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Chemical looping of metal nitride catalysts: low-pressure ammonia synthesis for energy storage†

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The activity of many heterogeneous catalysts is limited by strong correlations between activation energies and adsorption energies of reaction intermediates. Although the reaction is thermodynamically favourable at ambient temperature and pressure, the catalytic synthesis of ammonia (NH₃), a fertilizer and chemical fuel, from N₂ and H₂ requires some of the most extreme conditions of the chemical industry. We demonstrate how ammonia can be produced at ambient pressure from air, water, and concentrated sunlight as renewable source of process heat *via* nitrogen reduction with a looped metal nitride, followed by separate hydrogenation of the lattice nitrogen into ammonia. Separating ammonia synthesis into two reaction steps introduces an additional degree of freedom when designing catalysts with desirable activation and adsorption energies. We discuss the hydrogenation of alkali and alkaline earth metal nitrides and the reduction of transition metal nitrides to outline a promoting role of lattice hydrogen in ammonia evolution. This is rationalized *via* electronic structure calculations with the activity of nitrogen vacancies controlling the redox-intercalation of hydrogen and the formation and hydrogenation of adsorbed nitrogen species. The predicted trends are confirmed experimentally with evolution of 56.3, 80.7, and 128 μmol NH₃ per mol metal per min at 1 bar and above 550 °C *via* reduction of Mn₆N_{2.58} to Mn₄N and hydrogenation of Ca₃N₂ and Sr₂N to Ca₂NH and SrH₂, respectively.

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1. Introduction

Ammonia is one of the most important synthetic chemicals in today's economy. With an annual production of about 162 million metric tons,¹ NH₃ is irreplaceable as a fertilizer, responsible for growing the food for approximately half of the world's population.^{2,3} However, the catalytic synthesis of NH₃ from N₂ and H₂ is realized at some of the most severe process conditions of the chemical industry, *i.e.*, about 300 bar and 400–500 °C (ref. 4 and 5) (the Haber–Bosch process), and consumes

energy at 28–166 GJ per ton NH₃ (ref. 1 and 5) in the form of natural gas, coal, or Naphtha;¹ this is 1–2% of the world's annual energy production.⁶ About 15% of these net energy requirements are consumed for the technologically sophisticated high-pressure operations alone.¹ The fossil-fuel dependence links food security to natural gas price fluctuations and results in net CO₂ emissions of 1.9 tons (H₂ generation *via* steam reforming of natural gas) to 16.7 tons (H₂ generation *via* partial oxidation of coal) per ton NH₃.¹ Economies of scale dictate the need for large facilities producing typically 1000–3000 tons NH₃ per day,¹ which requires a highly developed infrastructure for production and distribution.² The conceivable development of a catalyst for a low-pressure and low-temperature Haber–Bosch process could theoretically alleviate these conditions. Although thermodynamically favorable at ambient temperature and pressure, no catalyst has been found that establishes reasonable reaction rates at these conditions,⁷ which has been rationalized with the scaling of the activation energy for the N₂ dissociation and the adsorption energy of nitrogen at the catalyst surface.^{7–9}

Beyond its irreplaceable use in agriculture, the use of NH₃ as a fuel is an attractive proposition since it is easily liquefied, rendering it a stable one-way hydrogen carrier and one of the most energy-dense zero-carbon fuels^{10,11} that can be used as a direct substitute for fossil fuels in internal combustion engines.¹² This, and the prospect of zero-CO₂-emission vehicles, have motivated the development of the “AmVeh” car prototype

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† Electronic supplementary information (ESI) available: Experimental and computational details, free energy plots for the NH₃ evolution and N₂ reduction with Co₃N/Co, Fe₄N/Fe, Mn₅N₂/Mn₄N, Mo₂N/Mo, CrN/Cr₂N, TaN/Ta₂N, NbN/Nb₂N, Li₃N/LiH, Ba₃N₂/BaH₂, Sr₃N₂/SrH₂, and Ca₃N₂/CaH₂, surface oxidation energetics, Δ*G*_{vac}[NH₃^{*}, yH^{*}] based on gas phase H₂ as hydrogen source, NH₃ evolution with Fe-doped Mn₄N, NH₃ evolution with Mn₆N_{2.58}, Ca₃N₂ and Sr₂N after correcting for partial nitride hydrolysis, NH₃ yield from Ca₃N₂ *vs.* time and H₂ gas flow rate. See DOI: 10.1039/c5sc00789e

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fueled by a 70% NH_3 /30% gasoline blend.¹³ Current combustion research is focused on increasing the energy substitution by NH_3 and improving the exhaust treatment for removing uncombusted NH_3 .^{13,14} Additionally, NH_3 can be used in alkaline fuel cells that decompose NH_3 into N_2 and H_2 fuel¹⁵ for direct electricity generation.¹⁶ The development of the electrocatalysts and the cell design are currently limiting the costs and efficiency of this technology.¹⁶ The synthesis of ammonia as a “solar fuel”,¹⁷ could conceivably be deployed beginning with the electrolysis of water with photovoltaic electricity¹⁸ (the generated H_2 , however, would require massive investments into infrastructure for compression, storage and transport, hindering its direct use). Instead, H_2 could be employed for the synthesis of more practical liquid ammonia-based fuels *via* the conventional Haber–Bosch process. However, this technology requires sophisticated multi-step high-pressure and high-temperature unit operations and high-value electricity to operate these units due to the limited activity of the employed heterogeneous catalysts.^{1,2,19}

One proposed means to circumvent the high-pressure and high-temperature requirements of the Haber–Bosch process is the electrochemical reduction of N_2 to synthesize NH_3 with solar-derived photovoltaic electricity at ambient pressure and temperature.^{20–22} NH_3 evolution at the cathode becomes thermodynamically favorable at an equilibrium potential of 0.1 V *vs.* the reversible hydrogen electrode, RHE,^{20,21} and electronic structure calculations have suggested materials may be found that would liberate NH_3 at about -0.5 V *vs.* RHE.^{21,23,24} However, no suitable electrocatalyst has been identified experimentally for these potentials – the observed rates of NH_3 evolution are low and the best reported Faradaic efficiencies are in the order of 0.2–2%,^{20,25} while more negative (stronger) potentials decrease the Faradaic efficiency further due to the competing hydrogen evolution reaction.

