



**HAL**  
open science

# Experimental screening of metal nitrides hydrolysis for green ammonia synthesis via solar thermochemical looping

Stéphane Abanades, Bertrand Rebiere, Martin Drobek, A. Julbe

► **To cite this version:**

Stéphane Abanades, Bertrand Rebiere, Martin Drobek, A. Julbe. Experimental screening of metal nitrides hydrolysis for green ammonia synthesis via solar thermochemical looping. *Chemical Engineering Science*, 2024, 283, pp.119406. 10.1016/j.ces.2023.119406 . hal-04251780

**HAL Id: hal-04251780**

**<https://hal.science/hal-04251780v1>**

Submitted on 20 Oct 2023

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# Experimental screening of metal nitrides hydrolysis for green ammonia synthesis via solar thermochemical looping

Stéphane Abanades<sup>1\*</sup>, Bertrand Rebiere<sup>2</sup>, Martin Drobek<sup>2</sup>, Anne Julbe<sup>2</sup>

<sup>1</sup> CNRS; Processes, Materials and Solar Energy laboratory (PROMES); 7 rue du Four Solaire; 66120 Odeillo Font-Romeu; France

<sup>2</sup> Institut Européen des Membranes (IEM); CNRS, ENSCM, Univ Montpellier; Place Eugène Bataillon; 34095 Montpellier; France

\* Corresponding author: stephane.abanades@promes.cnrs.fr

## Abstract

Ammonia is a fundamental chemical commodity for fertilizer and as a novel energy vector. Solar-driven ammonia synthesis is proposed as a sustainable alternative to the catalytic energy-intensive and CO<sub>2</sub>-emitting Haber-Bosch process. The considered thermochemical process aims to produce ammonia from nitrogen and water ( $N_2+3H_2O\rightarrow 2NH_3+1.5O_2$ ) via redox cycles using a solar heat source, thus bypassing the supply of H<sub>2</sub> or electricity. Metal oxide/nitride redox pairs can be employed for this cyclic process. The exothermal hydrolysis reaction of nitrides produces ammonia ( $M_xN_y+3H_2O\rightarrow 2NH_3+M_xO_y$ ), and is followed by one or several regeneration steps ( $M_xO_y+N_2\rightarrow M_xN_y+3/2O_2$ ) requiring a heat supply from concentrated solar energy. This study aims to experimentally identify the most suitable metal nitrides in the hydrolysis step for ammonia synthesis based on solar-driven chemical-looping. As a result, FeN, CrN, BN, and Si<sub>3</sub>N<sub>4</sub> turned out to be irrelevant candidates for NH<sub>3</sub> production, as the hydrolysis yield was poor up to 1000°C. In contrast, AlN, Li<sub>3</sub>N, Ca<sub>3</sub>N<sub>2</sub>, Mg<sub>3</sub>N<sub>2</sub>, TiN, and ZrN exhibited noteworthy reactivity depending on the temperature. The hydrolysis rate of AlN was significantly enhanced only above 1100°C, TiN showed an increasing NH<sub>3</sub> production rate with temperature (reaching 3.4 mmol/min/g at 1000°C), while an optimum at 750°C was unveiled for complete ZrN conversion (corresponding to the highest rate of 34.2 mmol/min/g). Hydrolysis of Li<sub>3</sub>N, Ca<sub>3</sub>N<sub>2</sub>, and Mg<sub>3</sub>N<sub>2</sub> was complete at lower temperatures (~200°C), with NH<sub>3</sub> yields of 5.9, 4.9, and 18.6 mmol/g, respectively. Solar-driven regeneration of metal nitrides at high temperature will be then necessary to demonstrate the complete feasibility of thermochemical cycles for green ammonia synthesis.

**Keywords:** ammonia synthesis, solar fuel, metal nitrides, chemical-looping, thermochemical cycles, hydrogen carrier.

## 1. Introduction

Ammonia is one of the most produced industrial chemical compounds with a current production of 168.1 million tons and annual growth of more than 2% to reach 197.2 million tons in 2026 (Mordor Intelligence LLP, 2021). Ammonia is a fundamental component of ammonium nitrate fertilizer. Hence, the main application sector is that of fertilizers for agriculture, while new applications as an energy carrier or as an effective means of hydrogen storage (Aziz et al., 2020) show a growing interest in proposing alternatives to fossil fuels. An increasing demand in ammonia is thus foreseen in the future. Ammonia as a clean fuel (and hydrogen carrier/vector) is promising since it can be stored more easily than hydrogen in the liquid form (NH<sub>3</sub> boiling point = -33.4 °C at 1 atm versus -253 °C for H<sub>2</sub>) and it offers a higher volumetric energy density (12.7 MJ/L) than liquid hydrogen (8.5 MJ/L). Furthermore, vast ammonia infrastructure already exists due to its extensive use for fertilizers.

The search for carbon-free alternatives and less energy-intensive solutions for NH<sub>3</sub> production represents a major challenge for the years to come. Indeed, ammonia is currently produced by the Haber-Bosch process ( $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ ,  $\Delta H^\circ = -91.9 \text{ kJ mol}^{-1}$ ) developed more than a century ago, which is highly energy-intensive and generates greenhouse gas (GHG) emissions (2.2 tons CO<sub>2</sub> / ton NH<sub>3</sub> (Rafiqul et al., 2005)). The ammonia production represents about 2% of the world consumption of fossil energy and generates over 420 million tons of

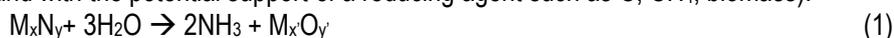
54 CO<sub>2</sub> per year, thus representing 1.2% of global anthropic CO<sub>2</sub> emissions (Liu et al., 2020). The Haber-Bosch  
55 process consists in reacting hydrogen (H<sub>2</sub>) with nitrogen (N<sub>2</sub>) using catalysts at high temperatures and pressures  
56 (400/650°C – 200/400 bars) and relies on fossil fuels. Indeed, the hydrogen required for the synthesis of ammonia  
57 is currently produced by steam reforming of natural gas, while N<sub>2</sub> is obtained by cryogenic separation of air. Both  
58 of these processes require a large input of energy, causing significant concomitant GHG emissions. Specific studies  
59 have been proposed to improve the efficiency of NH<sub>3</sub> synthesis unit by associating a tri-reforming reactor with a  
60 membrane unit (Damanabi et al., 2019). However, the use of ammonia as an energy carrier cannot be considered  
61 as a decarbonized source when using hydrogen of fossil origin. It is thus necessary to develop alternatives to the  
62 Haber-Bosch process. In order to make ammonia a sustainable energy carrier in the future, the decarbonation of  
63 its production and the use of a renewable energy source are necessary. The decarbonation of ammonia production  
64 can be achieved by using green hydrogen (produced by electrolysis) or by directly producing ammonia via new  
65 electrochemical or thermochemical processes. However, with the increasing deployment of hydrogen as an energy  
66 carrier in the transport sector or for industrial applications (e.g., for direct reduced iron and steel metallurgy (Bhaskar  
67 et al., 2020; Patisson and Mirgoux, 2020)), it becomes necessary to develop alternatives for ammonia production  
68 in order to avoid consuming the green hydrogen feedstocks that will be produced. The direct use of H<sub>2</sub> in the  
69 process should therefore be avoided, while preferring production from nitrogen and water.

70  
71 To avoid using the Haber-Bosch process, the synthesis of ammonia from renewable energies must be developed  
72 on an industrial scale (Wang et al., 2018). Accordingly, the primary energy source can be used either in the form  
73 of electricity or in the form of heat. The solar-driven production of ammonia by directly using the heat generated by  
74 solar concentrating systems with a higher energy conversion efficiency than electrolysis (because it is not limited  
75 by the efficiency of the intermediate electricity production) appears to be an ideal solution (Abanades, 2023). This  
76 method is advantageous because it can potentially produce ammonia from N<sub>2</sub> and H<sub>2</sub>O without electricity input or  
77 hydrogen consumption. The overall reaction is however highly endothermic ( $\text{N}_2 + 3\text{H}_2\text{O} \rightarrow 2\text{NH}_3 + \frac{3}{2}\text{O}_2$ ,  $\Delta H^\circ =$   
78  $633.6 \text{ kJ/mol}$ ), it cannot occur spontaneously due to the high stability of nitrogen and requires a significant energy  
79 input (either heat or electricity). Therefore, the use of concentrated solar energy for providing the reaction enthalpy  
80 represents a major interest. This reaction corresponds to the reverse of NH<sub>3</sub> combustion, achievable thanks to  
81 contribution of solar energy.

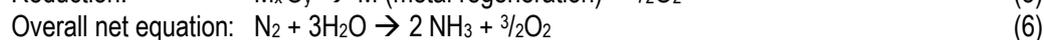
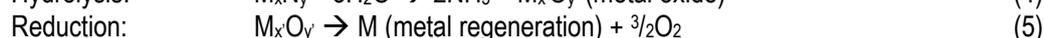
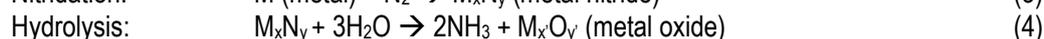
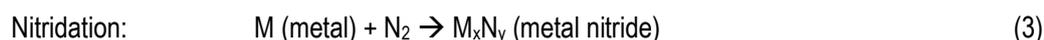
82  
83 Various alternative methods of ammonia production under mild conditions have been proposed, especially for solar  
84 energy integration in low-pressure green ammonia production technologies (Klaas et al., 2021). Possible processes  
85 include solid state synthesis, molten salt synthesis, thermochemical looping and photocatalytic routes.  
86 Electrochemical processes based on green electricity produced by renewable energies have been studied to  
87 synthesize ammonia, among which one can cite solid-state ammonia synthesis (SSAS) (Kishira et al., 2017;  
88 Kyriakou et al., 2017; Marnellos et al., 2000; Marnellos and Stoukides, 1998; Qing et al., 2016) or synthesis by  
89 means of molten salts (Murakami et al., 2005a, 2005b, 2003). Such electrochemical processes require electrodes  
90 and an electrolyte (solid or molten salts) and have the advantage of not requiring high pressures. However, in some  
91 electrochemical processes, the synthesis still makes use of N<sub>2</sub> and H<sub>2</sub>, it is thus necessary to privilege the processes  
92 rather based on the use of N<sub>2</sub> and water. Among the main drawbacks of such processes, it can be noticed that the  
93 electrodes generally include noble metals (Pd, Pt, Ru) (Ceballos et al., 2021), the NH<sub>3</sub> production rates are low,  
94 and the overall efficiency of the process remains limited by the conversion of the primary energy source into  
95 electricity. Other routes have considered the chemical looping of metal nitrides consisting of a reduction of N<sub>2</sub> with  
96 a looped metal nitride ( $\text{M}_a\text{N}_{b-\delta} + \delta/2 \text{N}_2 \rightarrow \text{M}_a\text{N}_b$ ), followed by separate hydrogenation of the lattice nitrogen in  
97 ammonia ( $\text{M}_a\text{N}_b + 3\delta/2 \text{H}_2 \rightarrow \text{M}_a\text{N}_{b-\delta} + \delta \text{NH}_3$ ) (Daisley and Hargreaves, 2023; Goto et al., 2021; Hunter et al., 2010;  
98 Laassiri et al., 2018; Michalsky et al., 2015a; Yang et al., 2022). However, such a process still relies on the use of  
99 H<sub>2</sub> as feedstock, since the net reaction remains unchanged ( $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$ ), and the exothermicity of this global  
100 reaction makes the use of solar energy less attractive.

101  
102 As an alternative to the Haber-Bosch process and the electrochemical synthesis of ammonia, this study aims to  
103 develop thermochemical processes for the production of ammonia from N<sub>2</sub> and H<sub>2</sub>O, using concentrated solar  
104 energy as a high-temperature heat source. Previous works have already been devoted to the development of solar-  
105 driven thermochemical redox cycles for water splitting to produce hydrogen (Abanades, 2022; Haeussler et al.,  
106 2019; Le Gal and Abanades, 2011; Xiao et al., 2012). Reduction of metal oxides using high-temperature solar heat  
107 has also been proved to be feasible (Chambon et al., 2010a, 2010b; Chuayboon and Abanades, 2019). Similarly,  
108 metal oxide/nitride redox cycles can be proposed. Chemical-looping ammonia production pathways have been

reviewed (Lai et al., 2022). The ammonia synthesis reaction from water and nitrogen can be decomposed into several steps, with high-temperature heat supplied by concentrated solar radiation as the only energy input. Such cycles for solar thermochemical ammonia production can be operated in two or three steps, using different reactive intermediate materials participating in the reactions. This makes possible the ammonia synthesis under milder conditions (atmospheric pressure and temperatures compatible with concentrated solar energy). For instance, two-step cycles involve a reaction of metal nitride with water vapour to produce ammonia and the metal oxide (Eq. 1), followed by an endothermic step (Eq. 2) corresponding to the regeneration of metal nitride from the nitridation reaction of the oxide with N<sub>2</sub> (and with the potential support of a reducing agent such as C, CH<sub>4</sub>, biomass).



A three-step cycle based on the metal oxide/nitride redox pair can also be considered with the same overall net reaction (Klaas et al., 2021) (note that equations are not balanced as they depend on the redox pair involved):



The main advantages of such cycles include: (i) the absence of a fossil energy source allowing the decarbonation of ammonia production, (ii) the use of hydrogen as a reactant is not required, (iii) the reaction carried out at atmospheric pressure, (iv) the absence of expensive catalysts and material consumption as the reactive materials are cycled, (v) the direct use of solar energy as a process heat source without intermediate production of electricity, thereby enhancing overall energy conversion efficiencies. Recent theoretical studies have identified possible oxide/nitride redox couples (Bartel et al., 2019), but to date very few experimental studies have demonstrated the feasibility of solar ammonia production by thermochemical cycles. Nitrides of chromium, aluminum, lithium, molybdenum and manganese were previously proposed and studied experimentally (Gálvez et al., 2008; Jain et al., 2017; Michalsky et al., 2015b; Michalsky and Pfromm, 2011). However, there is no available comprehensive experimental study comparing the ability of various nitrides to produce ammonia. In addition, high-throughput equilibrium analysis and computational screening were also performed for rapid identification of candidate materials (Bartel et al., 2019; Michalsky and Steinfeld, 2017). Regarding the synthesis of nitrides (regeneration step), the solar carbothermal reduction of metal oxides (Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, and ZrO<sub>2</sub>) in N<sub>2</sub> to produce nitrides was demonstrated (Murray et al., 1995), which confirmed the feasibility of nitrides synthesis from their oxides at high temperatures with the addition of a reducing agent. The economics and scale-up ability of the technology have been assessed (Gálvez et al., 2007b; Michalsky et al., 2012).

