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Towards anti-perovskite nitrides as potential nitrogen storage materials for chemical looping ammonia production: reduction of Co$_3$ZnN, Ni$_3$ZnN, Co$_3$InN and Ni$_3$InN under hydrogen

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Graphical abstract

Highlights
- Pure phase Co$_3$ZnN, Ni$_3$ZnN, Co$_3$InN, and Ni$_3$InN anti-perovskite nitrides have been prepared
- Ammonia in high yields is produced upon hydrogenation of the anti-perovskite nitrides at 400°C and 500°C
- Lattice nitrogen is removed from Ni$_3$ZnN and Ni$_3$InN in a topotactic manner

ABSTRACT: The ammonia production properties upon reduction in hydrogen of the anti-perovskite nitrides Co$_3$ZnN, Ni$_3$ZnN, Co$_3$InN, and Ni$_3$InN have been investigated. Single phases with ideal anti-perovskite structures (Space group: $Pm-3m$) were prepared for all the nitrides by the ammonolysis of the corresponding precursor oxides and all the nitrides were observed to produce ammonia in high yields when reacted with H$_2$/Ar. The cumulative ammonia production values at 400 °C were 3069, 2925, 289, and 1029 μmol-NH$_3$ g$^{-1}$ for Co$_3$ZnN, Ni$_3$ZnN, Co$_3$InN, and Ni$_3$InN, respectively and the order of the release rates was Ni$_3$ZnN > Co$_3$ZnN > Ni$_3$InN > Co$_3$InN. X-ray diffraction studies revealed that Co$_3$ZnN and Co$_3$InN were decomposed upon the loss of lattice N, whereas Ni$_3$ZnN and Ni$_3$InN were transformed into Ni$_3$Zn and Ni$_3$In via the intermediate phases Ni$_3$ZnN, and Ni$_3$InN. The crystal structures of these intermediate phases are related to their initial structures, indicating that the loss of lattice N in Ni$_3$ZnN and Ni$_3$InN was topotactic.

Keyword: anti-perovskite nitride, nitrogen storage material, chemical looping ammonia production, topotactic reaction

1. Introduction

Ammonia production, currently accomplished on the industrial scale via the Haber-Bosch Process, is a reaction of pivotal societal importance [1]. It can be credited with the sustenance of around 40% of the global population through the provision of an accessible route to synthetic
fertilizer. Around 174 million tonnes of ammonia are produced on the industrial scale annually [1] and production continues to grow. When considered in its entirety, including the production of the feedstream reagents, the Haber-Bosch Process currently accounts for around 1-2% of global energy demand [1]. The hydrogen required is generated currently from fossil sources and the process has been reported to be responsible for the production of about 2.5% of all fossil fuel based CO₂ emissions worldwide [1]. Accordingly, in view of the paramount importance of this reaction, recent studies have sought to address issues of sustainability. One topic of focus has been the possibility of the development of ammonia synthesis technology which would be suitable for operation on a local scale, being much smaller than the traditional Haber-Bosch plants which are operated on a large scale, where, for example, the local generation of fertilizer on a farm could be accomplished using hydrogen generated via electrolysis employing renewably derived energy such as that from wind power. In order to accomplish this, using heterogeneous catalysis, a step change in catalyst performance is necessary and, correspondingly, the development of new catalysts of enhanced activity with respect to the industrially employed iron-based [2] and ruthenium based [3] catalysts is an area of contemporary interest. It is widely believed that in order to achieve this, the limiting scaling relationship which has been reported for ammonia synthesis will need to be broken. Amongst catalysts investigated to date have been elctride supported metals in which novel mechanistic pathways are reported to be operative [4], the combination of lithium hydride and metals or metal nitrides which are proposed to circumvent scaling limitations via the transfer of reaction intermediates between phases [5], ternary [6,7] and quaternary [8] metal nitrides which might operate by nitrogen based Mars-van Krevelen mechanisms [9,10] and hydride and metal hydride based compositions [11,12] for which hydrogen based Mars-van Krevelen mechanisms may be
operational. In addition to the development of novel, more active, heterogeneous catalysts, photocatalytic [13] and electrocatalytic [14,15] processes have also been investigated.