This article introduces an alternative approach: splitting of a catalytic reaction into two separate reaction steps that are facilitated with a looped metal compound catalyst. We demonstrate this approach with looped metal nitride catalysts for solar-driven low-pressure synthesis of ammonia. Solar-driven thermochemical N_2 reduction could circumvent the high-pressure requirements of the Haber–Bosch process and the energetic deficiencies of the electrochemical N_2 reduction. This approach separates the NH_3 synthesis into two reaction steps:^{26–29} first, N_2 is reduced, typically, with a metal oxide and concentrated sunlight at elevated temperatures yielding a metal nitride. In a second step, the metal nitride is oxidized with H_2O to yield NH_3 and the restored metal oxide at lower temperatures. On paper, the optimization of the reactive materials^{30,31} and of the solar radiation receiver-reactor technology³² could allow us to approach solar-to-fuel energy conversion efficiencies of 70–75%, for solar radiation concentrated 5000-fold to 800–1500 °C.³³ However, while NH_3 can be formed at 1 bar and 200–500 °C by the oxidation of certain metal nitrides with H_2O ,^{27,34,35} recycling the metal oxide requires either a chemical reducing agent, such as biomass and/or syngas, or temperatures above 1500 °C.^{26–29}

We propose production of NH_3 and O_2 from H_2O and N_2 , without a sacrificial reducing agent and at moderate

temperatures, *via* solar-driven cleavage of H_2O into H_2 and O_2 (ref. 30 and 31) and subsequent fixation and hydrogenation of N_2 with H_2 into NH_3 at 1 bar and up to 800 °C using a looped metal nitride catalyst and concentrated solar energy. Looped metal nitrides may decouple scaling of the nitrogen adsorption energy with the activation energy for N_2 dissociation that typically limits the activity of Haber–Bosch catalysts,⁷ since the chemical potential of a metal nitride can be utilized in a low-temperature oxidation liberating NH_3 , while N_2 can be reduced *via* recycling the metal nitride at elevated temperatures. At the process scale, this approach does neither require electricity for NH_3 formation nor the infrastructure for supplying natural gas or coal and the know-how and technology for high-pressure operations. As indicated by our previous net-present value analysis of solar-driven NH_3 synthesis *via* metal nitride hydrolysis,²⁶ such a process can be economically more attractive in geographically, economically, or politically isolated regions than NH_3 from large-scale Haber–Bosch plants.

In a broader context, looped nitride catalysis is analogous to looped oxide catalysis with reduced metal oxides that provide oxygen vacancies for the abstraction of oxygen from, for instance, bio-oils upgraded with H_2 into hydrocarbons.³⁶ Looped nitride catalysts provide active lattice nitrogen that is converted with H_2 into NH_3 and nitrogen vacancies, with ideally high selectivity for NH_3 and no formation of N_2 and N_2H_4 . This is in contrast to the activity of redox materials, for instance, for solar-driven splitting of CO_2 and H_2O with total selectivity for CO , H_2 , and O_2 .^{33,37} In turn, established computational tools for the rational design of heterogeneous catalysts and electrocatalysts, such as free energy minimization to determine reaction paths,^{38,39} can be utilized to develop reducible metal nitride catalysts. In the following two Sections we employ electronic structure theory to determine and describe limiting reaction energetics for metal nitrides. Comparable to chemical looping applications, the oxygen vacancies of a looped oxide may be regenerated at high temperatures with concentrated solar energy, while the nitrogen vacancies of a looped nitride are refilled *via* solar-driven N_2 reduction. While we discuss trends in the bond strength of nitrogen adsorbates and lattice nitrogen, the presented principles are expected to apply analogously to the bond strength of oxygen, that governs the adsorption of oxygen at electrocatalysts for the oxygen reduction and evolution reactions (ORR/OER),^{40,41} the reversible oxygen vacancy formation at metal oxide surfaces for selective deoxygenation,⁴² and the oxygen exchange capacity of metal oxide redox materials for solar-driven CO_2 and H_2O splitting.^{31,33,37,43} The discussed metal nitrides form a bridge between materials with weak metal–nitrogen bonds for nitrogen activation^{44–46} and materials with strong metal–nitrogen bonds for hydrogen storage,^{10,11,47,48} such as certain Li-based compounds which may reversibly release H_2 at reasonable pressures and temperatures (*e.g.*, 0.4–20 bar and 195–285 °C for $\text{Li}_3\text{N}/\text{Li}_2\text{NH}$)⁴⁷ and that ideally do not liberate NH_3 .⁴⁹

In this article we suggest design principles – which we derive from both electronic structure calculations and experiments – that can inform the design of a metal nitride for solar-driven ammonia synthesis. Section 2.1 outlines the ammonia-



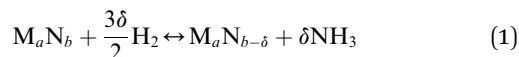
synthesis potential of metal nitrides that facilitate the incorporation of hydrogen into the bulk crystal lattice. This is rationalized in Section 2.2 *via* electronic structure calculations that describe how nitrogen vacancies control NH₃ evolution at the atomic scale. Sections 2.3 and 2.4 quantify the reaction kinetics of NH₃ evolution and experimentally demonstrate the augmented conversion of lattice nitrogen *via* hydrogenation of metal nitrides relative to the reduction of metal nitrides.

2. Results and discussion

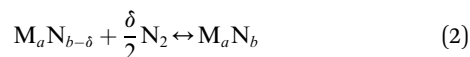
2.1 Thermochemical reactivity of metal nitride catalysts

We start by using literature data to provide basic reactivity principles for nitrides and to outline the pressure and temperature conditions of the proposed ammonia production *via* chemical looping of metal nitride catalysts. Similar to the Sabatier principle in catalysis,^{7,21,45} producing NH₃ from N₂ and H₂ *via* looping of a metal nitride catalyst should have an optimum stability of the metal–nitrogen bond. At one extreme, thermally unstable nitrides – such as Co₃Mo₃N, Ni₃N, Cu₃N and Zn₃N₂ – have been shown to yield much NH₃ *via* denitridation with H₂ at about 250–400 °C.^{44,46} However, the latter three materials are too unstable to be regenerated with N₂ at 1 bar⁴⁶ and a completely reversible recycling of Co₃Mo₃N from the formed Co₆Mo₆N requires long-time heating for 4 h in H₂/N₂.⁴⁴ On the other extreme, some more stable metal nitrides, when reacted with H₂, absorb hydrogen reversibly yielding mixtures of metal imide, amide and hydride (*e.g.*, Li₂NH, LiNH₂ and LiH from the reaction of Li₃N with H₂), rather than being selective to NH₃.^{47,48} These nitrides can liberate some NH₃ at elevated temperatures in the presence of H₂, *e.g.*, from LiNH₂ above 300 °C (*ref.* 47) and from Ca₃N₂ above 600 °C.⁵⁰ Ideally, an intermediate metal–nitrogen bond strength would balance these effects.