Solar ammonia production via thermochemical cycles based on metal nitrides is a suitable means for the decarbonation of the industrial process, reducing both its environmental impact and its energy/economic costs. Several innovative aspects of this approach can be mentioned. The solar process considered for ammonia production avoids the direct use of hydrogen as a feedstock, while being a green process without electricity supply. The cycles are solely based on metal nitrides as intermediate compounds and on solar heat for NH<sub>3</sub> production from N<sub>2</sub> and H<sub>2</sub>O as the only feedstocks. The development of active metal nitride materials for the hydrolysis step to synthesize NH<sub>3</sub> with high yields and the high-temperature solar-driven regeneration for the nitridation step are the main challenges for process performance enhancement, paving the way to industrial applications.

In particular, the reactivity of nitrides during hydrolysis must first be demonstrated experimentally to identify suitable candidates for solar ammonia synthesis. Experimental screening of metal nitrides hydrolysis has never been done before. There is no study comparing the reactivity of different nitrides in the literature. In addition, their ability to produce ammonia during hydrolysis must be quantified and suitable operating conditions must be identified for each candidate material. In this study, a series of metal nitrides was thus selected for an experimental screening of their reactivity towards the production of NH<sub>3</sub>. The aim was to identify the most suitable metal nitrides in the hydrolysis step to synthesize NH<sub>3</sub> with high yields and production rates. The reaction conversion, hydrolysis rate, and ammonia production capacity were evaluated by investigating the direct reaction of nitride powders with steam in a packed-bed reactor, and the influence of temperature was probed. Ammonia production was directly measured and quantified via continuous evolved gas analysis. Active metal nitride candidates with their corresponding performance for ammonia synthesis were identified.

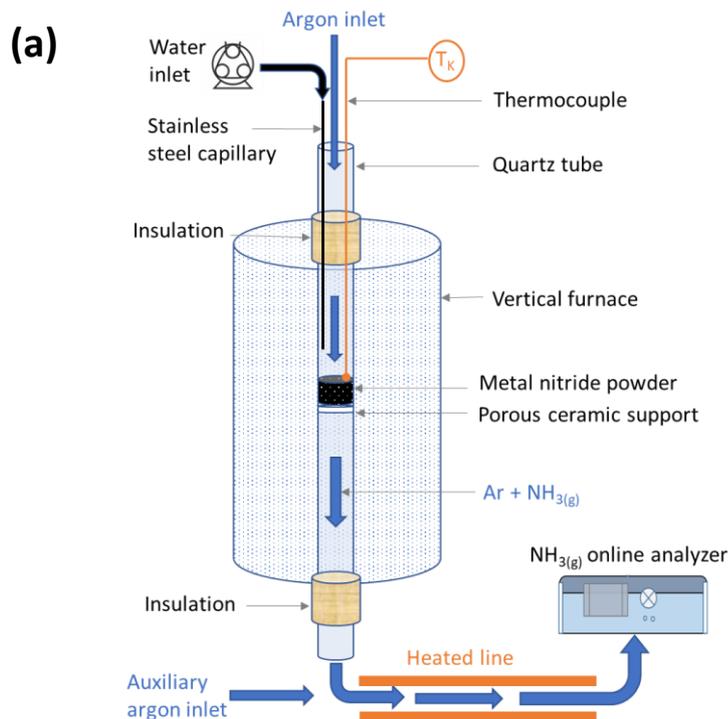
164  
165  
166  
167  
168  
169  
170  
171  
172  
173  
174  
175  
176  
177  
178  
179  
180  
181  
182  
183  
184  
185  
186  
187  
188  
189

## 2. Experimental set-up and methods

### 2.1 Experimental bench

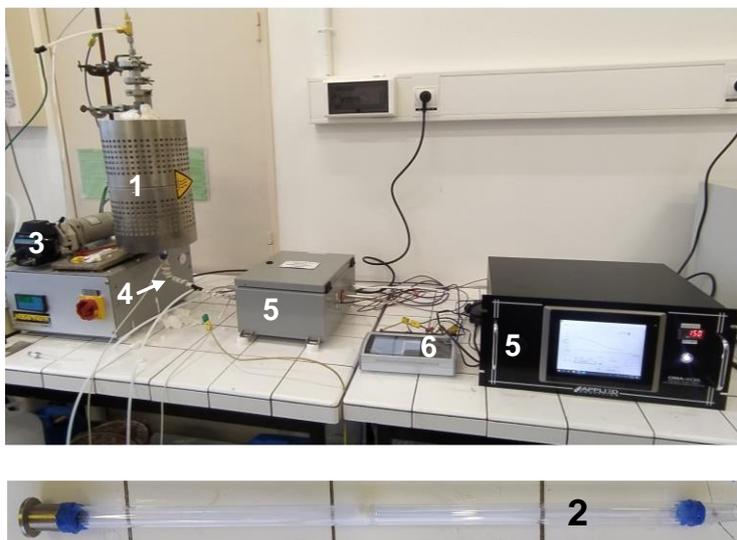
An experimental bench dedicated to the study of the hydrolysis step of metal nitrides with continuous evolved gas analysis has been specifically developed to perform nitrides screening and compare  $\text{NH}_3$  production rates. The experimental set-up (Figure 1) is composed of a vertical tubular furnace to study the production of  $\text{NH}_3$  at different temperatures. A tubular quartz reactor is placed inside the furnace. The metal nitride powder is loaded as a packed-bed ( $\sim 0.1\text{-}0.5\text{ g}$ ) inside the vertical tubular furnace in the center of the quartz tube (16 mm inside diameter, middle of the tube 175 mm from the ends) and supported by a porous ceramic (zirconia felt).

The reactor is connected to a gas inlet to inject the carrier gas (Ar, 99.999% purity) with a flow-rate controlled by a mass-flow controller (MFC, Brooks, range 0-1 NL/min). A stainless-steel capillary is placed inside the quartz tube to inject water vapor using a calibrated peristaltic pump (for liquid water flow-rate control). The water is then vaporized as it flows through the capillary and exits as steam which is transported by the Ar carrier gas through the powder bed. At the quartz tube outlet, a heated line ( $T > 120^\circ\text{C}$ ) is used to sample the exhaust gases towards an  $\text{NH}_3$  analyzer, avoiding any condensation of steam in which the soluble  $\text{NH}_3$  could be trapped. On this outlet, an auxiliary Ar input (MFC, Brooks, range 0-5 NL/min) is connected for the dilution of the  $\text{NH}_3$  concentration in order to maintain it within the detection range of the analyzer. The maximum  $\text{NH}_3$  concentration reached also depends on the initial mass of loaded nitride in the reactor, which must be thus controlled to avoid peak saturation. The exiting gas is analyzed using a dedicated UV-vis spectrophotometer (OMA-406, Applied Analytics, measurement cell heated to  $150^\circ\text{C}$ , range: 0-10000 ppm, calibrated with 5000 ppm  $\text{NH}_3$  calibration gas) to continuously measure the ammonia concentration during hydrolysis and monitor the progress of the reaction (one measurement performed every 5 s). The reaction temperature is measured by a K-type thermocouple reaching inside the powder bed. Both the sample bed temperature and the  $\text{NH}_3$  concentration are recorded continuously by data acquisition with a time step of 1 s.



190  
191  
192

(b)



193

194

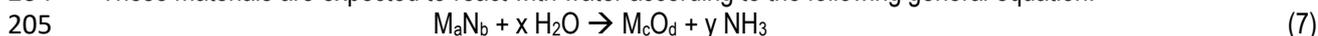
195 **Figure 1.** Experimental hydrolysis reactor and set-up: (a) Schematic of the packed-bed of commercial nitride  
196 powder in a vertical tubular furnace with continuous NH<sub>3</sub> analysis in the exit gas, (b) Photograph of the set-up (1.  
197 Tubular furnace; 2. Quartz tube reactor; 3. Peristaltic pump; 4. Heated line; 5. NH<sub>3</sub> analyzer; 6. Acquisition  
198 system).

199

## 200 2.2 Materials and methods

201 A series of ten commercial metal nitrides (Sigma Aldrich) was selected to investigate the hydrolysis reaction: AlN  
202 (purity ≥98%, metals basis), Li<sub>3</sub>N (99.4%), Ca<sub>3</sub>N<sub>2</sub> (99%), Mg<sub>3</sub>N<sub>2</sub> (99.6%), TiN (≥99.7%), CrN (Cr<sub>2</sub>N+CrN, ≥99.5%),  
203 Fe<sub>x</sub>N (x=2-4, ≥99.7%), BN (≥99.7%), Si<sub>3</sub>N<sub>4</sub> (99.9%), and ZrN (99.5%).

204 These materials are expected to react with water according to the following general equation:



206 Each material was thus tested during the hydrolysis reaction to compare the NH<sub>3</sub> production yields and the reaction  
207 rates at different temperatures.

208 The nitridation step was not studied in this work, but the carbothermal reduction of oxides in the presence of N<sub>2</sub>  
209 appears to be a favorable route for the regeneration of nitrides. For instance, the combined carbothermal reduction  
210 and nitridation of Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, SiO<sub>2</sub> and ZrO<sub>2</sub> oxides are thermodynamically possible upon increasing temperature  
211 based on their Gibbs free enthalpy variation (Murray et al., 1995).

212

213 The experimental conditions are summarized in Table S1 (Supplementary Information). The Ar carrier gas flow-  
214 rate was set at 0.2 NL/min and the water vapor flow-rate was 0.224 NL/min. The resulting steam molar content in  
215 the reactor was therefore 52.8%. At the reactor outlet, the gas was diluted with Ar (typically 1.25 NL/min) before  
216 being injected into the analyzer to avoid saturation of the analysis cell and to remain within the suitable  
217 measurement range of the gas analysis system (0-10000 ppm). The nitride mass loaded in the reactor was thus  
218 maintained low enough to avoid excessively high ammonia concentrations in the outlet gas and to prevent signal  
219 saturation, thus warranting reliable online analysis. The amount of NH<sub>3</sub> evolved from the hydrolysis reactions was  
220 quantified, as detailed in the following. The NH<sub>3</sub> mole fraction (y<sub>NH<sub>3</sub></sub>) was measured as a function of time. From  
221 these data, the production rate and the total amount of NH<sub>3</sub> can be calculated as follows:

$$222 Q_{\text{NH}_3} = \frac{y_{\text{NH}_3} \cdot Q_{\text{total}}}{m_{\text{nitride}}} \quad (8)$$

223

224 with Q<sub>NH<sub>3</sub></sub> the NH<sub>3</sub> production rate per unit mass of nitride (mol.min<sup>-1</sup>.g<sup>-1</sup>), y<sub>NH<sub>3</sub></sub> the NH<sub>3</sub> mole fraction at the reactor  
225 outlet, Q<sub>total</sub> the total outlet gas molar flow-rate after dilution (mol/min), and m<sub>nitride</sub> the nitride mass loaded into the  
226 reactor (g).

227

228 Q<sub>total</sub> depends on the studied nitride and the corresponding global reaction equation of the hydrolysis. Indeed, part  
229 of the injected steam is consumed during the reaction producing NH<sub>3</sub>. The outlet gas flow-rate corresponds to the  
230 sum of the outlet flow-rates of argon (Q<sub>Ar</sub>), unreacted steam (Q<sub>H<sub>2</sub>O,outlet</sub>) and NH<sub>3</sub>, and is therefore expressed by:

231  
232 
$$Q_{\text{total}} = Q_{\text{Ar}} + Q_{\text{H}_2\text{O},\text{outlet}} + m_{\text{nitride}} \cdot Q_{\text{NH}_3} \quad (9)$$

233  
234 For example, in the case of  $\text{Mg}_3\text{N}_2$  hydrolysis, the overall equation is given by:  
235 
$$\text{Mg}_3\text{N}_2 + 6 \text{H}_2\text{O} \rightarrow 3 \text{Mg}(\text{OH})_2 + 2 \text{NH}_3 \quad (10)$$
  
236

237 The flow-rate of unreacted steam can then be calculated as follows:  
238 
$$Q_{\text{H}_2\text{O},\text{outlet}} = Q_{\text{H}_2\text{O},\text{inlet}} - 3 \cdot Q_{\text{NH}_3} \quad (11)$$
  
239

240 By combining Eqs. (8), (9), and (11),  $Q_{\text{NH}_3}$  can be expressed as:  
241 
$$Q_{\text{NH}_3} = \frac{y_{\text{NH}_3} \cdot (Q_{\text{Ar}} + Q_{\text{H}_2\text{O},\text{inlet}})}{(1 + 2y_{\text{NH}_3}) \cdot m_{\text{nitride}}} \quad (12)$$
  
242

243 The total amount of  $\text{NH}_3$  produced (mol/g) is calculated by integrating the  $\text{NH}_3$  molar flow-rate over the hydrolysis  
244 step duration.

245 
$$n_{\text{NH}_3} = \int_0^t Q_{\text{NH}_3} \cdot dt \quad (13)$$
  
246

247 The performance metrics including global amounts of generated ammonia and production rates were expressed  
248 per unit mass of metal nitride (Eq. 8 and Eq. 13) for comparison purpose on the same basis.

249 The ammonia yield can then be obtained from:  
250 
$$X_{\text{NH}_3} = \frac{n_{\text{NH}_3}}{n_{\text{NH}_3,\text{max}}} \quad (14)$$
  
251

252 where  $n_{\text{NH}_3,\text{max}}$  is the theoretical maximum amount of  $\text{NH}_3$  calculated from the overall reaction equation.  
253

254 In addition, the structure and microstructure of fresh and hydrolyzed materials were characterized by different  
255 techniques to verify the powders conversion and to confirm that the reactions occur as expected.

256 Crystalline structure and phase identification were studied by X-ray diffraction (XRD) using a Panalytical X'PERT  
257 PRO diffractometer with the Cu K $\alpha$  radiation ( $\alpha_{\text{Cu}} = 0.15406 \text{ nm}$ , angular range =  $20\text{-}80^\circ$ ,  $2\theta$ , tube current 20 mA,  
258 potential 40 kV).