A further approach which has been of interest in the context of localised ammonia synthesis involves chemical looping in which production is accomplished via the reaction of a nitrogen containing reagent followed by its regeneration in a separate reaction step. A number of these studies have employed the hydrolysis of a nitride followed by its regeneration at high temperature employing N$_2$, e.g. [16,17]. It has been reported that the high temperatures required for renitridation could be accomplished from solar energy. By such routes, ammonia production from nitrogen, water and sunlight becomes possible making it entirely sustainable with a dramatically reduced carbon footprint. Related to this has been the report of a system for ammonia synthesis based upon hydrolysis of lithium nitride and its subsequent regeneration by electrochemical means [18]. Whilst it is less direct, the possible availability of sustainable hydrogen derived from water, means that looping approaches based upon hydrogenation of regenerable metal nitrides is also an area of interest. Accordingly, reports have been made of ammonia production via the hydrogenation of systems based upon binary metal nitrides including Re$_3$N [19], Ni$_3$N [20], Cu$_3$N [20], Zn$_3$N$_2$ [20], Ta$_3$N$_5$ [20,21] and manganese nitride [22] have been reported. In the current study, we extend these studies towards anti-perovskite nitrides (general formula A$_3$BN, see Figure 1 for their structure) which offer the possibility of tuning the reactivity of lattice nitrogen and regeneration via the controlled variation of the metal (i.e. A and B site) composition. The aim of this work is to establish composition – performance relationships which might prove to be of value for for the computationally aided design of more active heterogeneous catalysts [23]. In the current study, we report the lattice nitrogen hydrogenation characteristics of cobalt, nickel, zinc and indium based anti-perovskite nitrides. It is of interest to note that the removal and replenishment of lattice nitrogen from anti-perovskite
nitrides is in some way analogous to the exsolution of metal nanoparticles from perovskites which is an area of topical interest [24]. Also of relevance to the approach reported within the current manuscript are reports of the nitrogenation and hydrogenation characteristics of transition metal – iron intermetallic compounds [25] and the nitrogen absorption behaviour of zirconium vanadium iron and related alloys [26].

2. Experimental Details

2.1. Sample preparation

Polycrystalline samples of Co₃ZnN, Ni₃ZnN, Co₃InN, and Ni₃InN were synthesized by ammonolysis of precursor oxides which in turn were prepared from nitrate solutions. Stoichiometric amounts of Co(NO₃)₂·6H₂O (98.0–102.0%, Alfa Aesar), Ni(NO₃)₂·6H₂O (≥98%, Fluka), Zn(NO₃)₂·6H₂O (≥99.0%, Sigma Aldrich), and In(NO₃)₃·xH₂O (99.99%, Alfa Aesar) were dissolved in a minimal amount of HNO₃ aqueous solution (10%) and stirred at room temperature for 30 mins. The solution was dried at 120 °C overnight, followed by calcination in air at 400 °C for 3 h. The precursor oxides obtained were nitrided under a flow of NH₃ (99.98%, BOC, 95 mL min⁻¹) at 600 °C for 10 h employing a ramp rate of 2.5 °C min⁻¹, followed by subsequent cooling to room temperature under the flow of NH₃. The obtained nitrides were subsequently passivated applying a flow of 0.1% O₂/N₂/Ar (prepared by mixing 2% O₂/Ar and 99.998% N₂, BOC, 100 mL min⁻¹) at room temperature for 5 h in order to prevent bulk oxidation upon discharging samples from the reactor.

2.2. Characterization

Powder X-ray diffraction (XRD) measurements were conducted using an X’Pert PRO MPD (PANalytical) employing Cu Kα radiation (λ = 1.54056 Å). XRD patterns were collected in the 2θ
20–85° range with a step size of 0.0167°. Le Bail refinements for the XRD patterns obtained were performed using the Jana2006 program [27] with a pseudo-Voigt function in order to estimate lattice parameters. Energy dispersive X-ray spectroscopy (EDX) was collected using a XL30 ESEM (Philips/FEI) at an accelerating voltage of 20 kV. Specific surface areas were determined by Brunauer Emmett Teller (BET) analysis of 20 point nitrogen physisorption isotherms determined at −196 °C using a Quantachrome Quadrasorb Evo Analyser. Prior to measurements being undertaken, samples were degassed at 120 °C for 16 h under vacuum. N and H content analyses were conducted by combustion using an CE-440 Elemental Analyser (Exeter Analytical).