In principle, the reduction of a metal nitride yields NH₃ and a lower nitride phase:



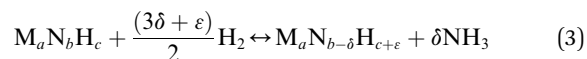
where M represents a metal, *a* and *b* are stoichiometric constants and δ is the amount of lattice nitrogen extracted. The cycle can be closed if the solid is regenerated with N₂:



Ideally, both reactions would have an exergonic region of temperature space, such that NH₃ is synthesized *via* a temperature-swing operation. Fig. 1A shows thermodynamic calculations of both reactions as functions of temperature for some representative systems. Unfortunately, none of these reactions exhibits this characteristic; instead, this figure generally identifies NH₃ evolution to be endergonic and N₂ reduction to be exergonic, except for Fe₄N and Co₃N (ESI[†]) with reversed reaction energetics. This can be understood due to the low thermal stability of Fe₄N and Co₃N.

To understand these trends, Fig. 2A shows the free energy of NH₃ evolution *vs.* the product of the number of d-electrons in the metal ground state, *N_d*, and the energy of these electrons, *E_d*. The analysis suggests increasing NH₃ evolution and decreasing stability of the metal–nitrogen bond with increasing occupancy of the d-states, which indicates their antibonding character. This phenomena is well known from the interaction of adsorbates at transition-metal surfaces.⁵² While we did not include Ni₃N, Cu₃N and Zn₃N₂ in this analysis due to limited thermodynamic data, the high NH₃ yields with these unstable metal nitrides⁴⁶ can be understood due to an even higher number of d-electrons, relative to Fe₄N. We suggest that the trade-off between NH₃ evolution and N₂ reduction may be optimized for doped transition-metal nitrides by targeting properties intermediate to those of Mn and Fe, that is, an *N_dE_d* of about –50 eV. Since the correlation of d-state occupancy and nitride reactivity is linked through the stability of the metal–nitrogen bond, for a ternary system *N_dE_d* may be defined in first approximation as the arithmetic average of the value for the metals that form metal–nitrogen bonds.

Instead, the yield of NH₃ could be increased with a material that facilitates exergonic NH₃ evolution *via* metal nitride oxidation at low temperatures and exergonic N₂ reduction at higher temperatures. We suggest that this can be achieved by partially substituting the lattice nitrogen with hydrogen, as we examine for the reaction:



where *c* is a stoichiometric constant and ε is the amount of incorporated lattice hydrogen. Fig. 1B shows an analogous plot for this reaction and suggests that the substitution of the nitrogen vacancies with hydrogen yields NH₃ exergonically at relatively low temperatures. The closing of the cycle:



now has a negative slope – making it exergonic at elevated temperatures – since the evolution of H₂ is entropically favored at elevated temperatures. This feature theoretically circumvents the limited activities of typical Haber–Bosch catalysts due to scaling of the adsorption energies of nitrogen-containing surface species and the activation energy for the N₂ dissociation. This may be achieved using a metal nitride that liberates NH₃ *via* oxidative hydrogenation with H₂ at relatively low temperatures. The chemical potential of the nitride is thereafter re-established *via* reductive N₂ dissociation at ambient pressure and moderately elevated temperatures. In these materials M is an alkali or alkaline earth metal, and thus we see a correlation with the bonding valence s-electrons in the metal ground state, shown with Fig. 2B. The data indicates that the average energy of the s-states, *i.e.*, the s-band center, can be employed as an approximate descriptor of the reactivity of complex metal nitrides that allow for hydrogen intercalation. We note the deviation of Li-based materials from the correlation of the alkaline earth metal-based compounds can be understood due to the alkali-nature of Li. Generally, such incorporation of





Fig. 1 Ammonia synthesis at 1 bar and up to 800 °C (computed from tabulated free energy data)⁵¹ via (A) metal nitride reduction with H₂ (eqn (1), dashed lines) and N₂ reduction with reduced metal nitrides (eqn (2), solid lines) and (B) metal nitride hydrogenation (eqn (3), dashed line) and N₂ reduction with metal hydrides (eqn (4), solid line). Shaded regions mark exergonic reactions. The equilibrium of NH₃ with 3/2H₂ and 1/2N₂ is shown as reference at 1 bar (dotted line; negative values corresponding to NH₃ evolution).

hydrogen into the solid is desirable for a solar-driven thermochemical ammonia synthesis as it enables lower temperature ammonia evolution.

2.2 Formation of nitrogen vacancies vs. lattice hydrogen

This Section uses electronic structure calculations to outline how nitrogen vacancies control the intercalation of hydrogen and the evolution of NH₃, focusing on the (0001) surfaces of Mn₂N and Sr₂N. To quantify the reactivity of these materials, Table 1 shows free energy changes for key vacancy and surface reactions. We can see a net-energy penalty for forming surface and bulk nitrogen vacancies that is by more than 1 eV higher for Sr₂N(0001) than for Mn₂N(0001). The energy penalty for the

nitrogen vacancy migration into the bulk, *i.e.*, $\Delta G_{\text{vac, bulk}} - \Delta G_{\text{vac}}$, is about equal. This suggests that the nitrogen vacancies of Sr₂N(0001) require more energy to be formed and are more reactive than those of Mn₂N(0001). This is a first indicator for the trend of surface adsorbates such as H* to fill vacancies. The strong hydrogen binding indicates that in the presence of H₂ both surfaces are expectedly covered with H*.

To understand the reaction mechanism of the lattice nitrogen with surface hydrogen, Fig. 3A and B show the energetics of forming 1/4 ML v_N at Mn₂N(0001) and Sr₂N(0001) yielding NH_x* ($x = 0, 1, 2$ or 3) from surface hydrogen (and partly H₂ gas, in cases where 1 ML H* does not supply enough hydrogen to yield a specific H*/NH_x* surface coverage). The analysis points out a few general trends: the conversion of

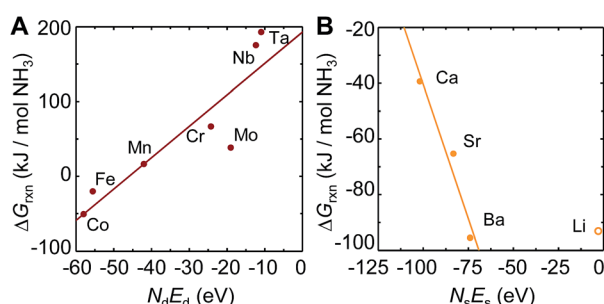


Fig. 2 Scaling of the free energy of the NH₃ evolution at 25 °C (computed from tabulated free energy data as described in Section 3.1) via metal nitride (A) reduction and (B) hydrogenation with the product of the number of electrons in the metal ground state, N , and the energy of these electrons, E , in the (A) d-states and (B) s-states. The metal marks the metallic constituent of the composition given with ESI.† Solid lines are fits to the data shown with solid symbols.