259 The morphology of the materials was observed with a Field Emission Scanning Electron Microscope (FESEM -  
260 Hitachi S4800) used to examine /compare the microstructure of the powders. An elemental chemical analysis  
261 cartography was carried out by EDX analysis (Energy Dispersive X-ray Spectroscopy, using a Zeiss Sigma 300  
262 with an accelerating voltage of 15 keV) to estimate the chemical composition and observe elements distribution  
263 (surface mapping) in the materials.

264  
265 In total, 44 hydrolysis runs were carried out with the experimental set-up in order to characterize the series of 10  
266 metal nitrides considered (Table S1).  
267

### 268 3. Results and discussion

#### 269 3.1 Aluminum nitride (AlN)

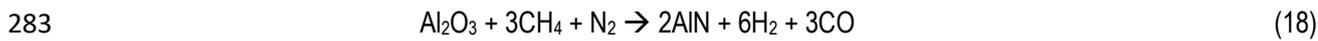
270 The hydrolysis of AlN can be written:  
271 
$$2\text{AlN} + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 2\text{NH}_3 \quad \Delta H^\circ = -274.1 \text{ kJ/mol} \quad (15)$$
  
272  
273

274 The theoretical production corresponds to one mole of  $\text{NH}_3$  per mole AlN, i.e., 24.4 mmol/g or 546.5 mL/g (based  
275 on the  $\text{H}_2$  equivalence, this corresponds to 36.6 mmol $\text{H}_2$ /g).  
276

277 The regeneration of the nitride may be achieved via the following route:  
278 
$$\text{Al}_2\text{O}_3 + \text{N}_2 \rightarrow 2\text{AlN} + \frac{3}{2}\text{O}_2 \quad \Delta H^\circ = 1039.7 \text{ kJ/mol} \quad (16)$$
  
279

280 This highly endothermic reaction is not thermodynamically favorable and the addition of a carbonaceous reducing  
281 agent (carbon or methane (Gálvez et al., 2008, 2007b, 2007a)) is necessary according to:

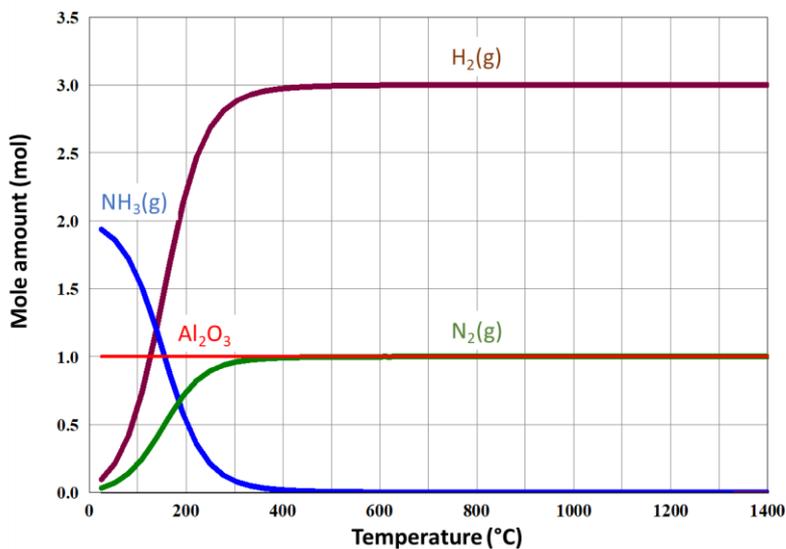
282 
$$\text{Al}_2\text{O}_3 + 3\text{C} + \text{N}_2 \rightarrow 2\text{AlN} + 3\text{CO} \quad (17)$$



284  
285 The solar-driven carbothermal reduction of  $\text{Al}_2\text{O}_3$  in  $\text{N}_2$  atmosphere has also been studied (Murray et al., 1995).

286  
287 Figure 2 shows the equilibrium composition of the  $2\text{AlN} + 3\text{H}_2\text{O}$  system (Eq. 15) as a function of temperature at 1  
288 bar. The hydrolysis reaction producing ammonia is thermodynamically favorable at low temperature (below  
289  $\sim 200^\circ\text{C}$ ), whereas  $\text{NH}_3$  is not stable above  $300^\circ\text{C}$  as it decomposes into  $\text{H}_2$  and  $\text{N}_2$  although a metastable state  
290 may exist without the presence of catalysts. It should be noted that similar thermodynamic equilibrium distributions  
291 are obtained regardless of the metal nitride considered, with  $\text{NH}_3$  being stable only below  $300^\circ\text{C}$ .

292

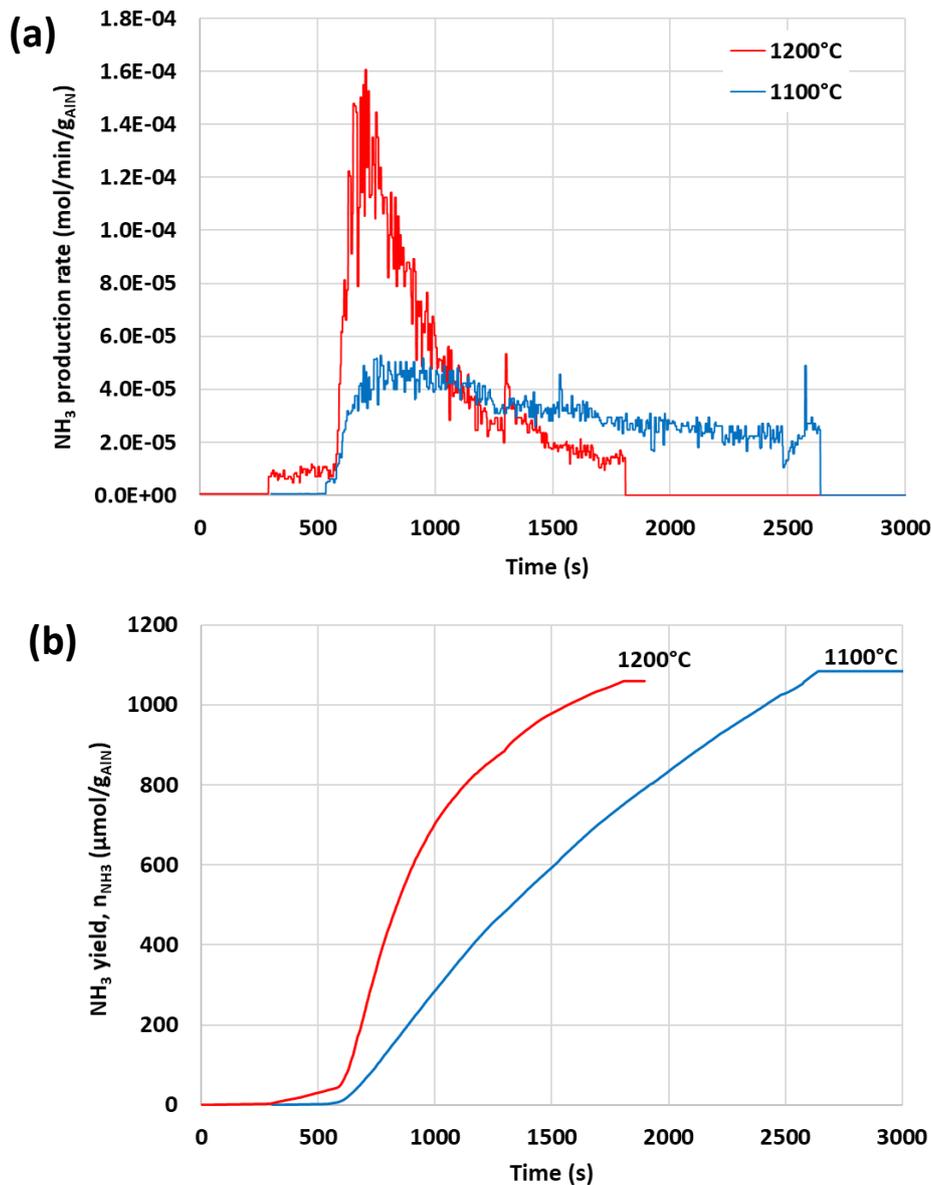


293  
294 **Figure 2.** Thermodynamic equilibrium composition of the  $2\text{AlN} + 3\text{H}_2\text{O}$  system as a function of the temperature at  
295 1 bar.  
296

297 A series of ten AlN hydrolysis runs was carried out at temperatures ranging from  $200^\circ\text{C}$  to  $1200^\circ\text{C}$ . Repeatability  
298 of the results was confirmed through different tests with similar conditions. The initial AlN mass did not significantly  
299 affect the mass-specific amount of ammonia produced (e.g., 1 mmol/g in run #13 vs. 1.1 mmol/g in run #14 at  
300  $1000^\circ\text{C}$ ). Increasing the temperature was found to significantly improve  $\text{NH}_3$  production. Indeed, the  $\text{NH}_3$  production  
301 rate was low below  $1000^\circ\text{C}$ , but it increased drastically above this temperature. This suggests that the reaction is  
302 hindered by kinetic limitations since the increase in temperature favors the reaction kinetics, although the reaction  
303 is not thermodynamically favorable at high temperatures. Actually, the slow kinetics at low temperatures does not  
304 allow thermodynamic equilibrium to be reached in a reasonable reaction time. Figure S1 represents the evolution  
305 of the  $\text{NH}_3$  production rate at  $550^\circ\text{C}$  and  $960^\circ\text{C}$ .  $\text{NH}_3$  was detected right from the steam was injected, with total  
306 production yields ( $n_{\text{NH}_3}$ ) of 0.66 and 0.77 mmol/g, respectively. The  $\text{NH}_3$  concentration reached a peak promptly  
307 then gradually decreased until reaching negligible values. During AlN sample heating, a weak  $\text{NH}_3$  production was  
308 measured around  $200^\circ\text{C}$  even in the absence of  $\text{H}_2\text{O}$  (Fig. S1b), which suggests a reaction of AlN with residual  
309 moisture.

310 Figure 3a shows the evolution of the  $\text{NH}_3$  production rates at  $1100^\circ\text{C}$  (hydrolysis of 155 mg AlN) and  $1200^\circ\text{C}$   
311 (hydrolysis of 156 mg AlN) as a function of time, which confirms the improved kinetics when increasing the  
312 temperature. During hydrolysis at  $1200^\circ\text{C}$ , the peak production rate of  $\text{NH}_3$  reached  $1.6 \cdot 10^{-4}$  mol/min/g versus  $5 \cdot 10^{-5}$   
313 mol/min/g at  $1100^\circ\text{C}$ . The total reaction duration decreased from about 40 min at  $1100^\circ\text{C}$  to 20 min at  $1200^\circ\text{C}$ .  
314 Therefore, heating the reactants favored the  $\text{NH}_3$  production rate although the reaction was thermodynamically less  
315 favorable. The cumulative production of  $\text{NH}_3$  reached about 1.1 mmol/g (which corresponds to an  $\text{NH}_3$  yield  $X_{\text{NH}_3}$   
316 of 4.5%). This total  $\text{NH}_3$  yield remained almost unchanged whatever the temperature (Fig. 3b). The high  
317 temperature necessary to reach a significant hydrolysis rate (above  $1000^\circ\text{C}$ ) can however represent an obstacle  
318 to the implementation of the  $\text{Al}_2\text{O}_3/\text{AlN}$  redox system, given that the  $\text{NH}_3$  yield is not improved above this  
319 temperature.

320



321  
 322  
 323 **Figure 3.**  $\text{NH}_3$  production during AlN hydrolysis at 1100°C and 1200°C: (a) evolution of  $\text{NH}_3$  production rate as a  
 324 function of time, (b) cumulative  $\text{NH}_3$  production as a function of time.  
 325

326 Characterization of the products was carried out to identify the main phases after the hydrolysis reaction and to  
 327 confirm the oxidation of the nitrides during ammonia synthesis upon exposure to steam. XRD analysis of materials  
 328 before and after two hydrolysis tests at 1000°C (Fig. 4) showed that the reaction was not complete because AlN  
 329 was still present in majority after reaction in both tests. In contrast, the products analysis after AlN hydrolysis at  
 330 1100°C and 1200°C (Fig. S2) showed that  $\text{Al}_2\text{O}_3$  was the main species with residual traces of AlN (in lower amount  
 331 at 1200°C than at 1100°C), which confirmed the efficient conversion of AlN to  $\text{Al}_2\text{O}_3$ . Some traces of  $\text{ZrO}_2$   
 332 (tetragonal) were also identified due the zirconia felt used as support for the packed-bed of nitride powder during  
 333 hydrolysis tests (this support could not be completely eliminated during the recovery of the packed-bed powder  
 334 after reaction).  
 335

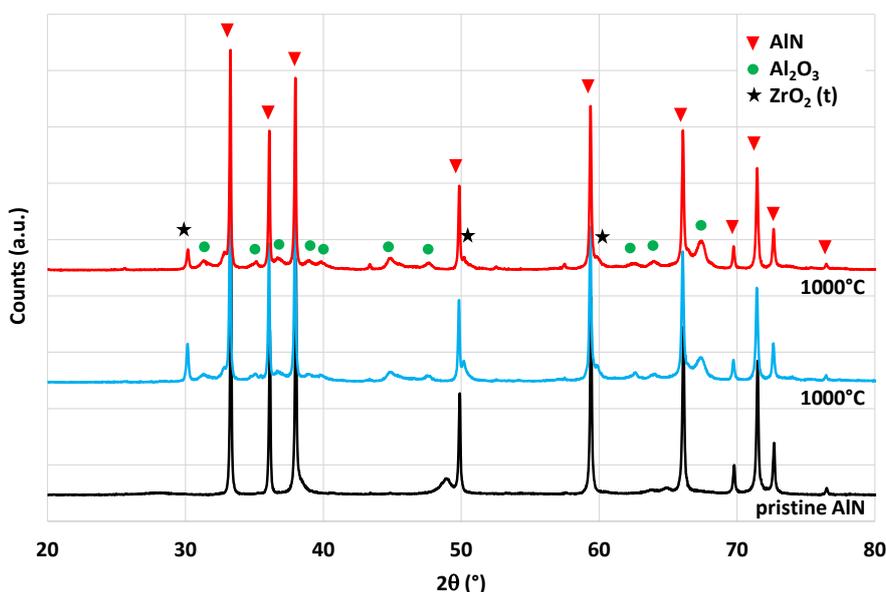


Figure 4. XRD patterns of AlN powders before and after hydrolysis at 1000°C.