2.3. Evaluation of ammonia production

Samples (0.2 g) were placed inside quartz microreactor tubes and were held in place centrally between quartz wool plugs and housed in a Carbolite tube furnace. Samples were heated under a flow of \( \text{H}_2/\text{Ar} \) (75% \( \text{H}_2 \), BOC, 60 mL min\(^{-1}\)) from room temperature to the target reaction temperature (400 or 500 °C) employing a ramp rate of 10 °C min\(^{-1}\). Samples were held for 6 h at the target temperature. The vent gas was flowed through 210 mL of \( \text{H}_2\text{SO}_4 \) solution (0.00108 M) and the change in conductivity was related to the production of \( \text{NH}_3 \).

3. Results and Discussion

The XRD patterns of the precursor oxides for Co\(_3\)ZnN (Co-Zn-O), Ni\(_3\)ZnN (Ni-Zn-O), Co\(_3\)InN (Co-In-O), and Ni\(_3\)InN (Ni-In-O) are presented in Figure 2. Co-Zn-O exhibited a cubic phase related to Co\(_3\)O\(_4\), although the lattice parameter based on the \( Fd-3m \) space group was 8.0971(7) Å, which is larger than the 8.065 Å of Co\(_3\)O\(_4\) [28] and which is indicative of Co-Zn-O being
Co$_3$Zn$_4$O$_4$, since the increase of lattice parameter with respect to Co$_3$O$_4$ is consistent with Zn substitution into the lattice [29]. The value of $\delta$ based on Vegard’s law was determined to be 0.85, which is in reasonable agreement with the synthesis value of $\delta$ = 0.75. The other precursor oxides, Ni-Zn-O, Co-In-O and Ni-In-O were found to be mixtures comprising NiO and ZnO, Co$_3$O$_4$ and In$_2$O$_3$, and NiO and In$_2$O$_3$, respectively.

All of the XRD patterns of the samples Co$_3$ZnN, Ni$_3$ZnN, Co$_3$InN, and Ni$_3$InN showed the expected cubic phase without any additional impurity phases being present (Figure 3). The estimated lattice parameters (Table 1) based on the ideal anti-perovskite structure with the space group of $Pm-3m$ were all in close agreement with the reported values of $a = 3.764$ Å for Co$_3$ZnN, $a = 3.766$ Å for Ni$_3$ZnN, $a = 3.8541(7)$ Å for Co$_3$InN, and $a = 3.8445(1)$ Å for Ni$_3$InN [30-32].

The N contents of Co$_3$ZnN, Ni$_3$ZnN, and Ni$_3$InN as determined by elemental analysis (Table 1) were also consistent with the expected values based on the $A_3B_N$ composition ($A = \text{Co, Ni}, B = \text{Zn, In}$), although the N content of Co$_3$InN was approximately 10% higher than that of theoretical value. Hydrogen, which could potentially be incorporated into the samples during the ammonolysis procedure, was not detected for any of the nitrides by combustion analysis. $A/B$ molar ratios of Co$_3$ZnN, Ni$_3$ZnN, and Ni$_3$InN estimated by EDX analysis were close the synthesis ratio of 3 for all nitrides although, as for the N analysis, that of Co$_3$InN was higher than expected.

One possibility is that In in Co$_3$InN might have been partially lost during synthesis since the melting point of In metal (157 °C) is much lower than the temperature of the ammonolysis reaction (600 °C) and this requires further investigation. The surface areas of Co$_3$ZnN, Ni$_3$ZnN, Co$_3$InN, and Ni$_3$InN were found to be 3, 5, 4, and 3 m$^2$ g$^{-1}$, respectively (Table 1).