Table 1 Theoretical reactivity of the (0001) surface

Energy (eV)	Reaction ^a	Mn ₂ N	Sr ₂ N
ΔG_{vac}	$N_{\text{lat}}^{\text{s}} + \frac{3}{2} \text{H}_2 = v_{\text{N}}^{\text{s}} + \text{NH}_3$	0.50	1.52
$\Delta G_{\text{vac, bulk}}$	$N_{\text{lat}}^{\text{ss}} + \frac{3}{2} \text{H}_2 = v_{\text{N}}^{\text{ss}} + \text{NH}_3$	0.82	1.88
$\Delta G_{\text{ads}}[\text{H}^*]$	$* + \frac{1}{2} \text{H}_2 = \text{H}^*$	−0.79	−0.45
$\Delta G_{\text{ads}}[2\text{H}^*]^b$	$2* + \text{H}_2 = 2\text{H}^*$	−1.30	−1.10
$\Delta G_{\text{ads}}[\text{H}_2\text{O}^*]$	$* + \text{H}_2\text{O} = \text{H}_2\text{O}^*$	— ^c	−0.64
$\Delta G_{\text{ads}}[\text{OH}^*]$	$* + \text{H}_2\text{O} = \text{OH}^* + \frac{1}{2} \text{H}_2$	−1.47	−2.20
$\Delta G_{\text{ads}}[\text{OH}^*, \text{H}^*]$	$2* + \text{H}_2\text{O} = \text{OH}^* + \text{H}^*$	−1.81	−2.73

^a Lat, s, and ss mark the lattice nitrogen, surface and subsurface.

^b Dissociative hydrogen adsorption at increased surface coverage of 1/2 ML H*. ^c H₂O dissociated to OH* and H*.



Fig. 3 Free energy diagrams for (A and B) forming $1/4$ ML v_N yielding $1/4$ ML NH_x^* and (C and D) hydrogenating NH_{x-1}^* to NH_x^* and $y = 0$ (circles), $1/4$ (diamonds), $1/2$ (squares), and $3/4$ (triangles) ML H^* adatoms on (A and C) $Mn_2N(0001)$ and (B and D) $Sr_2N(0001)$ at $25^\circ C$ and 1 bar. Lines are a guide only. The shaded regions mark energetically favourable surface reactions.

lattice nitrogen into v_N and N^* is exergonic at $Mn_2N(0001)$ in the absence of H^* and increasingly complicated in the presence of an increasing H^* coverage. That is, H^* appears to act as a surface “poison” for the adsorption of N^* or NH^* at $Mn_2N(0001)$. Second, while $1/4$ ML N^* is not formed on $Sr_2N(0001)$ with $1/4$ ML v_N , which is independent of the H^* coverage (± 0.04 eV), the formation of v_N at $Sr_2N(0001)$ is more favorable if the lattice nitrogen yields NH^* or NH_2^* in presence of $1/2$ – $3/4$ ML H^* relative to 0 – $1/4$ ML H^* . That is, H^* prevents the filling of v_N at $Sr_2N(0001)$ by surface nitrogen. Such energetic promotion of the vacancy formation by H^* co-adsorbates is absent at $Mn_2N(0001)$ where H^* mostly hinders formation of NH_x^* with $x = 0, 1$ or 2 . We note the endergonic formation of NH_3^* that is stabilized by H^* at both surfaces indicates that the direct formation of $1/4$ ML NH_3^* from lattice nitrogen and $3/4$ ML H^* is unlikely. Furthermore, departures and “crossover” from these free energy trends are due to the source of the hydrogen and the rearrangement of adsorbates (ESI†).

Fig. 3C and D show the energy required to hydrogenate adsorbed nitrogen, which indicates a similar trend: the higher the degree of under-coordination of the adsorbed nitrogen at the surface the easier it is to hydrogenate the nitrogen, which involves breaking surface-nitrogen bonds. Fig. 4 shows that these bonds are favorably formed at three-fold metal sites with charge localization between the adsorbate and the nitrogen vacancy. This is opposed, for instance, to three clearly defined metal-carbon bonds for C^* adsorbates at $Mo_2C(001)$.⁹ The most notable exception from this trend is the highly unfavorable hydrogenation of N^* to NH^* at low H^* coverage on $Sr_2N(0001)$ which is discussed in the following.



Fig. 4 Charge density differences (C and F), in units of the elementary charge per \AA^3 at the height of the adsorbate N nucleus, between (B) N^* at $Mn_2N(0001)$ with $1/4$ ML v_N and (A) the stoichiometric surface and the balance N, and for the hydrogenation of (D) $1/4$ ML N^* to (E) NH^* .

The optimized adsorption geometries are given with Fig. 5. The figure shows intercalation of hydrogen at $Sr_2N(0001)$ that is not observed at $Mn_2N(0001)$. In absence of surface hydrogen, the strong Sr–N bonds result in unstable $1/4$ ML N^* that is filling the vacancies at $Sr_2N(0001)$, which is visualized by the identical geometries shown with panels (2a and 2b) of Fig. 5, while $Mn_2N(0001)$ yields a stable $1/4$ ML N^* surface coverage (Fig. 5, panels 1a and 1b). In presence of surface hydrogen, Fig. 5 shows that the energetic promotion of forming $1/4$ ML v_N and NH^* or NH_2^* at high H^* coverage at $Sr_2N(0001)$ but not at $Mn_2N(0001)$ (shown with Fig. 3A and B) is due to filling of v_N by H^* yielding lattice hydrogen at $Sr_2N(0001)$ (Fig. 5, panels 2c and 2d vs. 1c and 1d). These calculations show hydrogen intercalating at the surface. The tendency of this lattice hydrogen to diffuse further into the bulk leading to formation of hydrides is outlined in Section 2.1. Finally, hydrogenating $1/4$ ML N^* with H^* to NH^* is energetically demanding at $Sr_2N(0001)$ relative to $Mn_2N(0001)$ (Fig. 3C and D) since it requires formation of $1/4$ ML v_N at $Sr_2N(0001)$ (Fig. 5, panels 2e and 2f vs. 1e and 1f).

In summary, the lattice nitrogen activity was outlined to control the formation and hydrogenation of adsorbed nitrogen and the formation of lattice hydrogen. These trends are analogous to the reactivity of the bulk metal nitrides.