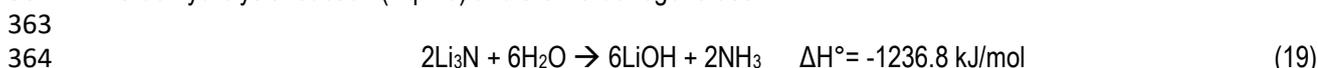
336  
337  
338

339 A semi-quantitative EDX analysis was carried out for the powders collected after hydrolysis at 1100°C and 1200°C  
340 to confirm the complete conversion of the nitride during the reaction. Tables S2-3 report the atomic composition of  
341 the powders on different analysis zones (Figs. S3-4). For both temperatures, the Al/O ratio was close to the atomic  
342 composition of Al<sub>2</sub>O<sub>3</sub> with Al/O = 0.57 at 1100°C and Al/O = 0.69 at 1200°C. The absence of nitrogen (below the  
343 detection limit) also denotes that AlN hydrolysis was complete at these temperatures and AlN was efficiently  
344 converted to Al<sub>2</sub>O<sub>3</sub> after reaction. It should be noted that nitrogen is a light element that is difficult to detect and that  
345 it may be present in an amount lower than the detection limit of the analysis method. Figures S5 and S6 show SEM  
346 micrographs and X-ray elemental mapping of powders after hydrolysis at 1100°C and 1200°C. The distribution of  
347 Al and O is homogeneous, which means that these elements are evenly distributed over the sample surface.  
348 Although complete AlN conversion was observed above 1000°C, the NH<sub>3</sub> production yield was low compared to  
349 the maximum achievable value from Eq. (15), which is explained by the thermal instability of NH<sub>3</sub>. Indeed, ammonia  
350 is not stable at high temperatures according to thermodynamics (Figure 2) and can decompose into N<sub>2</sub> and H<sub>2</sub>. The  
351 NH<sub>3</sub> yield was therefore likely limited by the thermodynamically favorable dissociation of NH<sub>3</sub>. These results are  
352 consistent with previous kinetic studies performed by thermogravimetric analysis (Gálvez et al., 2007a), in which a  
353 reaction conversion close to 95% was reported at 1100°C and 1200°C, and 68% at 950°C using a mixture 80%  
354 H<sub>2</sub>O-Ar. However, the reaction rate was drastically reduced under 10% H<sub>2</sub>O-Ar with a reaction extent of 40% at  
355 1200°C after 20 min (complete reaction after ~100 min) and 20% at 1100°C after 30 min. This study also reported  
356 a maximum NH<sub>3</sub> yield of 88% obtained at 1000°C for a reaction extent of 93%, which decreased at higher  
357 temperatures. Importantly in this study, ammonia was not directly detected and measured by gas analysis, but  
358 indirectly quantified by mass balance.

359  
360

### 3.2 Lithium nitride (Li<sub>3</sub>N)

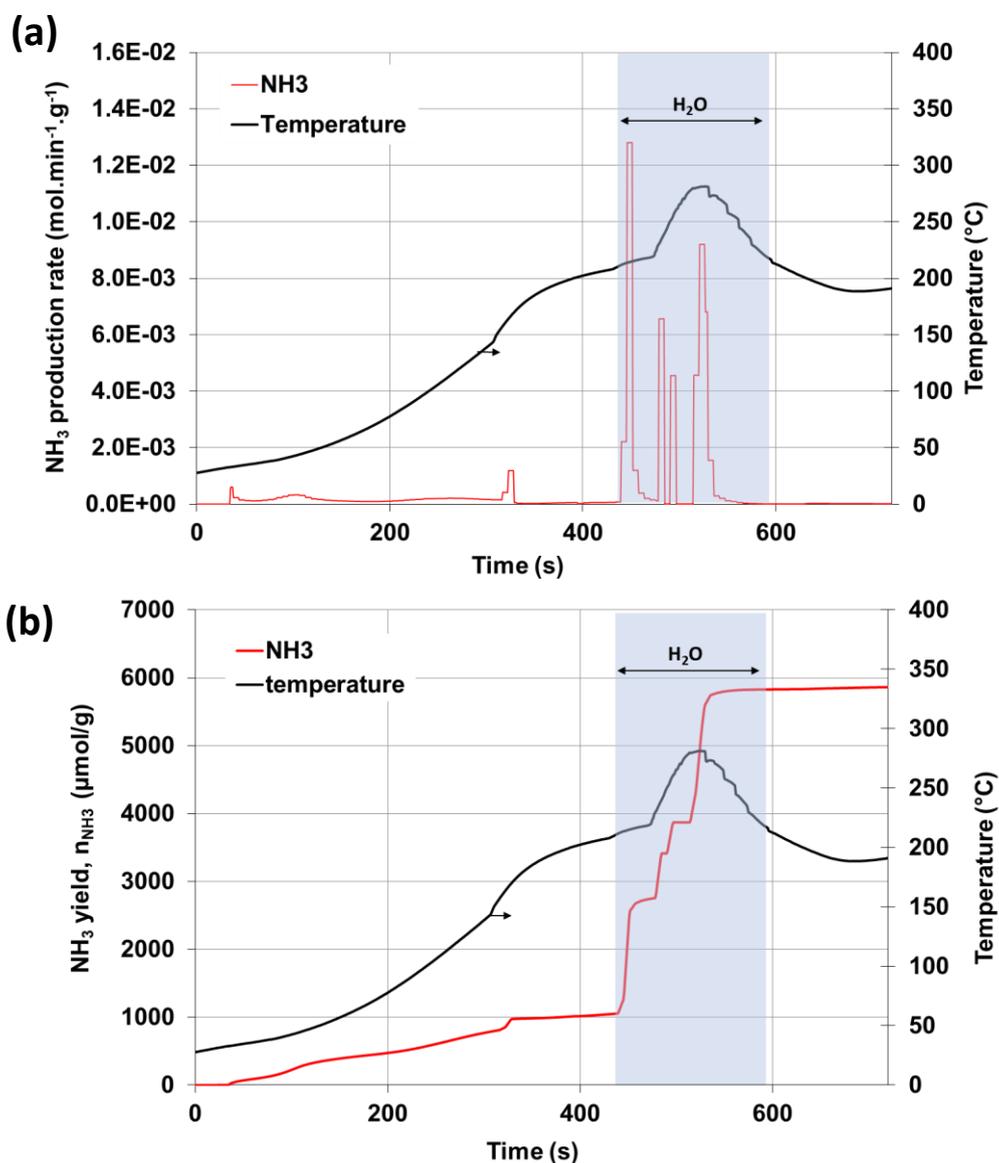
361 The synthesis of ammonia from lithium nitride was considered by Jain et al. (Jain et al., 2017), considering both the  
362 nitride hydrolysis reaction (Eq. 19) and the nitride regeneration.



366 The theoretical amount of NH<sub>3</sub> produced corresponds to one mole NH<sub>3</sub> per mole Li<sub>3</sub>N, thus 28.7 mmol/g (642.9  
367 mL/g) and 43.1 mmol<sub>H<sub>2</sub></sub>/g relative to the H<sub>2</sub> equivalence. Lithium is a light element, which results in a high mass-  
368 specific NH<sub>3</sub> production potential, relative to the mass of material.

369  
370 Figure 5a shows the evolution of the NH<sub>3</sub> production rate during Li<sub>3</sub>N hydrolysis (107 mg) at 200°C. The reaction  
371 rate was fast and several successive peaks in NH<sub>3</sub> production were observed due to unstable steam injection  
372 caused by discontinuous droplet feeding. The hydrolysis reaction was completed in less than 2 min. The maximum  
373 NH<sub>3</sub> production rate reached 1.28.10<sup>-2</sup> mol/min/g and the total NH<sub>3</sub> yield reached 5.9 mmol/g (Figure 5b),

374 corresponding to a hydrolysis yield of 20.3%. A prompt and substantial increase in temperature (+80°C) was also  
 375 observed during the reaction, which can be attributed to the heat generated by the strongly exothermic reaction.  
 376 As a result, the product was sintered but could be recovered for solid phase characterization. According to XRD  
 377 (Fig. S7), the  $\text{Li}_3\text{N}$  powder was totally converted after hydrolysis with the presence of  $\text{LiOH}$  phase. These results  
 378 are in agreement with previous work on the reaction of lithium nitride with water vapor at 100°C showing major  
 379 formation of  $\text{NH}_3$  detected by gas chromatography (Jain et al., 2017).  
 380



381  
 382 **Figure 5.**  $\text{NH}_3$  production during  $\text{Li}_3\text{N}$  hydrolysis at 200°C: (a) evolution of  $\text{NH}_3$  production rate as a function of  
 383 time, (b) cumulative  $\text{NH}_3$  production as a function of time.  
 384  
 385

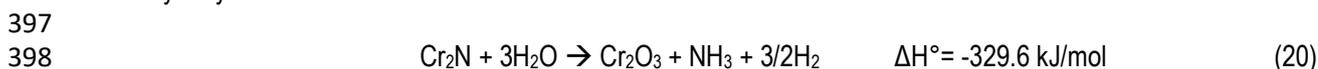
### 386 3.3 Chromium ( $\text{Cr}_2\text{N}/\text{CrN}$ ), boron (BN), iron ( $\text{Fe}_x\text{N}$ ), and silicon ( $\text{Si}_3\text{N}_4$ ) nitrides

387 Chromium, iron, boron, and silicon nitrides did not show a high reactivity during hydrolysis regardless of the  
 388 temperature considered. Experimental results for the hydrolysis of these nitrides are given in the following without  
 389 detailed characterization as they were not identified as suitable candidates for ammonia production.  
 390

391 Chromium nitride was previously considered for solar ammonia production (Michalsky and Pfromm, 2011). The  
 392 reduction of  $\text{Cr}_2\text{O}_3$  was carried out in  $\text{N}_2$  with the help of a reducing agent such as  $\text{CO}$  or  $\text{H}_2$ , resulting in the formation  
 393 of a  $\text{CrN}$  and  $\text{Cr}_2\text{N}$  mixture. Then, a small amount of  $\text{NH}_3$  was measured during hydrolysis in this previous work,

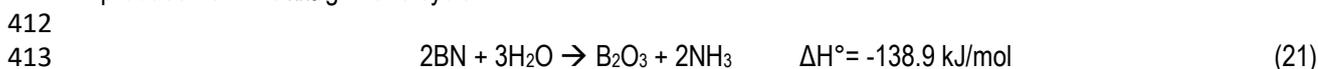
394 which was attributed to the slow corrosion kinetics of this nitride (also well known for its application as a protective  
395 coating).

396 The hydrolysis reaction can be written as follows:



399  
400 The hydrolysis of commercial chromium nitride (520 mg) composed of a mixture of Cr<sub>2</sub>N and CrN phases (Fig. S8,  
401 mean Cr/N atomic ratio of 1.7 measured by EDX) was investigated at temperatures of 570°C and 950°C. Figure  
402 S9a shows the NH<sub>3</sub> production profile as a function of time with steam injections at 570°C and 950°C. Whatever  
403 the temperature, the NH<sub>3</sub> production remained very low with peak production rates of 1.10<sup>-6</sup> mol/min/g and 7.8.10<sup>-6</sup>  
404 mol/min/g at 570°C and 950°C, respectively. The cumulated value of NH<sub>3</sub> production during CrN hydrolysis was  
405 also weak and did not exceed 10 μmol/g (Figure S9b). These results are in agreement with previous studies  
406 (1.07×10<sup>-4</sup> mol NH<sub>3</sub>/mol Cr/min reported by Michalsky and Pfromm, 2011) and the main reason for this low  
407 production was attributed to the preferential formation of N<sub>2</sub> by nitride decomposition instead of NH<sub>3</sub> formation.

408  
409 Boron nitride was identified in a theoretical study as a potential candidate material for solar thermochemical NH<sub>3</sub>  
410 synthesis (Bartel et al., 2019). Equilibrium calculations identified the BN/B<sub>2</sub>O<sub>3</sub> redox couple with the ability to  
411 produce 10 mmol<sub>NH<sub>3</sub></sub>/g in one cycle.



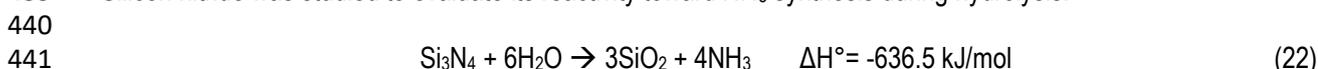
414  
415 In order to experimentally test the feasibility of ammonia synthesis, the hydrolysis of commercial boron nitride (198  
416 mg) was carried out in this work at different temperatures (pure cubic BN phase was identified by XRD, Fig. S8).  
417 Figure S10a shows the NH<sub>3</sub> production profile at 370°C, 700°C, and 970°C. As a result, very weak production rates  
418 were observed at the lowest temperatures while a peak production rate of 1.10<sup>-5</sup> mol/min/g was reached at 970°C.  
419 However, the cumulated production yield remained low with only 31 μmol<sub>NH<sub>3</sub></sub>/g (Figure S10b). After the reaction,  
420 the material was vaporized and could not be recovered. Therefore, contrary to theoretical predictions, boron nitride  
421 did not show suitable hydrolysis reactivity for ammonia synthesis at the different temperatures studied.

422  
423 Iron nitride was also previously identified as a potential material for ammonia synthesis (Bartel et al., 2019) and  
424 was thus considered in this work. Commercial iron nitride is labeled with a Fe<sub>x</sub>N composition (x in the range 2-4).  
425 A mean Fe/N atomic ratio of 3.2 was measured by EDX. A phase mixture of mainly Fe<sub>4</sub>N with Fe<sub>3</sub>N was identified  
426 by XRD (Fig. S8).

427 The NH<sub>3</sub> production profile from Fe<sub>x</sub>N (400 mg) at 250°C, 550°C, and 1000°C is shown in Figure S11. At 250°C,  
428 no production was detected. At 550°C, a peak of NH<sub>3</sub> production was measured with a maximum value at 3.2.10<sup>-4</sup>  
429 mol/min/g but no further NH<sub>3</sub> was significantly observed at 1000°C. The total cumulative production of NH<sub>3</sub> at 550°C  
430 was 230 μmol/g (Figure S11b), which remains well below the theoretically predicted 10 mmol/g. In addition, part of  
431 the material was melted and sublimated after the test (rust-colored deposit on the walls of the quartz tube denoting  
432 the presence of Fe<sub>2</sub>O<sub>3</sub>).

