Zn d-states, as discussed in the electronic supplementary material.

To understand the difference in the sensitivity of the scaling between the free energy of the nitrogen vacancy formation and the number of electrons in the dopant d-states, which is shown in figures 2 and 3, we compute the partial charge localized at the lattice nitrogen, respectively. Generally, a high amount of net-positive charge localized at the dopant and a high amount of net-negative charge localized at the lattice nitrogen correlate with stable lattice nitrogen. The steeper slope of scaling of the free energy of the nitrogen vacancy formation with the partial dopant charge for $D_{0.5Mo1.5N}$ versus $D_{0.25Mn1.75N}$ suggests that the dopant donates nearly the same amount of charge in both materials which, however, has a stronger effect on the bonding of the lattice nitrogen in $D_{0.5Mo1.5N}$ relative to $D_{0.25Mn1.75N}$. The larger increase or decrease of charge density at the lattice nitrogen when doping $D_{0.5Mo1.5N}$ versus $D_{0.25Mn1.75N}$, shown in figure 8b, appears owing to the dopant concentration in the metal nitride.

Doping Mo2N with twice the amount of metal, compared with Mn2N, yields nearly twice the amount of charge density.
change in average at the lattice nitrogen, relative to the undoped metal nitride. Previous studies have suggested that the bonding of nitrogen in metal nitrides can be controlled via metal doping [49]. The trends discussed here indicate that the stability of the lattice nitrogen in transition-metal nitrides can be controlled with the type and the amount of a metal dopant owing to the anti-bonding character of the dopant d-states as well as owing to the amount of charge density transferred to the lattice nitrogen.

Comparable to the trends in the quantity of the charge density transfer, forming nitrogen vacancies in ternary metal nitrides shows also trends in the geometry of the charge distribution. Figure 9a analyses changes in the charge density owing to the formation of nitrogen vacancies in Mo$_2$N. Darker-shaded areas mark regions with accumulated charge (charge sinks), whereas lighter areas mark regions from which charge is withdrawn (charge sources). As shown schematically in figure 9b, the stability trends of the lattice nitrogen can be understood from attractive and repulsive electronic interactions between charge density sinks and sources.

In detail, doping Mo$_2$N with Sc or Ti results in stronger binding of the lattice nitrogen compared with no doping, as shown with figure 3. For these dopants, the charge density difference near the dopant exhibits four 3d lobes that are nearly equally pronounced. For the V, Cr and Mo dopants, the binding of the lattice nitrogen decreases while the charge density starts to accumulate at the dopant, next to the lattice nitrogen. When doping with Mn, Fe, Co and Ni the binding of the lattice nitrogen decreases further while charge density also accumulates at the lattice nitrogen. This suggests that the weaker binding of the lattice nitrogen is due electronic repulsion between two charge sinks. This also explains why the binding of the lattice nitrogen does not decrease further when further increasing the occupancy of the dopant d-states, i.e. when doping with Cu and Zn. For the Cu dopant, the spatial polarization of the charge density difference at the dopant weakens while it nearly changes its polarization for the Zn dopant, which appears to cancel the repulsion between two charge sinks. This correlates with an increase in the stability of the lattice nitrogen in Mo$_2$N when doping with Zn.

Further details of this analysis are given in the electronic supplementary material, showing the charge density differences owing to doping in Mn$_2$N.

4. Conclusion

Complementing the production of solar fuels and chemicals via synthetic photosynthesis, NH$_3$ fertilizer from solar-driven N$_2$ and H$_2$O splitting could aid in the global and decentralized production of solar-derived food and biofuels. Renewable NH$_3$ fuel might be an attractive alternative to carbon-based fuels derived from solar-powered CO$_2$ and H$_2$O splitting, the central reactions of synthetic photosynthesis. In this sense, this work contributes with novel design principles for metal nitride redox materials to the development of a global project on artificial photosynthesis which, in turn, could raise the public profile of this field and may assist in funding the development of solar ammonia production.

Here, we have outlined the process conditions required to produce NH$_3$ from H$_2$O and N$_2$ with a metal nitride redox material and concentrated solar radiation at ambient pressure. This can be achieved with Mo$_2$N that is oxidized with H$_2$O at approximately 500°C and recycled from the formed MoO$_2$. ~

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**Figure 9.** (a) Charge density differences (in units of the elementary charge per Å$^2$) owing to the formation of nitrogen vacancies in D$_{2h}$Mo$_2$N (shown at the height of the nitrogen nucleus). The first panel in the first row is a schematic of the metal nitride crystal geometry with solid and dashed circles marking atoms in the upper and lower plane of the bulk models, respectively. The first panel in the first row is a schematic of the metal nitride crystal geometry with solid and dashed circles marking atoms in the upper and lower plane of the bulk models, respectively. (b) A schematic of the correlation between the nitrogen binding strength and the charge density and location near the nitrogen vacancy. M, V and D mark the parent metal, the nitrogen vacancy and the dopant, whereas a ‘×’ mark the accumulation of positive or negative charge, respectively. (Online version in colour.)
with $N_2/CO$ at 750°C and below $4.0 \times 10^{-1}$ bar $p_{CO_2}$. As an alternative, $NH_3$ can be formed with $Mn_3N_2$ that is oxidized with $H_2O$ at or above 500°C and recycled from the formed $MoN$ with $N_2/HzO$ at 1000–1230°C and below $1.5 \times 10^{-5}$ bar $p_{H_2O}$. Owing to the intermediate thermochromical stability of $MnN_2$ and $MoN$, the fast formation kinetics of $MnN_2$ and relative fast apparent solid-state diffusion of nitrogen in $MnN_{2.56}$, manganese nitride was identified as an ideal candidate for the development of ternary metal redox materials. To further decrease the correlated stability of the metal oxide, the design of ternary manganese-based metal nitrides focuses on destabilizing the lattice nitrogen. We have employed electronic structure theory to show that the stability of the lattice nitrogen in transition metal nitrides can be increased or decreased to a desirable process-and-redox material-dependent value via doping with transition metals. This was verified experimentally for manganese nitride doped with iron. The electronic structure trends of transition-metal nitrides suggest that nitrogen bonding is destabilized with an increasing occupancy of the anti-bonding dopant $d$-states.

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**References**