2.3 Ammonia from partial reduction of metal nitrides

In the following two Sections we study the role of nitrogen vacancies experimentally by comparing the reactivity of Mn-based transition-metal nitrides to the reactivity of Ca- and Sr-based alkaline earth metal nitrides. This Section characterizes the NH_3 evolution *via* the reduction of manganese nitride.

Fig. 6A shows the evolution of ammonia from the reaction of manganese nitride with H_2 . The yield of NH_3 relative to the lattice nitrogen available for the reaction was at maximum ~ 8 mol% NH_3 after 60 min at $700^\circ C$. The location of the optimum at an intermediate temperature is presumably due to slow reaction kinetics at lower temperatures and thermal decomposition of NH_3 at higher temperatures. At low NH_3 yields we observe decreasing NH_3 yields with time, which is presumably due to partial stripping of NH_3 with the H_2 routed through the liquid absorbent. Since we observe this effect only for NH_3 yields between 10^{-5} to 3×10^{-3} , NH_3 stripping is assumed to not significantly affect NH_3 evolution with higher yields above



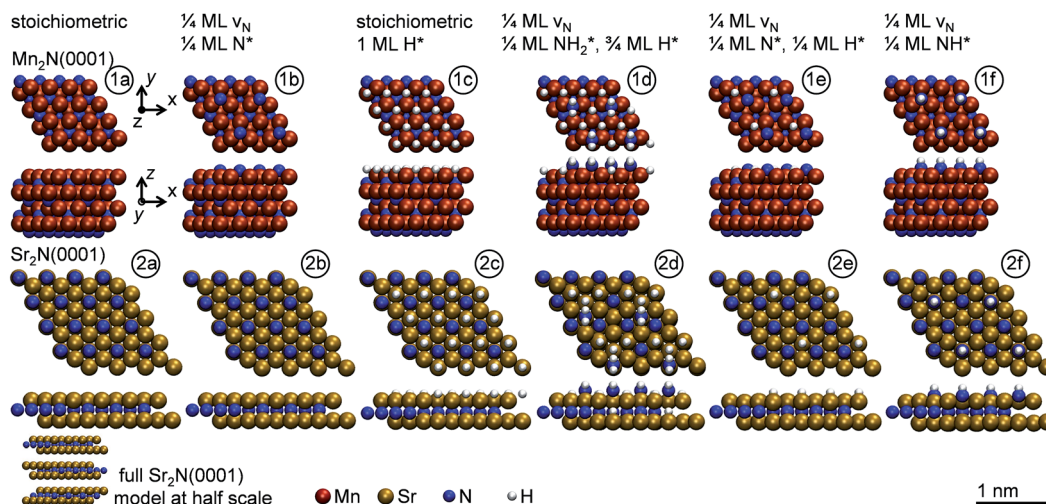


Fig. 5 Optimized adsorption geometries for the indicated surface conditions (top two lines) of (1a to 1f) $\text{Mn}_2\text{N}(0001)$ and (2a to 2f) $\text{Sr}_2\text{N}(0001)$. The view along the y -axis of the $\text{Sr}_2\text{N}(0001)$ model is limited to the upper layer.

300 °C. More important, the ammonia evolution at 550 and 700 °C is described best by a reaction- or gas diffusion-limited kinetic model with an activation energy estimated from an Arrhenius plot of $98 \pm 7 \text{ kJ mol}^{-1}$. This indicates that the kinetics of the NH_3 formation with H_2 are more sensitive to temperature than the steam hydrolysis of Mn_4N with an activation energy of 63 kJ mol^{-1} , where oxygen intercalation fills the nitrogen vacancies.³⁴

Fig. 6B shows the composition of the solid after the reaction with H_2 . Increasing temperature decreases the fraction of $\text{Mn}_6\text{N}_{2.58}$ and yields a maximum Mn_4N fraction near 700 °C. This suggests that NH_3 is formed through the reduction of a higher nitride into a lower nitride phase that contains less nitrogen and that decomposes thermally at 1000 °C to Mn and N_2 .⁵¹ The thickness of the reaction front through a particle with constant volume (*i.e.*, $L = X_{\text{N}} \rho_{\text{nitride}}^{-1} A_{\text{BET}}^{-1}$, where ρ_{nitride} is the density of the reacting nitride and X_{N} is the fraction of liberated lattice nitrogen), can be estimated based on a nitrogen mass balance to be 54 nm or 46 nm for NH_3 evolution at 700 °C from

$\text{Mn}_6\text{N}_{2.58}$ or Mn_4N , respectively. Fig. 6 suggests that this bulk reaction is limited at the surface: by gas-phase diffusion or the surface reaction, that is by the formation of nitrogen vacancies and the hydrogenation of surface nitrogen. We note, attempting to control the lattice nitrogen reactivity *via* doping Mn_4N with Fe did not increase the NH_3 evolution at 700 °C (ESI†), which may be due to the catalytic activity of Fe in establishing the chemical equilibrium in NH_3 , N_2 and H_2 gas mixtures.⁴

For comparison, some metal nitrides that cannot be regenerated with 1 bar N_2 may yield significant quantities of NH_3 . Ni_3N , Cu_3N , Zn_3N_2 and Ta_3N_5 may liberate 30, 25, 23, and 13 mol% of their lattice nitrogen as NH_3 when reacted for at least 30 min at 250, 250, 400, and 700 °C, respectively.⁴⁶ Ammonia yields decrease when reacting H_2 with more stable nitrides: such as to 8 mol% with $\text{Co}_3\text{Mo}_3\text{N}$ for 60 min at 400 °C.⁴⁴ Manganese nitrides can be formed from N_2 at 1 bar, as shown with Fig. 1A, and spent iron-doped manganese nitrides can be regenerated with N_2 , as shown for three consecutive cycles with Fig. S3.† However, stable performance and long-term stability of metal nitrides, in form of pellets or porous structures for instance,^{31,33,37} have to be assessed in the future.

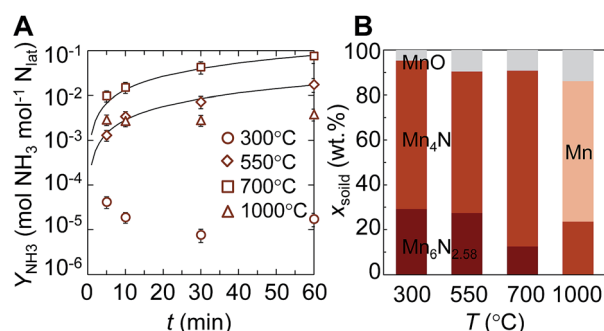


Fig. 6 NH_3 evolution *via* isothermal transition-metal nitride reduction: (A) NH_3 yield vs. time and (B) solid weight fractions from the reaction of Mn_4N with H_2 at 1 bar vs. temperature. Error bars are *via* error propagation within a 95% confidence interval. Solid lines are shrinking-core models for the data at 550 °C and 700 °C controlled by the chemical reaction or gas phase diffusion.