433 XRD analysis of the material after hydrolysis was carried out (Figure S12), which revealed the presence of different  
434 iron oxide phases (FeO, Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub>), without any nitride phase being detected. This shows that NH<sub>3</sub>  
435 production is not correlated to the oxidation state of the material after hydrolysis. In other words, ammonia formation  
436 may not occur even if the material is fully oxidized after hydrolysis. The nitrogen released can indeed form species  
437 other than NH<sub>3</sub> (such as N<sub>2</sub>) or NH<sub>3</sub> can be thermally decomposed before exiting the reactor.

438  
439 Silicon nitride was studied to evaluate its reactivity toward NH<sub>3</sub> synthesis during hydrolysis.



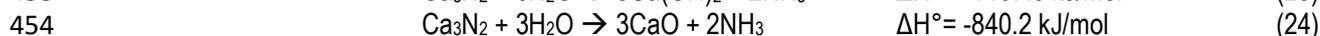
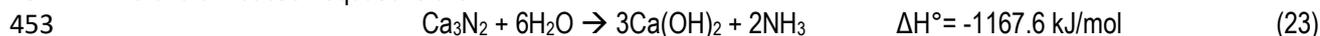
442  
443 Figure S13a shows the NH<sub>3</sub> production profile during three consecutive hydrolysis tests of Si<sub>3</sub>N<sub>4</sub> (322 mg) at 220°C,  
444 520°C, and 980°C. Peaks of NH<sub>3</sub> production rate were observed at the three temperatures and reached 9.10<sup>-6</sup>,  
445 2.1.10<sup>-4</sup> and 2.6.10<sup>-4</sup> mol/min/g, respectively. The production rate was enhanced when the temperature increased.  
446 The cumulative amounts of NH<sub>3</sub> remained low for each temperature and were respectively 5, 65, and 183 μmol/g  
447 (Figure S13b). According to XRD (Fig. S14), the Si<sub>3</sub>N<sub>4</sub> phase was still the main one detected after hydrolysis,  
448 confirming the negligible nitride powder conversion.

449

### 450 3.4 Calcium nitride (Ca<sub>3</sub>N<sub>2</sub>)

451 The hydrolysis of calcium nitride has been thoroughly investigated given the good reactivity towards NH<sub>3</sub> synthesis.

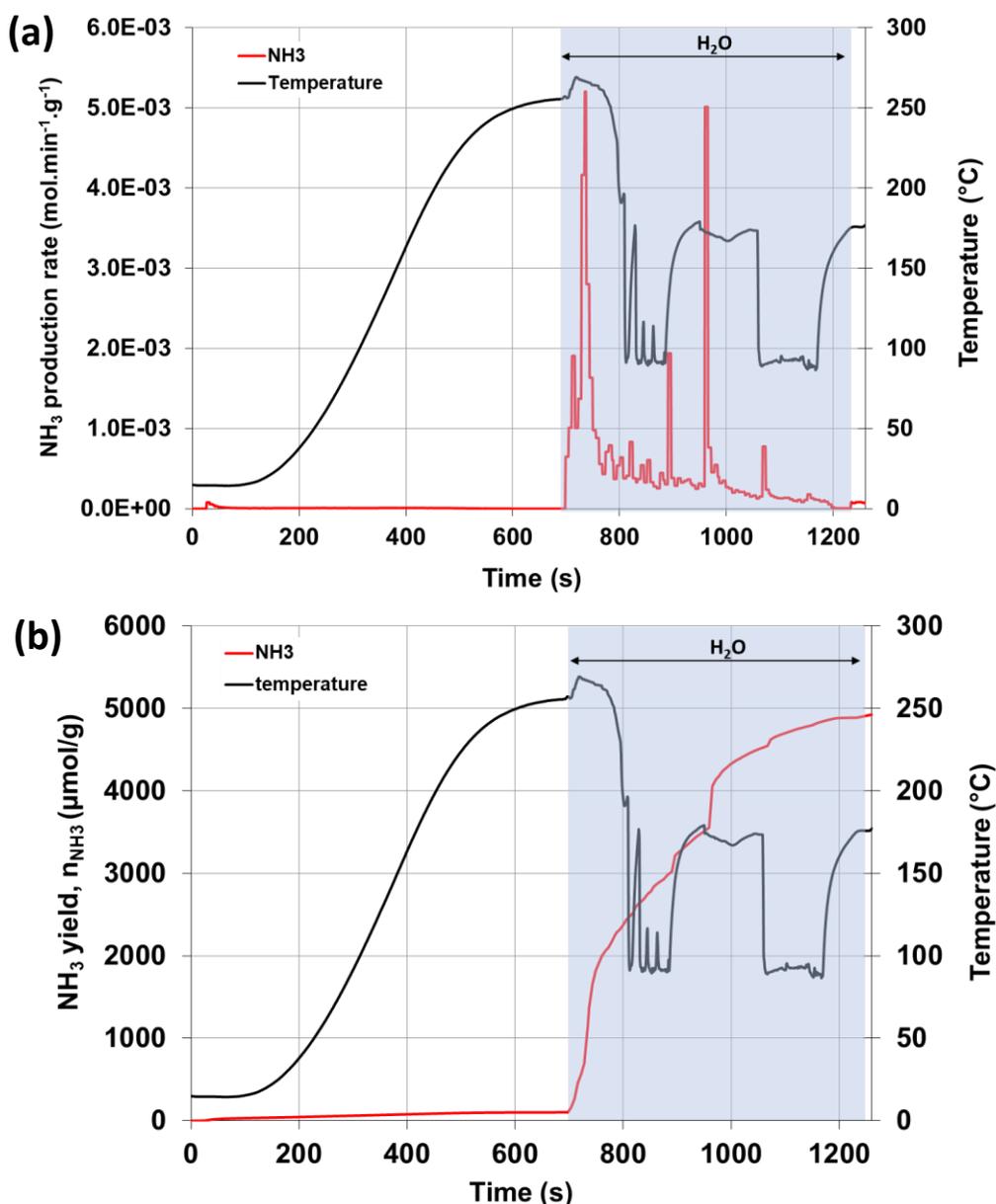
452 The overall reaction equations are:



455

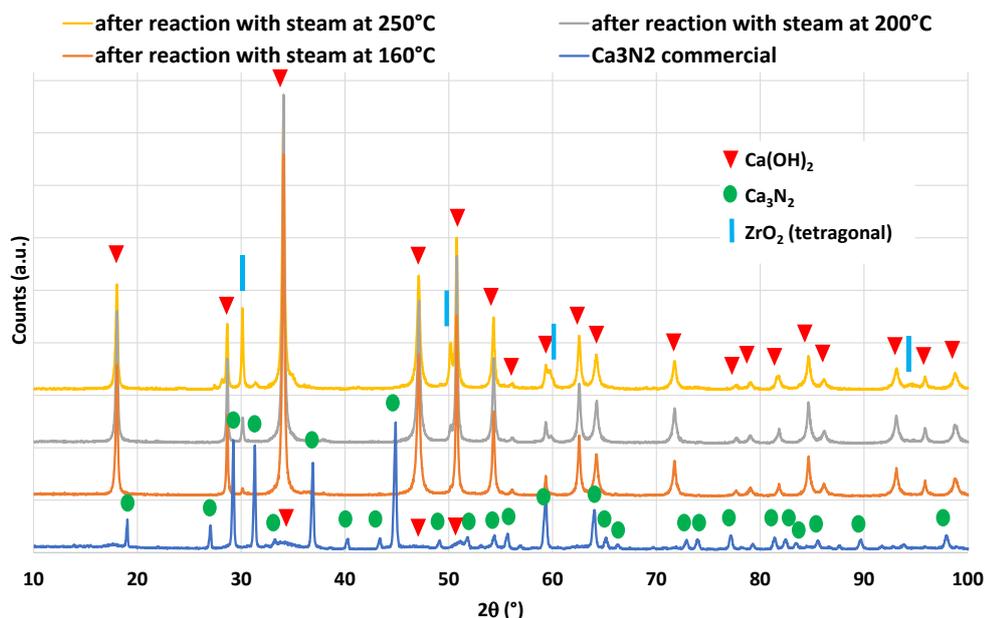
456 Based on Eq. (23), the theoretical maximum NH<sub>3</sub> production is 13.5·10<sup>-3</sup> mol/g. Figure 6 shows the NH<sub>3</sub> production  
457 profile during Ca<sub>3</sub>N<sub>2</sub> hydrolysis (100 mg) at 250°C. Calcium nitride is highly reactive during hydrolysis with a peak  
458 production rate of NH<sub>3</sub> reaching 5.2·10<sup>-3</sup> mol/min/g and an overall reaction duration of about 10 min. Steam was  
459 injected at a reactor temperature of 250°C inducing a slight temperature increase (260°C) due to the exothermal  
460 reaction, but strong temperature variations between 170°C and 90°C were then observed, which can be explained  
461 by the energy consumed by the vaporization of water and falling droplets on the thermocouple. Figure 6b plots the  
462 cumulative production of NH<sub>3</sub> during Ca<sub>3</sub>N<sub>2</sub> hydrolysis, reaching a value of 4.9·10<sup>-3</sup> mol/g in less than 10 min  
463 (corresponding to 36.5% of the theoretical maximum production). The strong temperature drop during hydrolysis  
464 (up to ~100°C) may be responsible for the incomplete NH<sub>3</sub> yield. Additional tests were carried out between 170 and  
465 290°C and confirmed complete reactions in less than 10 min with an overall NH<sub>3</sub> yield increasing with temperature  
466 (~14 mmol/g when the temperature was maintained above 200°C during hydrolysis), as shown in Figure S15. The  
467 measured NH<sub>3</sub> production thus corresponds to about 100% of the theoretical maximum production when the  
468 temperature is high enough.

469



470  
 471 **Figure 6.** NH<sub>3</sub> production during Ca<sub>3</sub>N<sub>2</sub> hydrolysis at 260°C: (a) evolution of NH<sub>3</sub> production rate as a function of  
 472 time, (b) cumulative NH<sub>3</sub> production as a function of time.  
 473

474 The material was characterized by XRD before and after hydrolysis at different temperatures to identify the existing  
 475 phases and compare with the fresh material (Figure 7). Whatever the hydrolysis temperature (160°C, 200°C or  
 476 250°C), the nitride phase disappeared and Ca(OH)<sub>2</sub> was the main phase identified, which denotes a total oxidation  
 477 of the nitride (and a hydration of CaO). A complete conversion of the nitride with water was thus confirmed by XRD.  
 478 A tetragonal ZrO<sub>2</sub> phase was also detected, due to zirconia felt as a powder support in the reactor. Also note the  
 479 absence of CaO, as calcium hydroxide is stable and does not decompose at these temperatures.  
 480



481  
482 **Figure 7.** XRD patterns of calcium nitride powders before and after hydrolysis at different temperatures.  
483

484 EDX analysis of the powder hydrolyzed at 270°C was carried out. Table S4 reports the atomic composition of the  
485 powder, which shows the absence of nitrogen trace in the sample thus confirming the complete nitride conversion.  
486 With a composition of 33%<sub>at</sub> Ca and 65.7%<sub>at</sub> O, the Ca/O ratio is 0.5, thus corresponding to the atomic ratio in  
487 Ca(OH)<sub>2</sub>. Traces of zirconium are also detected and correspond to the powder felt support used during the tests.  
488 Figure S16 shows the SEM and EDX elemental mapping of the sample composed of Ca and O evenly distributed  
489 on the surface.

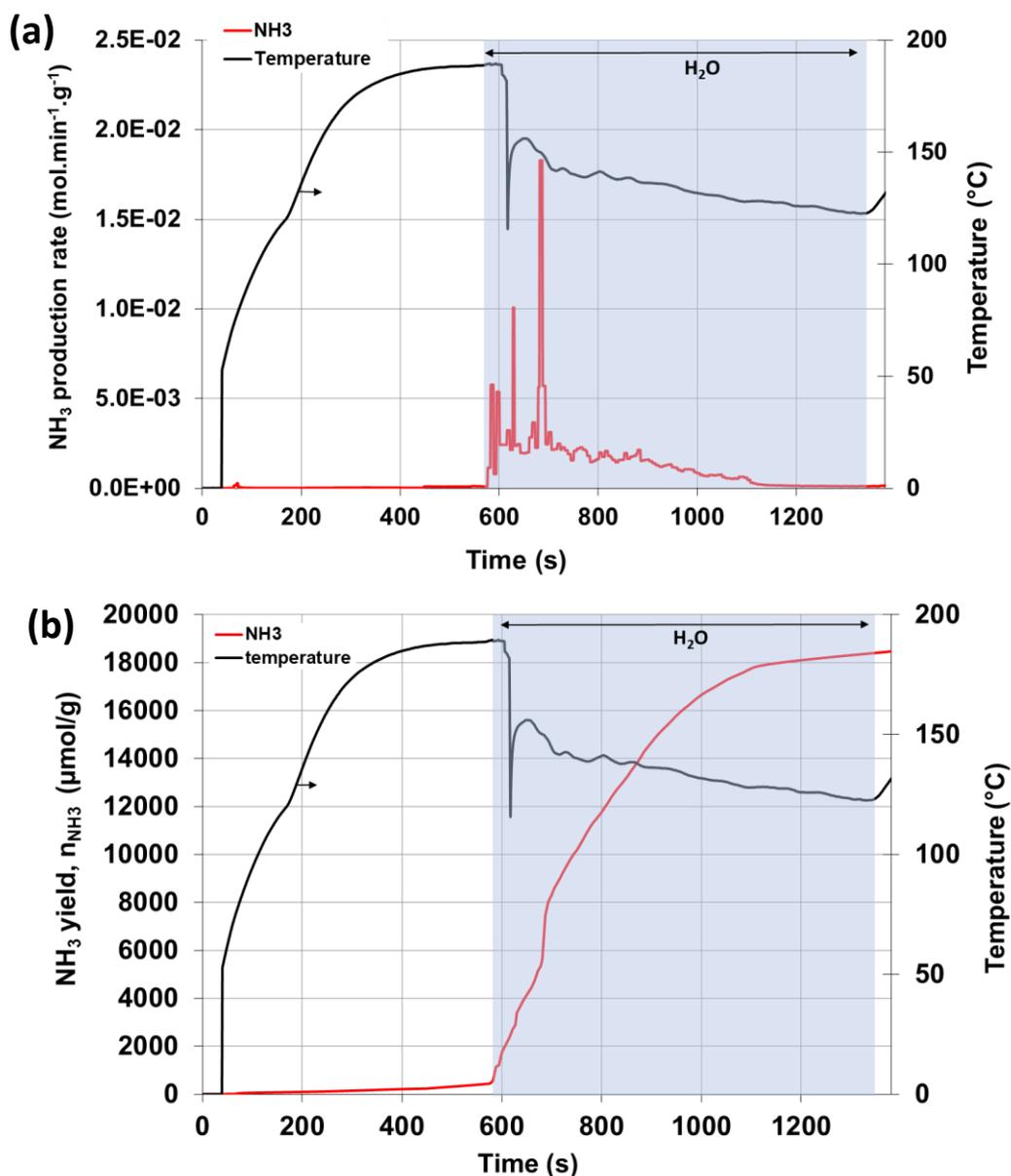
### 490 3.5 Magnesium nitride (Mg<sub>3</sub>N<sub>2</sub>)