Ammonia production under 75% H$_2$/Ar was investigated in order to determine the reactivity of the lattice N in these nitrides. The ammonia production profiles are presented in Figure 4. All of
The nitrides were found to produce ammonia and the production amounts at 400 °C were 3069, 2925, 289, and 1029 μmol-NH₃ g⁻¹ for Co₃ZnN, Ni₃ZnN, Co₃InN, and Ni₃InN, respectively (Figure 4a and Table 2). The nitrides did not complete ammonia production within 6 h at 400 °C. On the other hand, all of the nitrides except for Co₃InN completed ammonia production in 6 h at 500 °C (Figure 4b) which is consistent with their post-reaction N analysis (Table 1). The production amounts at 500 °C were 3491, 3461, 1523, and 2804 μmol-NH₃ g⁻¹ for Co₃ZnN, Ni₃ZnN, Co₃InN, and Ni₃InN, respectively (Figure 4b and Table 2). These values are generally higher than for Li-Mn-N (2072 μmol-NH₃ g⁻¹ for 5 h at 500 °C) [22]. Furthermore, these production amounts correspond to the consumption of 93, 92, 42, and 85% of the total available N content of the samples respectively. These values are ca. 1.7–3.9 times higher than the reported values for Li-Mn-N (24% for 5 h at 500 °C) [22].

Significant differences amongst the nitrides were observed in terms of their ammonia production rates which, estimated from the production amount in 30 min after the temperature reached 400 °C, were 752, 2082, 61, and 220 μmol-NH₃ g⁻¹ h⁻¹ for Co₃ZnN, Ni₃ZnN, Co₃InN, and Ni₃InN, respectively. These values do not correspond to initial production since small amounts of ammonia (1–6% against theoretical maximum) were produced from these nitrides during the temperature increase. The ammonia production rates of the Ni-containing nitrides were ca. 2.8–3.6 times higher than the corresponding Co-containing nitrides and the Zn-containing nitrides were 9.5–12.3 times higher than the corresponding In-containing nitrides. The highest ammonia production rate observed for Ni₃ZnN (2082 μmol-NH₃ g⁻¹ h⁻¹) was ca. 3.2 times higher than the catalytic ammonia production under 75% H₂/N₂ Co₃Mo₃N (652 μmol-NH₃ g⁻¹ h⁻¹ at 400 °C under 0.1 MPa) [33]. N balance calculations based upon the elemental analyses reported in Table 1 and the total ammonia production reported in Table 2 are indicative of the vast majority of the lost lattice N producing NH₃ with the contribution of N₂ formation potentially being much
less significant. In most instances lattice and ammonia balances are within ca. 10% of the total, with the notable exception of the Co$_3$InN system where, for example, post-reaction N analyses may be influenced by oxidation of materials following their exposure to air.

The post-400°C reaction XRD pattern of Co$_3$ZnN (hereafter $A_3BN$ samples reacted at $T$ °C are referred to as $A_3BN-T$) showed the presence of ZnO and Co metal in addition to unreacted Co$_3$ZnN (Figure 5a), meaning that Co$_3$ZnN decomposed into Zn metal and Co metal upon the loss of lattice N. Unreacted Co$_3$ZnN was not observed in the Co$_3$ZnN-500 XRD pattern. ZnO was most probably formed during post-reaction exposure to air since Zn metal is easily oxidized in air even at room temperature [34]. Decomposition into Zn$_3$N$_2$ followed by subsequent oxidation to ZnO seems unrealistic because the ca. 93% and 94% of the N lost was related to ammonia production at 400 and 500 °C, respectively. In contrast, the XRD pattern of Ni$_3$ZnN-400 exhibited Ni$_3$Zn ($Fm-3m$) [35] and an unknown phase (denoted by $\alpha$ in Figure 5a). The unknown phase is likely to be an intermediate phase such as Ni$_3$Zn$_x$ ($a = 3.6630(3)$ Å) since its space group is the same as Ni$_3$Zn ($Pm-3m$). The existence of an intermediate phase whose crystal structure is same as Ni$_3$ZnN indicates the release of lattice N to be topotactic. Since such a topotactic reaction does not require additional energy corresponding to the rearrangement of the component metal species, Ni$_3$ZnN showed a higher ammonia production rate than Co$_3$ZnN at 400 °C. The XRD pattern of Ni$_3$ZnN-500 showed only the single phase of Ni$_3$Zn, corresponding to the complete loss of lattice N from Ni$_3$ZnN at 500 °C.