2.4 Ammonia from formation of hydrogenated metal nitrides

Some alkali and alkaline earth metal nitrides may yield ammonia exergonically from the reaction with H_2 due to the intercalation of hydrogen, as discussed in Section 2.1. The electronic structure calculations reported in Section 2.2 outline how the reactivity of the bulk metal nitrides correlates with the activity of the nitrogen vacancies. With the experimental results in this Section we show the ready evolution of ammonia and the corresponding hydrogenated metal compounds from the nitrides of Ca and Sr under H_2 .

The liberation of the lattice nitrogen of Ca_3N_2 and Sr_2N as NH_3 may be limited kinetically at the low temperatures that are favored thermodynamically, as was shown with Fig. 1.

Therefore, Ca_3N_2 and Sr_2N , as well as $\text{Mn}_6\text{N}_{2.58}$ as reference, were reacted with H_2 at 1 bar and a range of temperatures including the low and high end of the spectrum, 220–850 °C. Fig. 7A shows the NH_3 yield over the course of three heating cycles. Sr_2N liberates NH_3 nearly instantaneously during the initial heating period, which is followed by a continuous and comparably slight increase of the NH_3 yield. The absolute NH_3 yield from Ca_3N_2 is lower than that from Sr_2N , but both alkaline earth metal nitrides liberate NH_3 faster and in significantly larger quantities than the transition-metal nitride.

The minimum apparent reaction rates of hydrogenating lattice nitrogen with H_2 into NH_3 are estimated with 0.9 ± 0.2 , 1.3 ± 0.4 and $2.1 \pm 0.2 \mu\text{mol NH}_3 (\text{mol metal} \times \text{s})^{-1}$ for $\text{Mn}_6\text{N}_{2.58}$, Ca_3N_2 and Sr_2N respectively. Since OH and H_2O adsorb strongly at alkaline earth metal nitrides (Table 1), this is accounting for partial nitride hydrolysis by traces of adsorbed water, although neither Sr_2N nor Ca_3N_2 appeared visually oxidized after the reaction. These reaction rates of Ca_3N_2 and Sr_2N and significant formation of up to 12 mol% NH_3 from Ca_3N_2 that we observed with a late onset between 30–60 min heating at various H_2 flow rates (ESI†) indicate that NH_3 is formed from the reaction of lattice nitrogen and H_2 . For comparison, these yields are higher than the previously reported 1 mol% NH_3 from Ca_3N_2 heated for 120 min at 800 °C in H_2 , which can be understood due to the unfavorable $\text{NH}_3\text{--N}_2/\text{H}_2$ equilibrium that is established during these early studies by F. Haber, *et al.*⁵⁰

The intercalation of hydrogen can be observed for Ca_3N_2 yielding mainly Ca_2NH and Sr_2N yielding SrH_2 : Fig. 7B shows the composition of Ca_3N_2 , determined *via* XRD, after the reaction with H_2 . Increasing temperature increases the formation of Ca_2NH , with nominally 25 mol% lattice hydrogen. From the yield of Ca_2NH , the activation energy of the NH_3 evolution is about $42 \pm 7 \text{ kJ mol}^{-1}$. However, the different surface morphologies, shown with Fig. 8, and the slightly different BET surface areas, given with Table S1 (ESI†), of the nitrides indicate that this value of the activation energy cannot be compared directly to the activation energy of the NH_3 evolution from



Fig. 8 Scanning electron micrographs of the metal nitrides.

manganese nitride, given in Section 2.3. The lower activation energy of Ca_3N_2 is, however, qualitatively in agreement with the higher NH_3 evolution rate with Ca_3N_2 , relative to $\text{Mn}_6\text{N}_{2.58}$. Furthermore, a 58% higher NH_3 evolution rate from Sr_2N with a 16% lower specific surface area relative to Ca_3N_2 indicates that the reported results are not solely due to the available surface area. These results confirm that the intercalation of the two alkaline earth metal nitrides by hydrogen promotes the ammonia evolution from the lattice nitrogen at the surface.

3. Methods

3.1 Thermochemical equilibrium calculations

To guide the design of looped metal nitride catalysts, the thermochemical equilibrium of various bulk metal nitrides, H_2 , and their reaction products was determined at 1 bar and as a function of temperature from tabulated free energy data.⁵¹ Per convention, negative free energy differences mark exergonic reactions.

3.2 Electronic structure calculations

To determine the NH_3 -evolution-controlling mechanism at the atomic scale, hexagonal $\zeta\text{-Mn}_2\text{N}$ and trigonal Sr_2N were modeled *via* density functional theory (DFT), performed with the open-source planewave pseudopotential periodic electronic-structure code DACAPO.^{53–55} Atomic manipulations were handled in the Atomic Simulation Environment (ASE)⁵⁶ and exchange–correlation interactions were treated by the revised Perdew–Burke–Ernzerhof (RPBE) functional of Hammer, Hansen, and Nørskov⁵⁷ derived in the generalized gradient approximation (GGA). A k -point sampling of $4 \times 4 \times 4$ for bulk and $4 \times 4 \times 1$ for surface calculations was used for sampling of the Brillouin zone in the x , y and z directions, with the z direction orthogonal to the surface slab. A Fermi–Dirac smearing of 0.1 eV was used to achieve convergence and results were extrapolated to 0 K. The linesearch BFGS algorithm was employed for relaxing atomic geometries until the maximum force on any unconstrained atom was less than $0.05 \text{ eV } \text{\AA}^{-1}$. To avoid remnant stress in the calculations, the lattice constants were chosen as the DFT-calculated lattice constants (*i.e.*, $(a, c) = (2.81, 4.44) \text{ \AA}$ for Mn_2N , and $(3.90, 21.15) \text{ \AA}$ for Sr_2N), which are within 2.2% of the experimental values (*i.e.*, $(a, c) = (2.84, 4.51) \text{ \AA}$ for Mn_2N ,⁵⁸ and $(3.86, 20.70) \text{ \AA}$ for Sr_2N ⁵⁹). Calculations for Mn_2N were spin-polarized. All surface calculations were performed for the (0001) facet with $2 \times 2 \times 4$ or $2 \times 2 \times 6$ metal atoms in the x , y and z directions of the Mn_2N or Sr_2N slab. The surfaces were modeled with 10 Å of vacuum perpendicular to the surface with the lower layers of the slab constrained to the



Fig. 7 NH_3 evolution *via* metal nitride hydrogenation at various temperatures: (A) NH_3 yield vs. time (arithmetic average of three experiments) from the reactions of Ca_3N_2 , Sr_2N , and $\text{Mn}_6\text{N}_{2.58}$ with H_2 at 1 bar, shown on the upper panel, and the corresponding temperature profile, on the lower panel; (B) weight fraction of Ca_3N_2 heated for 60 min under H_2 (XRD analyses in air). Error bars are *via* error propagation within a 95% confidence interval. Solid lines are a guide only.



bulk geometry while the atoms in the upper two layers were always optimized to zero-force positions. The interaction between the dipole moments of surfaces was decoupled *via* introduction of a dipole layer in the vacuum.