491 The hydrolysis reaction of commercial magnesium nitride (101 mg) was studied, with the following overall  
492 equations:



495  
496 The calculated maximum NH<sub>3</sub> production is 19.8·10<sup>-3</sup> mol/g. Figure 8 shows the NH<sub>3</sub> production profile during the  
497 hydrolysis of Mg<sub>3</sub>N<sub>2</sub> at 190°C. During steam injection, the temperature dropped rapidly due to water vaporization.  
498 A substantial production of NH<sub>3</sub> was measured with a maximum peak rate of 1.8·10<sup>-2</sup> mol/min/g and an overall  
499 reaction duration of less than 10 min, as confirmed by the NH<sub>3</sub> production returning to zero before the end of steam  
500 injection. The cumulative production of NH<sub>3</sub> during Mg<sub>3</sub>N<sub>2</sub> hydrolysis at 190°C was 18.6·10<sup>-3</sup> mol/g (Figure 8b),  
501 which corresponds to 94% of the maximum theoretical NH<sub>3</sub> yield.  
502

503 Other tests were also carried out at slightly different temperatures (from 120 to 275°C) and confirmed the  
504 repeatability of the results with complete conversion achieved after about 5 to 10 min of hydrolysis reaction.  
505



**Figure 8.** NH<sub>3</sub> production during Mg<sub>3</sub>N<sub>2</sub> hydrolysis at 190°C: (a) evolution of NH<sub>3</sub> production rate as a function of time, (b) cumulative NH<sub>3</sub> production as a function of time.

506  
507  
508  
509  
510  
511  
512  
513  
514  
515  
516

The magnesium nitride powder was characterized by XRD before and after hydrolysis at different temperatures in order to identify the main phases after reaction and to compare them with the pristine material (Figure 9). The nitride phase completely disappeared after reaction whatever the temperature (200°C or 270°C) and both MgO and Mg(OH)<sub>2</sub> were formed, which demonstrates the complete nitride conversion. The peaks related to MgO were higher than those related to Mg(OH)<sub>2</sub> at the highest temperature, which highlights the decomposition of Mg(OH)<sub>2</sub> to MgO with increasing temperature. Some ZrO<sub>2</sub> (tetragonal) from the felt support was also detected, as already mentioned previously for the other materials.

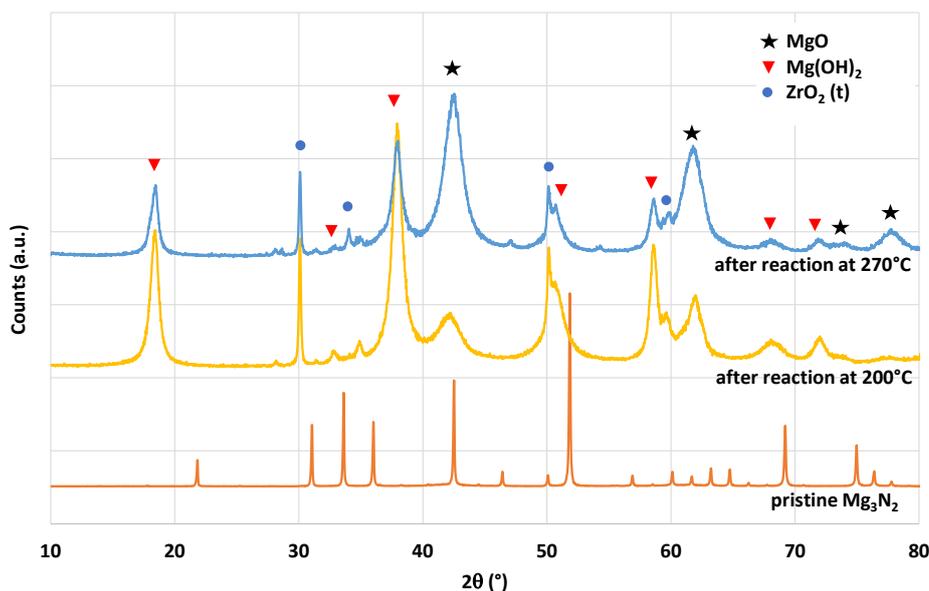


Figure 9. XRD patterns of magnesium nitride powders before and after hydrolysis at different temperatures.

517  
518  
519

EDX analysis of the powder hydrolyzed at 270°C was performed and the atomic composition is reported in Table S5. No trace of nitrogen was detected, which confirms the complete nitride conversion. With a composition of 35.3%<sub>at</sub> Mg and 61.6%<sub>at</sub> O, the Mg/O ratio is 0.57, corresponding to an intermediate ratio between MgO and Mg(OH)<sub>2</sub> in agreement with the results of XRD analysis. Traces of zirconium are also detected corresponding to the felt support.

Figure S17 shows SEM and EDX elemental mapping related to the atomic composition of the sample. The powder is composed of Mg and O evenly distributed over the surface.

525  
526  
527

### 3.6 Titanium nitride (TiN)

Titanium nitride was considered for solar production of NH<sub>3</sub>, with the following hydrolysis reaction equation:

529  
530

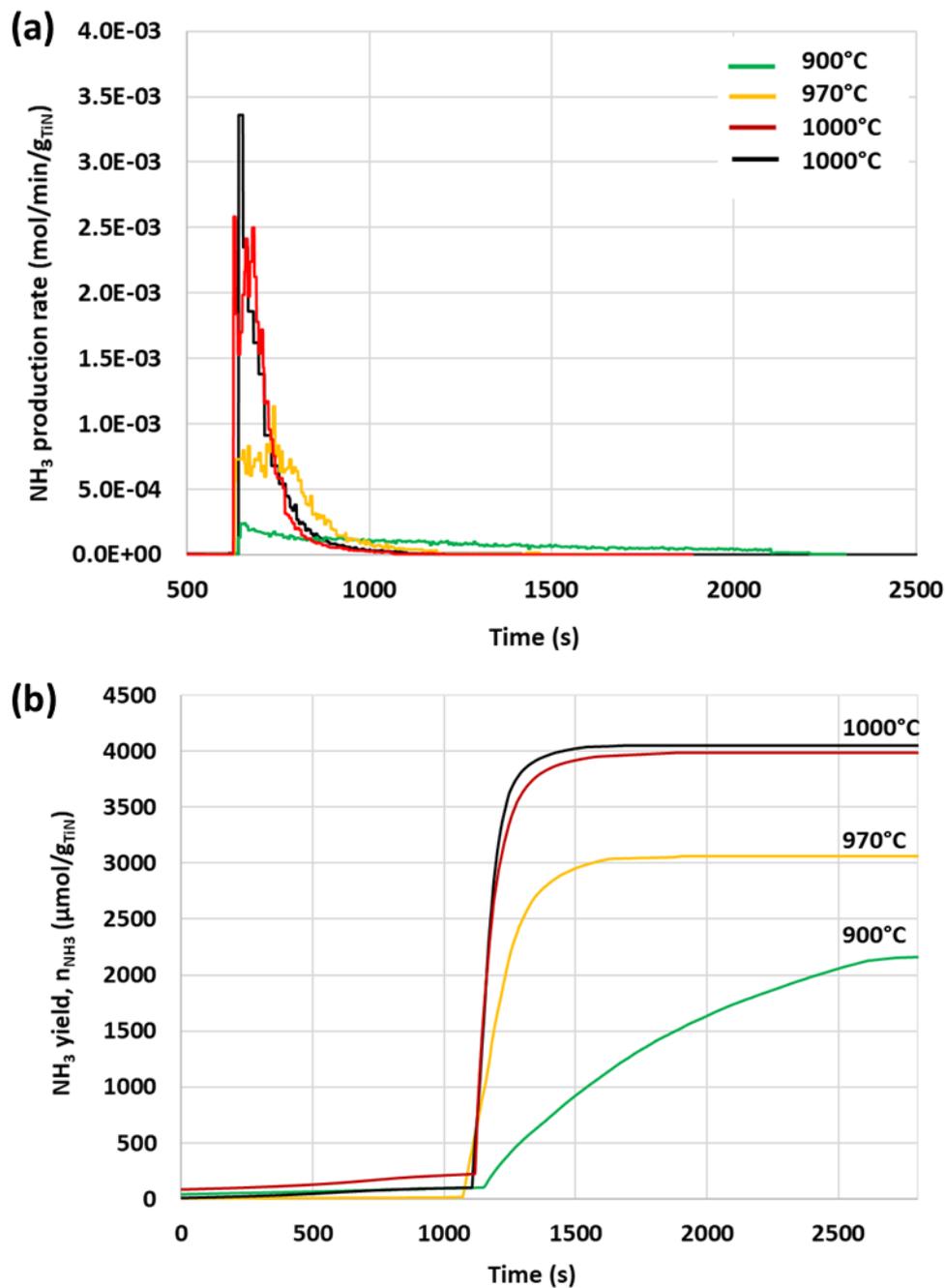


531  
532

Titanium can also form oxy-nitride species of varying composition and stoichiometry, which can impact the overall equation. Based on Eq. (27), the theoretical maximum production of NH<sub>3</sub> is 16.1·10<sup>-3</sup> mol/g. According to thermodynamics (Fig. S18), the formation of NH<sub>3</sub> is only predicted below 300°C because it decomposes at higher temperatures, and secondary oxide and oxy-nitride minor phases are predicted at higher temperatures (above ~800°C).

Figure 10a shows the evolution of the NH<sub>3</sub> production rate during TiN hydrolysis at 900°C, 970°C, and 1000°C. Although the reaction was not thermodynamically favored at high temperatures, the peak production rate increased with increasing temperature due to a kinetically-controlled reaction. The NH<sub>3</sub> production rate rose from 2.4·10<sup>-4</sup> mol/min/g at 900°C, to 3.4·10<sup>-3</sup> mol/min/g at 1000°C. The reaction duration was short whatever the temperature since NH<sub>3</sub> production was completed in less than ~3-4 min, indicating fast kinetics. Other hydrolysis reactions carried out at 250°C and 500°C did not produce NH<sub>3</sub>, which means that the temperature must be high enough to obtain noticeable kinetics. Figure 10b shows the cumulative production of NH<sub>3</sub> during TiN hydrolysis at different temperatures. The NH<sub>3</sub> production increased significantly with temperature as it was 2.16 mmol/g at 900°C, 3.06 mmol/g at 970°C, and 4.05 mmol/g at 1000°C.

543  
544  
545  
546  
547



**Figure 10.** NH<sub>3</sub> production during TiN hydrolysis at 900°C, 970°C and 1000°C: (a) evolution of NH<sub>3</sub> production rate as a function of time, (b) cumulative NH<sub>3</sub> production as a function of time.

548  
549  
550  
551  
552  
553  
554  
555  
556  
557

XRD analysis of titanium nitride powders before and after hydrolysis at different temperatures was carried out (Figure 11). TiO<sub>2</sub> (rutile) was observed as the main phase after hydrolysis at each temperature considered. The initial TiN phase was still detected at 900°C but remained in very low amount. The intensity of TiN peaks relative to TiO<sub>2</sub> decreased when temperature increased, confirming an improvement in reaction extent. ZrO<sub>2</sub>(t) from the felt support was also detected, consistently with previous results.

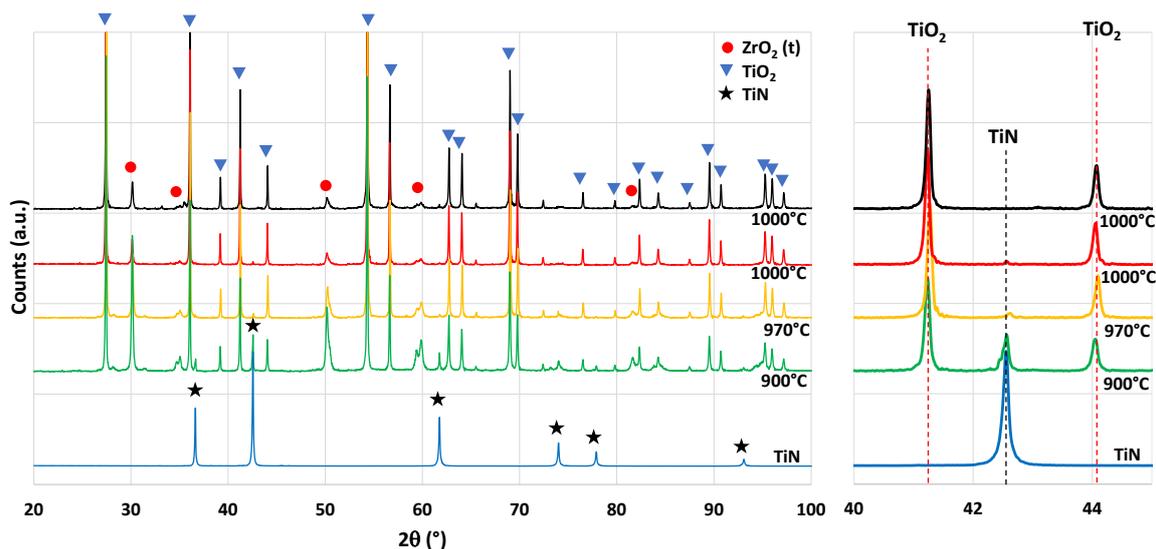


Figure 11. XRD patterns of TiN powders before and after hydrolysis at different temperatures.