A similar explanation for the ammonia production rate can be applied for the relation between Ni$_3$InN and Co$_3$InN. The XRD pattern of Co$_3$InN-400 evidenced Co metal and unreacted Co$_3$InN (Figure 5b). In addition to these phases, CoIn$_2$ [36] was also detected in the XRD pattern of Co$_3$InN-500. These observations mean that Co$_3$InN decomposed into Co metal and CoIn$_2$ upon
the loss of lattice N. In contrast, the XRD pattern of Ni,InN-400 showed unreacted Ni,InN, a small amount of Ni metal, and an unknown phase (denoted as β in Figure 5b). The unknown phase is likely to be an intermediate phase such as Ni,InN, \((a = 3.78394(18) \text{ Å})\) which has the same space group as Ni,InN (Pm-3m). As for Ni,ZN, Ni,InN topotactically released N atoms upon initial reaction to form an intermediate phase Ni,InN. This could be the reason that the ammonia release rate of Ni,InN was higher than Co,InN at 400 °C. The XRD pattern of Ni,InN-500 showed Ni,In (P63/mmc) [37] with small amount of Ni metal, consistent with the complete loss of N from Ni,InN at 500 °C.

The 9.5 times higher ammonia rate of Ni,ZN compared to Ni,InN at 400 °C cannot be explained solely on the basis of comparative surface areas (Table 1) since the area of Ni,ZN is less than twice that of Ni,InN (Table 1) and SEM investigation of all the materials investigated (Figure S1 in the Supplementary Information) demonstrates them to have quite irregular morphology. Ammonia production by nitrides under the H2/Ar atmosphere is assumed to proceed through a Mars-van Krevelen like mechanism \([21,22]\), which comprises surface reactions and bulk diffusion of N atoms. Regarding the surface reactions, adsorption and dissociation of hydrogen molecules to produce H species, the reaction of the H species with lattice N atoms to form ammonia, and the desorption of the ammonia molecules are involved in ammonia production. Differences in the chemical affinities between Zn and In can be anticipated to affect these reactions resulting in the difference in the ammonia production rates between Ni,ZN and Ni,InN. Regarding N diffusion in the bulk, the bonding environment of N with surrounding atoms is important. In the case of Ni,BN (\(B = \text{Ga}\)), first-principle calculations have revealed that covalent-ionic and ionic interactions occur between Ni-N and B-N, respectively \([38]\). The difference in the electronegativity of Zn (1.65) against N (3.04) is larger than that of In (1.78), suggesting Zn-N bonding in Ni,ZN to be more ionic than the In-N bonding in Ni,InN.
Moreover, the Ni-N bond distances were calculated to be *ca.* 1.88 and 1.93 Å for Ni$_3$ZnN and Ni$_3$InN, respectively. These differences would be expected to affect the activation energy for the diffusion of N atoms. Further studies applying the Avrami-Erofe'ev relationship [39] and first-principle calculations should be undertaken to determine the dominant effect for the high ammonia release in Ni$_3$ZnN.

An obvious next step is to investigate the nitrogen cycling properties of these materials in which regeneration and further nitrogen discharge will be investigated. In addition, it is notable that addition of dopants including lithium in the case of manganese nitride [22], cobalt in the case of tantalum nitride [21,40] and ruthenium/alumina in the case of titanium-iron intermetallic compounds [25] have been reported to influence beneficially the lattice nitrogen conversion and/or uptake characteristics.