The correlated electronic structure of certain metal oxides is not well described with simple GGA methods. This is sometimes addressed by the inclusion of an empirical Hubbard U term that accounts for on-site Coulomb repulsion and exchange interactions, thereby correcting self-interaction errors, when modeling certain metal oxides,^{60–62} while other metal oxides have been modeled well without the additional U parameter⁶³ (and references therein). The value of U can be determined self-consistently,⁶² however, commonly it is chosen by fitting the experimental band gap⁶⁰ or reaction energetics (resulting in a consistent offset of the free energy of reaction with varying U).⁶⁴ Introducing nitrogen into a transition metal lattice may lead to partial electron localization with a minor increase in the metal oxidation state, compared to the presence of lattice oxygen.⁶⁵ Hence, transition metal nitrides, including Mn_2N , are typically modeled without a Hubbard U correction.^{23,66} Verifying this and assessing the use of GGA + U methods for metal nitride surfaces is an important point. In a prospective article, we will show how adsorption energies respond to the value of U only for metal compounds that possess a (pseudo) band gap. While Sr_2N and Mn_2N are metallic conductors,^{58,59} Sr_2N exhibits localized N 2p states.⁶⁷ Thus, whether GGA + U methods may improve the accuracy of DFT-computed adsorption energies at Sr_2N surfaces deserves further study.

To aid in our description of nitride activity from first principles, four free-energies are defined. First, ΔG_{vac} is the free energy required to form a nitrogen vacancy, v_{N} , at the surface:

$$\Delta G_{\text{vac}} \equiv G_{\text{s}}[v_{\text{N}}] - (G_{\text{s}} - G_{\text{N}}^{\text{r}}) \quad (5)$$

where G_{s} is the free energy of the intact surface, $G_{\text{s}}[v_{\text{N}}]$ is the free energy of the surface with 1/4 monolayer (ML, relative to the number of surface metal atoms) v_{N} and G_{N}^{r} is the reference energy of nitrogen in the gas phase, respectively.

Next, $\Delta G_{\text{ads}}[A^*]$ is the adsorption energy of the adsorbate(s) A (an asterisk indicates an adsorbed species):

$$\Delta G_{\text{ads}}[A^*] \equiv G_{\text{s}}[A^*] - (G_{\text{s}} + G_{\text{A}}^{\text{r}}) \quad (6)$$

where $G_{\text{s}}[A^*]$ is the free energy of the surface with the adsorbate(s) and G_{A}^{r} the free energy of the reference adsorbate(s).

Third, $\Delta G_{\text{vac}}[\text{NH}_x^*, y\text{H}^*]$ is the free energy change to create adsorbed NH_x species while creating nitrogen vacancies and leaving y adsorbed H's at the surface; that is to form 1/4 ML v_{N} at a surface with z ML H^* ($z = 0, 1/4, 1/2, 3/4$ or 1) yielding 1/4 ML NH_x^* ($x = 0, 1, 2$ or 3, corresponding to 0, 1/4, 1/2 or 3/4 ML H^*) and y ML H^* remaining at the surface ($y = 0, 1/4, 1/2$ or 3/4):

$$\Delta G_{\text{vac}}[\text{NH}_x^*, y\text{H}^*] \equiv G_{\text{s}}[v_{\text{N}}, \text{NH}_x^*, y\text{H}^*] - (G_{\text{s}}[z\text{H}^*] + (x + y - z)G_{\text{H}}^{\text{r}}) \quad (7)$$

where $G_{\text{s}}[v_{\text{N}}, \text{NH}_x^*, y\text{H}^*]$, $G_{\text{s}}[z\text{H}^*]$ and G_{H}^{r} are the energy of the surface after or before the formation of v_{N} and the reference energy of the balance hydrogen gas.

Finally, $\Delta G_{\text{hyd}}[\text{NH}_x^*, y\text{H}^*]$ is the energy for hydrogenating NH_{x-1}^* with $(y + 1)$ pre-adsorbed H^* , leaving NH_x^* and $y\text{H}^*$:

$$\Delta G_{\text{hyd}}[\text{NH}_x^*, y\text{H}^*] \equiv G_{\text{s}}[v_{\text{N}}, \text{NH}_x^*, y\text{H}^*] - G_{\text{s}}[v_{\text{N}}, \text{NH}_{x-1}^*, (y + 1)\text{H}^*] \quad (8)$$

where $G_{\text{s}}[v_{\text{N}}, \text{NH}_{x-1}^*, (y + 1)\text{H}^*]$ is the energy of the surface before the hydrogenation.

Details on the local optimization procedures, references energies, conversion of electronic energies to free energies, and adsorption energetics in presence of OH and H_2O and at oxynitride surfaces are given with ESI†.

3.3 Metal nitride preparation

Manganese was nitridated³⁴ by heating 2 g Mn in N_2 under two different thermal conditions; first, for 120 min at 700 °C which yielded 59–67 wt% $\epsilon\text{-Mn}_4\text{N}$ and 25–34 wt% $\zeta\text{-Mn}_6\text{N}_{2.58}$ (denoted as Mn_4N), and second, for 240 min at 750 °C which yielded 91–94 wt% $\zeta\text{-Mn}_6\text{N}_{2.58}$ (denoted as $\text{Mn}_6\text{N}_{2.58}$). We note ζ -phase manganese nitride ranges from 28.6–33.3 mol% lattice nitrogen including Mn_5N_2 , $\text{Mn}_6\text{N}_{2.58}$, and Mn_2N .⁵⁸ The nitride characterization is summarized with Table S1 (ESI†). Fe-doped Mn nitride, $\text{Fe/Mn}_4\text{N}$, was prepared by heating 2 g of an equimolar mixture Mn and Fe powder for 120 min in N_2 yielding 26 ± 1 wt% $\epsilon\text{-Mn}_4\text{N}$ and 16 ± 1 wt% $\zeta\text{-Mn}_6\text{N}_{2.58}$. All Mn-containing powders were pretreated at 60 °C for 10 min in air to remove water. Ca_3N_2 and Sr_2N ^{34,68} were prepared by heating 4.4 g metal pieces for 240 min (Ca) or 420 min (Sr) in N_2 and milling for about 5 min with mortar and pestle. The fraction of hydroxides formed when handling Ca_3N_2 or Sr_2N during the X-ray diffraction (XRD) analysis in air were disregarded in NH_3 yield calculations since these materials were otherwise handled in Ar. All N_2 flows were $1.9 \pm 0.1 \text{ L}_{(\text{STP})} \text{N}_2 \text{ min}^{-1}$.