558  
559  
560  
561  
562  
563  
564  
565  
566  
567

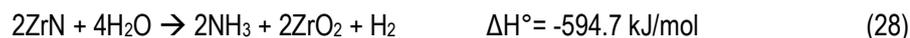
EDX analysis of TiN powders hydrolyzed at 900°C, 970°C, and 1000°C was performed and Table S6 reports the atomic compositions. The Ti/O ratio is 0.52 at 1000°C, corresponding approximately to TiO<sub>2</sub> composition. No trace of nitrogen was detected at any hydrolysis temperature, which means it is below the detection limit. The traces of zirconium correspond to the felt support.

Figures S19-S21 show the SEM and EDX elemental mapping of powders hydrolyzed at 900, 930 and 1000°C, confirming the homogeneous distribution of the Ti and O elements.

### 3.7 Zirconium nitride (ZrN)

The final material tested in this study of nitride hydrolysis for NH<sub>3</sub> production was zirconium nitride (ZrN).

569  
570  
571  
572



As for Ti, Zr can form oxy-nitrides which can modify the overall equation of the reaction. Based on Eq. (28), the theoretical maximum production of NH<sub>3</sub> is 11.0 · 10<sup>-3</sup> mol/g.

The NH<sub>3</sub> production profiles during ZrN hydrolysis were studied at 550°C, 620°C, 750°C, 820°C, 920°C, and 1000°C (Figures 12 and S22). An increase in the peak production rate was measured until it reached an optimum at 750°C and decreased at higher temperatures (Table 1). The maximum NH<sub>3</sub> production rate at 750°C reached 34.2 mmol/min/g (767 mL/min/g), which was the highest reaction rate obtained among the nitrides tested. The period of NH<sub>3</sub> production was short, as the reaction was completed in less than about 2-3 min, except at the lowest temperature of 550°C where the kinetics were much slower. Figure 12b reports the cumulative production of NH<sub>3</sub> during ZrN hydrolysis at different temperatures, with an optimum at 750°C corresponding to a maximum NH<sub>3</sub> production yield of 12.3 mmol/g (Fig. S23).

579  
580  
581  
582  
583  
584

Table 1. Peak production rates and yields of NH<sub>3</sub> during ZrN hydrolysis at different temperatures.

	Peak production rate (mmol/min/g)	Peak production rate (mL/min/g)	Yield of NH <sub>3</sub> (mmol/g)
550°C	0.50	11.3	7.9
620°C	17.6	393.4	11.4
750°C	34.2	767.0	12.3
820°C	21.8	488.9	11.2
920°C	25.1	562.2	8.3
1000°C	15.7	352.9	2.1
1010°C	1.16	26.0	0.75

585  
586  
587

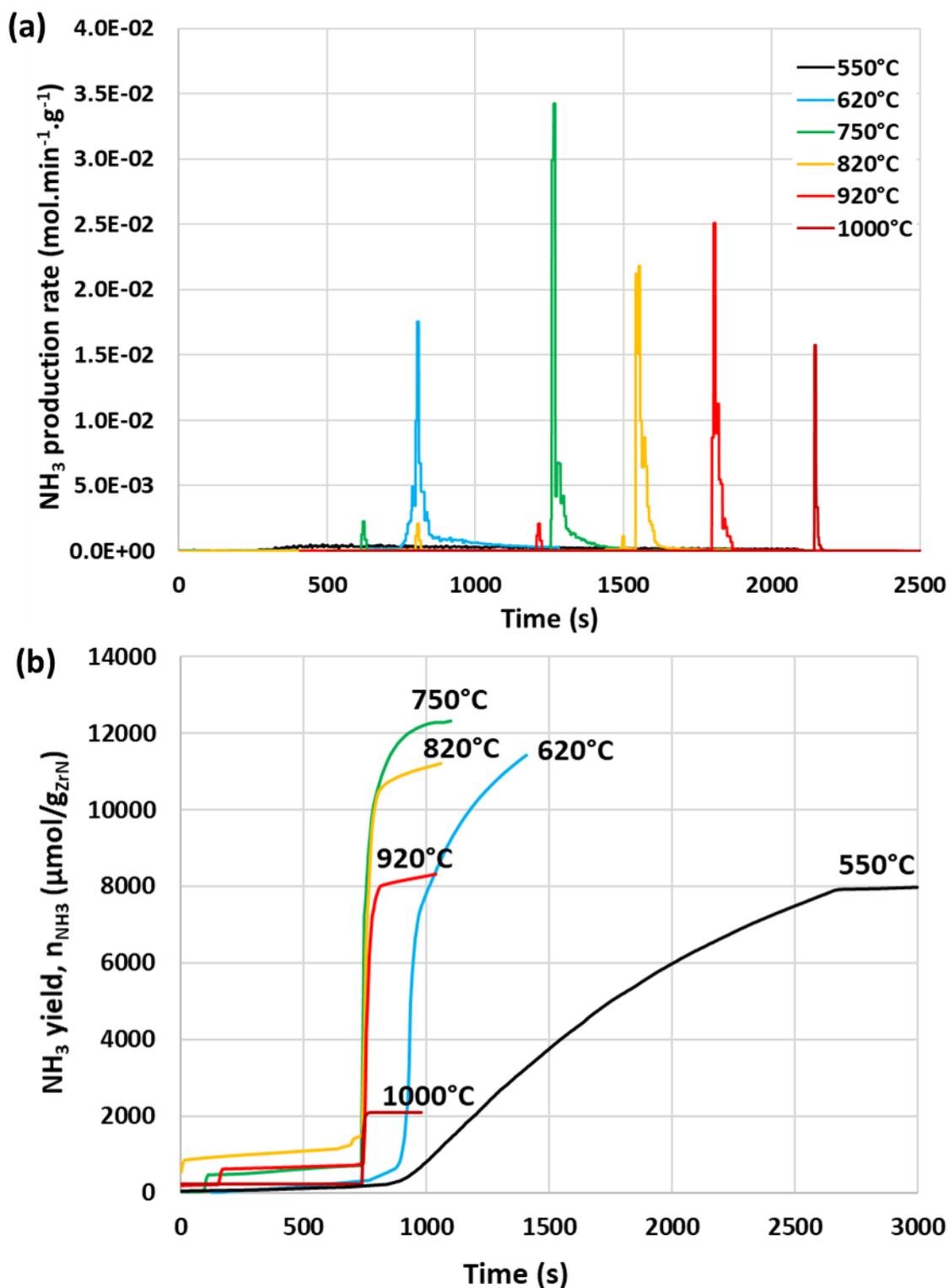


Figure 12.  $\text{NH}_3$  production during ZrN hydrolysis at different temperatures: (a) comparison of  $\text{NH}_3$  production rate, (b) cumulative  $\text{NH}_3$  production as a function of time.

589  
590  
591  
592  
593  
594  
595  
596  
597

XRD analysis of zirconium nitride powders before and after hydrolysis at different temperatures (Figure 13) shows that  $\text{ZrO}_2$  (monoclinic and tetragonal) is the main phase after the reaction at any temperature. The intensity ratio of peaks related to monoclinic  $\text{ZrO}_2$  increases with temperature. The initial ZrN phase is still observed especially at 550°C and 620°C, and it disappears at higher temperatures, which confirms the enhanced hydrolysis extent when increasing the temperature.

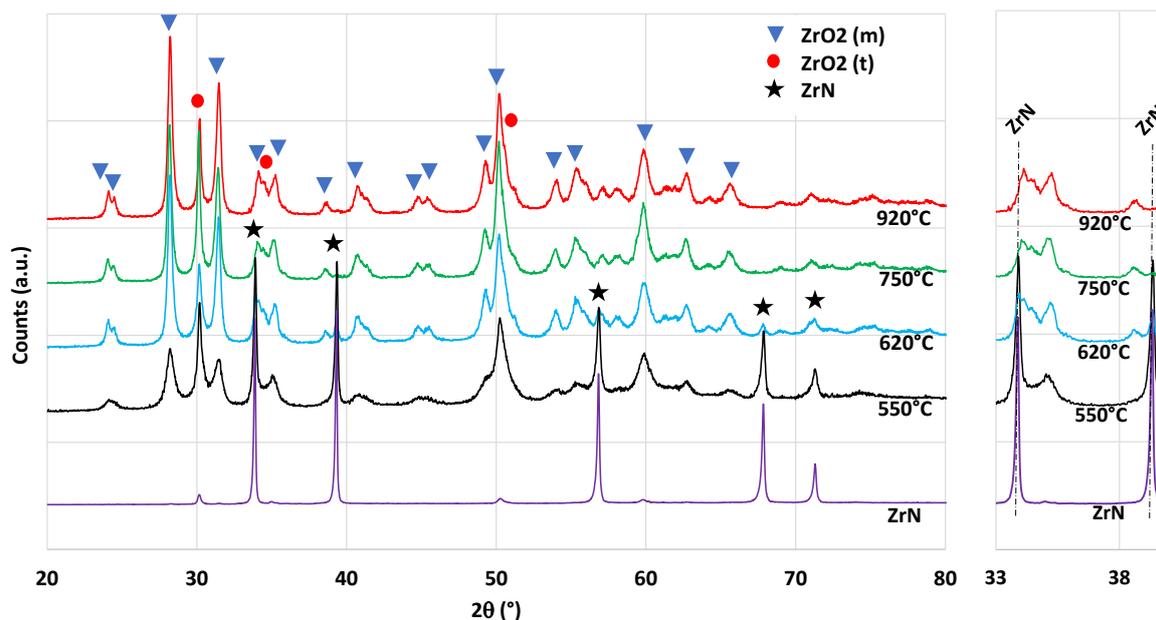


Figure 13. XRD patterns of ZrN powders before and after hydrolysis at different temperatures.

598  
599  
600  
601  
602  
603  
604  
605  
606  
607  
608  
609

EDX analysis of powders hydrolyzed at 620°C, 750°C, 820°C, and 920°C was performed and Table S7 reports the atomic composition, confirming the overall ZrO<sub>2</sub> composition after hydrolysis (Zr/O ratio of ~0.5). Some nitrogen was always detected, except for the powder hydrolyzed at 750°C, in agreement with the maximum conversion observed at this temperature.

Figures S24-S27 show the SEM and EDX elemental mapping of powders hydrolyzed at 620, 750, 820, and 920°C. A homogeneous distribution of Zr, O and N is evidenced.

This study successfully demonstrated the production of ammonia from the hydrolysis of ZrN with fast rates and optimum conversion at 750°C. The next step will focus on the solar regeneration of nitrides from ZrO<sub>2</sub> oxide.

#### 4. Conclusion

610  
611  
612  
613  
614  
615  
616  
617  
618  
619  
620  
621  
622  
623  
624  
625  
626  
627  
628  
629  
630  
631  
632  
633  
634

The production of ammonia via two-step cycles relying on N<sub>2</sub> and H<sub>2</sub>O as the only feedstocks is an attractive approach, as it uses solar heat as the process energy input and additionally bypasses the use of H<sub>2</sub>. Active materials involved in such thermochemical cycles (metal oxide/nitride redox pairs) must be identified and optimized to demonstrate the feasibility of the solar ammonia production process. A series of ten metal nitrides was experimentally tested for ammonia production from nitrides hydrolysis. Iron (FeN), chromium (CrN), boron (BN), and silicon (Si<sub>3</sub>N<sub>4</sub>) nitrides gave no significant NH<sub>3</sub> production, and therefore cannot be considered as suitable candidate materials for thermochemical ammonia production cycles. Among the considered nitrides, the most attractive materials turned out to be AlN, Li<sub>3</sub>N, Ca<sub>3</sub>N<sub>2</sub>, Mg<sub>3</sub>N<sub>2</sub>, TiN, and ZrN because they exhibit a noteworthy reactivity during hydrolysis and a significant production of NH<sub>3</sub>. The influence of temperature was studied for each material and proved to have a strong impact on the reaction conversion and the NH<sub>3</sub> yield. AlN hydrolysis occurred significantly above 1000°C with maximum rates at 1200°C (0.16 mmol/min/g), but the NH<sub>3</sub> yield remained moderate (1.1 mmol/g) presumably due to decomposition at high temperatures. TiN and ZrN also required high temperatures for NH<sub>3</sub> production. A maximum NH<sub>3</sub> production rate of 3.4 mmol/min/g was measured at 1000°C for TiN (NH<sub>3</sub> yield of 4.1 mmol/g), while an optimum temperature of 750°C was revealed for ZrN yielding the highest NH<sub>3</sub> production rate of 34.2 mmol/min/g (NH<sub>3</sub> yield of 12.3 mmol/g). The hydrolysis reactions of Li<sub>3</sub>N, Ca<sub>3</sub>N<sub>2</sub>, and Mg<sub>3</sub>N<sub>2</sub> were the most exothermic and thus required low temperatures (around 200°C) to achieve complete conversion, with total NH<sub>3</sub> yields of 5.9, 4.9, and 18.6 mmol/g, respectively. The hydrolysis rate of Ca<sub>3</sub>N<sub>2</sub> and Mg<sub>3</sub>N<sub>2</sub> was slightly lower than that of Li<sub>3</sub>N, TiN, and ZrN.