### 4. Conclusions

Anti-perovskite nitrides Co$_3$ZnN, Ni$_3$ZnN, Co$_3$InN, and Ni$_3$InN were prepared via ammonolysis using corresponding precursor oxides, and the reactivity of N atoms in these nitrides were investigated using ammonia synthesis as a model reaction. All of these nitrides released N atoms as ammonia under a flow of H$_2$/Ar. Ni-nitrides Ni$_3$ZnN and Ni$_3$InN showed higher ammonia production rate than Co-nitrides Co$_3$ZnN and Co$_3$InN, respectively. XRD measurement revealed that the existence of intermediate phases Ni$_3$ZnN, and Ni$_3$InN, which should be the main factor for the higher ammonia production rates. TGA measurements suggested the regenerabilities for Ni$_3$ZnN and Ni$_3$InN but further experiments are needed.

**Declaration of interests**
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.

**Author credit statement**

YG and AD undertook the experimental work in JSJH’s laboratory and under his supervision.

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**Fig. 1.** Crystal structure of $A_3BN$ anti-perovskite with the space group of $Pm-3m$. The green, gray, and blue spheres represent atoms in $A$ site, atoms in $B$ site, and N atoms, respectively.

**Fig. 2.** XRD patterns of precursor oxides Co-Zn-O, Ni-Zn-O, Co-In-O, and Ni-In-O.
Fig. 3. XRD patterns of as prepared Co$_3$ZnN, Ni$_3$ZnN, Co$_3$InN, and Ni$_3$InN.
Fig. 4. Ammonia production profiles of as prepared Co$_2$ZnN, Ni$_2$ZnN, Co$_3$InN, and Ni$_3$InN under the flow of 75% H$_2$/Ar at (a) 400 °C and (b) 500 °C.
Fig. 5. XRD patterns of post-reaction samples (a) Co$_3$ZnN-400, Co$_3$ZnN-500, Ni$_3$ZnN-400 and Ni$_3$ZnN-500 and (b) Co$_3$InN-400, Co$_3$InN-500, Ni$_3$InN-400 and Ni$_3$InN-500.
Table 1. Physical characteristics of the $A_3BN$ anti-perovskite nitrides

| Compound    | Lattice parameter (Å) | N content$^a$ (wt%) | $A/B$ molar ratio$^d$ | SSA$^e$ (m$^2$ g$^{-1}$) |
|-------------|------------------------|---------------------|-----------------------|--------------------------|
|             |                        | Theoretical$^c$     | As prepared           | Post reacted at 400 °C   | Post reacted at 500 °C   |                      |
| Co$_3$ZnN  | 3.7585(2)              | 5.47                | 5.28 ± 0.03           | 0.66 ± 0.01              | 0.06 ± 0.01              | 3.40 ± 0.20          |
| Ni$_3$ZnN  | 3.76481(8)             | 5.48                | 5.30 ± 0.03           | 1.21 ± 0.01              | 0.03 ± 0.01              | 3.27 ± 0.14          |
| Co$_3$InN  | 3.85672(8)             | 4.58                | 5.07 ± 0.08           | 4.04 ± 0.02              | 2.09 ± 0.02              | 3.70 ± 0.50          |
| Ni$_3$InN  | 3.85830(6)             | 4.59                | 4.61 ± 0.01           | 2.72 ± 0.02              | 0.05 ± 0.01              | 3.36 ± 0.08          |

$^a$Calculated on the basis of the ideal cubic perovskite structure (Space group: $Pm-3m$; $Z = 1$).

$^b$Determined by elemental analysis. $^c$Estimated on the basis of $A_3BN$ composition ($A$ = Co Ni, $B$ = Zn, In). $^d$Evaluated by EDX. $^e$Evaluated by BET analysis.

Table 2. Ammonia production yields of the anti-perovskite nitrides

| compound | Ammonia production (μmol-NH$_3$ g$^{-1}$)   |
|----------|--------------------------------------------|
|          | Theoretical$^c$ | 400 °C | 500 °C |
| Co$_3$ZnN | 3770            | 3069   | 3491   |
| Ni$_3$ZnN | 3784            | 2925   | 3461   |
| Co$_3$InN | 3620            | 289    | 1523   |
| Ni$_3$InN | 3291            | 1029   | 2804   |

$^a$Estimated on the basis of N content in the as prepared samples. $^b$Determined from the decrease in the conductivity of the H$_2$SO$_4$ solution ($0.00108$ M) through which the reaction vent gas was flowed.