3.4 Reduction of Mn_4N and $\text{Mn}_6\text{N}_{2.58}$ with H_2

To probe the reactivity of manganese nitride, 651 ± 2 mg Mn_4N containing 3.01 ± 0.01 mmol lattice nitrogen was heated in a quartz boat with a tube furnace at ambient pressure. The tube furnace was a HTF55347C model, Lindberg/Blue, with a quartz tube that was purged before each experiment for 10 min with N_2 to remove residual O_2 and H_2O . The temperature was ramped from 100 to 300 °C or from 400 to 550, 700 and 1000 °C respectively. H_2 was supplied at $0.5 \pm 0.1 \text{ L}_{(\text{STP})} \text{H}_2 \text{ min}^{-1}$ and final temperatures were held for 60 min. The gas leaving the furnace was routed through a liquid absorbent consisting of $50 \pm 5 \text{ mL}_{(\text{STP})} 10 \text{ mM HCl}$, chilled with ice-cold H_2O . Five mL samples were taken at 0, 5, 10, 30 and 60 ± 0.5 min after the reaction temperature was reached. These samples were analyzed for NH_3 as described below. After 60 min the furnace was cooled to below 100 °C. Solids were stored at 4 °C. All liquids were stored at room temperature. Additionally, the NH_3 evolution from Fe-doped Mn_4N was quantified (ESI†).

3.5 Hydrogenation of Ca_3N_2 and Sr_2N with H_2

The optimum temperature for reacting Ca_3N_2 with $0.5 \pm 0.1 \text{ L}_{(\text{STP})} \text{H}_2 \text{ min}^{-1}$ was determined using the experimental setup



described in Section 3.4 without the absorption vessel. The powder (476 ± 170 mg, *i.e.*, 6 ± 2 mmol lattice nitrogen) was held for 60 min at 300, 500, 700 and 1000 °C and analyzed for the loss of lattice nitrogen. All Ca-containing solids were stored under Ar at 4 °C. The effect of the H₂ flow rate on the NH₃ yield from Ca₃N₂ was tested (ESI†). To compare the NH₃ evolution kinetics between metal nitride reduction (Mn₆N_{2.58}) and hydrogenation (Ca₃N₂ and Sr₂N), 519 ± 18 mg metal nitride ($2.8\text{--}7.0$ mmol lattice nitrogen) were heated in 0.5 ± 0.1 L_(STP) H₂ min^{−1} from 220 to 850 ± 5 °C. After holding temperatures for 2 min, the furnace was cooled to 250 °C. The temperature change was repeated in triplicate. Liquid samples were taken at 250, 550 and 850 °C while the solids were analyzed after three cycles, reintroduced into the furnace, heated for 120 min at 750 °C in 1.9 ± 0.1 L_(STP) N₂ min^{−1} and analyzed anew.

3.6 Analytical

Solids were weighed (AE260 DeltaRange balance, ± 0.1 mg, Mettler) and analyzed *via* XRD (Miniflex II diffractometer, Cu-target X-ray tube, Rigaku, 5–80° 2 θ range, 1 or 10° 2 θ per min scan speed, PDXL Software Version 1.6.0.0 for quantitative solid phase analysis). The XRD analysis was in air which explains minor metal oxide and hydroxide fractions. To confirm N₂ reduction energy-dispersive X-ray spectroscopy (EDS) was employed using a S-3500N scanning electron microscope (SEM, 20 keV, Hitachi; Link Pentafet 7021 X-ray detector and Inca Energy X-ray analysis software, both Oxford Instruments). The specific BET surface area, A_{BET}, was analyzed using N₂ at NanoScale Inc., Manhattan, KS. NH₃ was quantified with an NH₃ Ion Selective Electrode and a pH/ISE Controller model 270 (both Denver Instrument). The concentration of dissolved NH₃ was estimated with zeroing for the signal from pure water. As estimated from the pH change, the formation of N₂H₄ was negligible relative to NH₃ formation in all reported experiments. The outlet of the absorption vessel was equipped with an NH₃ gas detection tube (0.25–3 or 5–70 ppm NH₃ detection range, Dräger). Ammonia yield, Y_{NH₃}, is reported as the molar ratio of NH₃ captured by the absorbent at a given time relative to the lattice nitrogen stored in the solid initially. The data is fitted to a kinetic model limited by the reaction or gas phase diffusion (ESI†).

3.7 Chemicals

Mn (99.9%, −325 mesh) and Fe (99.9%, −325 mesh) were from Noah Technologies, Ca (99%, granular) and NH₄Cl (99.5%) were from Acros, Sr (99%, pieces) was from MP Biomedicals and NaOH (99.6%, pellets) and HCl (12.1 N) were from Fisher Scientific. H₂O was deionized (Direct-Q 3 UV, Millipore) and degassed with Ar. H₂, N₂ and Ar (all UHP Zero grade) were from Lin weld.

4. Conclusions

We have introduced chemical looping of metal nitride catalysts for solar-driven synthesis of ammonia at ambient pressure from overall, water, N₂, and concentrated sunlight as source of renewable process heat. Augmented NH₃ evolution due to the

formation of lattice hydrogen was correlated to the exergonic character of the hydrogenation of alkali and alkaline earth metal nitrides *vs.* endergonic reduction of transition-metal nitrides. These trends were confirmed experimentally and rationalized *via* electronic structure calculations which showed that the lattice nitrogen activity controls hydrogen intercalation and the energetics of forming and hydrogenating adsorbed nitrogen. The energy of the metal d-states was discussed as a quantitative descriptor for the design of ternary metal nitrides with reactivities between those of Fe- and Mn-based nitrides, while the energy of the metal s-states may guide the design of, for instance Li-doped, alkaline earth metal nitrides for an NH₃ evolution promoted by the intercalation of surface hydrogen. Stable NH₃ evolution and long-term mechanical stability of metal nitride catalysts, in form of pellets or porous ceramics for instance, have to be assessed in the future.

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