This study thus demonstrated the feasibility of sustainable ammonia synthesis from a novel clean process ultimately based on concentrated solar energy as the process heat source. Noteworthy ammonia production performance was achieved with the identified metal nitrides. Thermochemical ammonia production based on nitrides cycles is a suitable means for industrial process decarbonation. Future work will focus on the regeneration step of the metal nitrides using concentrated solar energy at high temperatures. The most reactive nitrides were found to be Li<sub>3</sub>N,

635 Ca<sub>3</sub>N<sub>2</sub>, Mg<sub>3</sub>N<sub>2</sub>, TiN and ZrN. The solar-driven nitridation reaction of the corresponding oxides (Li<sub>2</sub>O, CaO, MgO,  
636 TiO<sub>2</sub>, and ZrO<sub>2</sub>) must therefore be characterized as a function of temperature and reducing agent to demonstrate  
637 the complete cycles of nitride chemical looping for ammonia synthesis.  
638

#### 639 **Declaration of Competing Interest**

640 The authors declare that they have no known competing financial interests or personal relationships that could  
641 have appeared to influence the work reported in this paper.  
642

#### 643 **Acknowledgments**

644 This work was partially funded by the CNRS Energy Unit (Cellule Energie) through the PEPS AMMOSOL project.  
645 The authors acknowledge the support from the PCM characterization platform (E. Bêche) at PROMES-CNRS  
646 during the XRD analysis.  
647

#### 648 **Appendix A. Supplementary material**

649 The following is the Supplementary material related to this article.  
650

651 Supplementary material contains a summary of the experimental conditions and the corresponding total amounts  
652 of NH<sub>3</sub> produced during the different hydrolysis tests, additional NH<sub>3</sub> production data for metal nitrides hydrolysis,  
653 materials characterization including XRD analysis data and SEM/EDX imaging/elemental mapping.  
654

#### 655 **Data availability**

656 Data will be made available on request.  
657

658

#### 659 **References**

- 660
- 661 Abanades, S., 2023. A Review of Oxygen Carrier Materials and Related Thermochemical Redox Processes for  
662 Concentrating Solar Thermal Applications. *Materials* 16, 3582. <https://doi.org/10.3390/ma16093582>
- 663 Abanades, S., 2022. Redox Cycles, Active Materials, and Reactors Applied to Water and Carbon Dioxide Splitting  
664 for Solar Thermochemical Fuel Production: A Review. *Energies* 15, 7061.  
665 <https://doi.org/10.3390/en15197061>
- 666 Aziz, M., Wijayanta, A.T., Nandiyanto, A.B.D., 2020. Ammonia as Effective Hydrogen Storage: A Review on  
667 Production, Storage and Utilization. *Energies* 13, 3062. <https://doi.org/10.3390/en13123062>
- 668 Bartel, C.J., Rumpitz, J.R., Weimer, A.W., Holder, A.M., Musgrave, C.B., 2019. High-Throughput Equilibrium  
669 Analysis of Active Materials for Solar Thermochemical Ammonia Synthesis. *ACS Appl. Mater. Interfaces*  
670 11, 24850–24858. <https://doi.org/10.1021/acsami.9b01242>
- 671 Bhaskar, A., Assadi, M., Nikpey Somehsaraei, H., 2020. Decarbonization of the Iron and Steel Industry with  
672 Direct Reduction of Iron Ore with Green Hydrogen. *Energies* 13, 758.  
673 <https://doi.org/10.3390/en13030758>
- 674 Ceballos, B.M., Pilia, G., Ramaiyan, K.P., Banerjee, A., Kreller, C., Mukundan, R., 2021. Roads less traveled:  
675 Nitrogen reduction reaction catalyst design strategies for improved selectivity. *Current Opinion in*  
676 *Electrochemistry* 28, 100723. <https://doi.org/10.1016/j.coelec.2021.100723>
- 677 Chambon, M., Abanades, S., Flamant, G., 2010a. Solar thermal reduction of ZnO and SnO<sub>2</sub>: Characterization of  
678 the recombination reaction with O<sub>2</sub>. *Chemical Engineering Science* 65, 3671–3680.  
679 <https://doi.org/10.1016/j.ces.2010.03.005>
- 680 Chambon, M., Abanades, S., Flamant, G., 2010b. Design of a Lab-Scale Rotary Cavity-Type Solar Reactor for  
681 Continuous Thermal Dissociation of Volatile Oxides Under Reduced Pressure. *Journal of Solar Energy*  
682 *Engineering* 132, 021006. <https://doi.org/10.1115/1.4001147>
- 683 Chuayboon, S., Abanades, S., 2019. Clean magnesium production using concentrated solar heat in a high-  
684 temperature cavity-type thermochemical reactor. *Journal of Cleaner Production* 232, 784–795.  
685 <https://doi.org/10.1016/j.jclepro.2019.05.371>
- 686 Daisley, A., Hargreaves, J.S.J., 2023. Metal nitrides, the Mars-van Krevelen mechanism and heterogeneously  
687 catalysed ammonia synthesis. *Catalysis Today* 423, 113874.  
688 <https://doi.org/10.1016/j.cattod.2022.08.016>

689 Damanabi, A.T., Servatan, M., Mazinani, S., Olabi, A.G., Zhang, Z., 2019. Potential of tri-reforming process and  
690 membrane technology for improving ammonia production and CO<sub>2</sub> reduction. *Science of The Total*  
691 *Environment* 664, 567–575. <https://doi.org/10.1016/j.scitotenv.2019.01.391>

692 Gálvez, M.E., Frei, A., Halmann, M., Steinfeld, A., 2007a. Ammonia Production via a Two-Step Al<sub>2</sub>O<sub>3</sub>/AlN  
693 Thermochemical Cycle. 2. Kinetic Analysis. *Ind. Eng. Chem. Res.* 46, 2047–2053.  
694 <https://doi.org/10.1021/ie061551m>

695 Gálvez, M.E., Halmann, M., Steinfeld, A., 2007b. Ammonia Production via a Two-Step Al<sub>2</sub>O<sub>3</sub>/AlN Thermochemical  
696 Cycle. 1. Thermodynamic, Environmental, and Economic Analyses. *Ind. Eng. Chem. Res.* 46, 2042–  
697 2046. <https://doi.org/10.1021/ie061550u>

698 Gálvez, M.E., Hischer, I., Frei, A., Steinfeld, A., 2008. Ammonia Production via a Two-Step Al<sub>2</sub>O<sub>3</sub>/AlN  
699 Thermochemical Cycle. 3. Influence of the Carbon Reducing Agent and Cyclability. *Ind. Eng. Chem.*  
700 *Res.* 47, 2231–2237. <https://doi.org/10.1021/ie071244w>

701 Goto, Y., Daisley, A., Hargreaves, J.S.J., 2021. Towards anti-perovskite nitrides as potential nitrogen storage  
702 materials for chemical looping ammonia production: Reduction of Co<sub>3</sub>ZnN, Ni<sub>3</sub>ZnN, Co<sub>3</sub>InN and Ni<sub>3</sub>InN  
703 under hydrogen. *Catalysis Today* 364, 196–201. <https://doi.org/10.1016/j.cattod.2020.03.022>

704 Haeussler, A., Abanades, S., Jouannaux, J., Drobek, M., Ayrál, A., Julbe, A., 2019. Recent progress on ceria  
705 doping and shaping strategies for solar thermochemical water and CO<sub>2</sub> splitting cycles. *AIMS Materials*  
706 *Science* 6, 657–684. <https://doi.org/10.3934/mat.2019.5.657>

707 Hunter, S.M., McKay, D., Smith, R.I., Hargreaves, J.S.J., Gregory, D.H., 2010. Topotactic Nitrogen Transfer:  
708 Structural Transformation in Cobalt Molybdenum Nitrides. *Chem. Mater.* 22, 2898–2907.  
709 <https://doi.org/10.1021/cm100208a>

710 Jain, A., Miyaoka, H., Kumar, S., Ichikawa, T., Kojima, Y., 2017. A new synthesis route of ammonia production  
711 through hydrolysis of metal – Nitrides. *International Journal of Hydrogen Energy* 42, 24897–24903.  
712 <https://doi.org/10.1016/j.ijhydene.2017.08.027>

713 Kishira, S., Qing, G., Suzu, S., Kikuchi, R., Takagaki, A., Oyama, S.T., 2017. Ammonia synthesis at intermediate  
714 temperatures in solid-state electrochemical cells using cesium hydrogen phosphate based electrolytes  
715 and noble metal catalysts. *International Journal of Hydrogen Energy* 42, 26843–26854.  
716 <https://doi.org/10.1016/j.ijhydene.2017.09.052>

717 Klaas, L., Guban, D., Roeb, M., Sattler, C., 2021. Recent progress towards solar energy integration into low-  
718 pressure green ammonia production technologies. *International Journal of Hydrogen Energy* 46, 25121–  
719 25136. <https://doi.org/10.1016/j.ijhydene.2021.05.063>

720 Kyriakou, V., Garagounis, I., Vasileiou, E., Vourros, A., Stoukides, M., 2017. Progress in the Electrochemical  
721 Synthesis of Ammonia. *Catalysis Today* 286, 2–13. <https://doi.org/10.1016/j.cattod.2016.06.014>

722 Laassiri, S., Zeinalipour-Yazdi, C.D., Catlow, C.R.A., Hargreaves, J.S.J., 2018. The potential of manganese  
723 nitride based materials as nitrogen transfer reagents for nitrogen chemical looping. *Applied Catalysis B:*  
724 *Environmental* 223, 60–66. <https://doi.org/10.1016/j.apcatb.2017.04.073>

725 Lai, Q., Cai, T., Tsang, S.C.E., Chen, X., Ye, R., Xu, Z., Argyle, M.D., Ding, D., Chen, Y., Wang, J., Russell, A.G.,  
726 Wu, Y., Liu, J., Fan, M., 2022. Chemical looping based ammonia production—A promising pathway for  
727 production of the noncarbon fuel. *Science Bulletin* 67, 2124–2138.  
728 <https://doi.org/10.1016/j.scib.2022.09.013>

729 Le Gal, A., Abanades, S., 2011. Catalytic investigation of ceria-zirconia solid solutions for solar hydrogen  
730 production. *International Journal of Hydrogen Energy* 36, 4739–4748.  
731 <https://doi.org/10.1016/j.ijhydene.2011.01.078>

732 Liu, X., Elgowainy, A., Wang, M., 2020. Life cycle energy use and greenhouse gas emissions of ammonia  
733 production from renewable resources and industrial by-products. *Green Chem.* 22, 5751–5761.  
734 <https://doi.org/10.1039/D0GC02301A>

735 Marnellos, G., Stoukides, M., 1998. Ammonia Synthesis at Atmospheric Pressure. *Science* 282, 98–100.  
736 <https://doi.org/10.1126/science.282.5386.98>

737 Marnellos, G., Zisekas, S., Stoukides, M., 2000. Synthesis of Ammonia at Atmospheric Pressure with the Use of  
738 Solid State Proton Conductors. *Journal of Catalysis* 193, 80–87. <https://doi.org/10.1006/jcat.2000.2877>

739 Michalsky, R., Avram, A.M., Peterson, B.A., Pfromm, P.H., Peterson, A.A., 2015a. Chemical looping of metal  
740 nitride catalysts: low-pressure ammonia synthesis for energy storage. *Chem. Sci.* 6, 3965–3974.  
741 <https://doi.org/10.1039/C5SC00789E>

742 Michalsky, R., Parman, B.J., Amanor-Boadu, V., Pfromm, P.H., 2012. Solar thermochemical production of  
743 ammonia from water, air and sunlight: Thermodynamic and economic analyses. *Energy* 42, 251–260.  
744 <https://doi.org/10.1016/j.energy.2012.03.062>  
745 Michalsky, R., Pfromm, P.H., 2011. Chromium as reactant for solar thermochemical synthesis of ammonia from  
746 steam, nitrogen, and biomass at atmospheric pressure. *Solar Energy* 85, 2642–2654.  
747 <https://doi.org/10.1016/j.solener.2011.08.005>  
748 Michalsky, R., Pfromm, P.H., Steinfeld, A., 2015b. Rational design of metal nitride redox materials for solar-driven  
749 ammonia synthesis. *Interface Focus* 5, 20140084. <https://doi.org/10.1098/rsfs.2014.0084>  
750 Michalsky, R., Steinfeld, A., 2017. Computational screening of perovskite redox materials for solar  
751 thermochemical ammonia synthesis from N<sub>2</sub> and H<sub>2</sub>O. *Catalysis Today* 286, 124–130.  
752 <https://doi.org/10.1016/j.cattod.2016.09.023>  
753 Mordor Intelligence LLP, 2021. Ammonia Market - Growth, Trends, COVID-19 Impact, and Forecasts (2021 -  
754 2026) (No. 6036753).  
755 Murakami, T., Nishikiori, T., Nohira, T., Ito, Y., 2003. Electrolytic Synthesis of Ammonia in Molten Salts under  
756 Atmospheric Pressure. *J. Am. Chem. Soc.* 125, 334–335. <https://doi.org/10.1021/ja028891t>  
757 Murakami, T., Nohira, T., Ogata, Y.H., Ito, Y., 2005a. Electrolytic Ammonia Synthesis in Molten Salts under  
758 Atmospheric Pressure Using Methane as a Hydrogen Source. *Electrochem. Solid-State Lett.* 8, D12.  
759 <https://doi.org/10.1149/1.1870633>  
760 Murakami, T., Nohira, T., Ogata, Y.H., Ito, Y., 2005b. Electrochemical Synthesis of Ammonia and Coproduction of  
761 Metal Sulfides from Hydrogen Sulfide and Nitrogen under Atmospheric Pressure. *J. Electrochem. Soc.*  
762 152, D109. <https://doi.org/10.1149/1.1904984>  
763 Murray, J., Steinfeld, A., Fletcher, E., 1995. Metals, nitrides, and carbides via solar carbothermal reduction of metal  
764 oxides. *Energy* 20, 695–704. [https://doi.org/10.1016/0360-5442\(95\)00032-C](https://doi.org/10.1016/0360-5442(95)00032-C)  
765 Patisson, F., Mirgautx, O., 2020. Hydrogen Ironmaking: How It Works. *Metals* 10, 922.  
766 <https://doi.org/10.3390/met10070922>  
767 Qing, G., Kikuchi, R., Kishira, S., Takagaki, A., Sugawara, T., Oyama, S.T., 2016. Ammonia Synthesis by N<sub>2</sub> and  
768 Steam Electrolysis in Solid-State Cells at 220°C and Atmospheric Pressure. *J. Electrochem. Soc.* 163,  
769 E282–E287. <https://doi.org/10.1149/2.0161610jes>  
770 Rafiqul, I., Weber, C., Lehmann, B., Voss, A., 2005. Energy efficiency improvements in ammonia production—  
771 perspectives and uncertainties. *Energy* 30, 2487–2504. <https://doi.org/10.1016/j.energy.2004.12.004>  
772 Wang, L., Xia, M., Wang, H., Huang, K., Qian, C., Maravelias, C.T., Ozin, G.A., 2018. Greening Ammonia toward  
773 the Solar Ammonia Refinery. *Joule* 2, 1055–1074. <https://doi.org/10.1016/j.joule.2018.04.017>  
774 Xiao, L., Wu, S.-Y., Li, Y.-R., 2012. Advances in solar hydrogen production via two-step water-splitting  
775 thermochemical cycles based on metal redox reactions. *Renewable Energy* 41, 1–12.  
776 <https://doi.org/10.1016/j.renene.2011.11.023>  
777 Yang, S., Zhang, T., Yang, Y., Wang, B., Li, J., Gong, Z., Yao, Z., Du, W., Liu, S., Yu, Z., 2022. Molybdenum-  
778 based nitrogen carrier for ammonia production via a chemical looping route. *Applied Catalysis B:  
779 Environmental* 312, 121404. <https://doi.org/10.1016/j.apcatb.2022.121404>  
780  
781