# Production of ammonia via a chemical looping process based on metal imides as nitrogen carriers

Wenbo Gao<sup>1,2</sup>, Jianping Guo<sup>1,3\*</sup>, Peikun Wang<sup>1,2</sup>, Qianru Wang<sup>1,2</sup>, Fei Chang<sup>1,2</sup>, Qijun Pei<sup>1,2</sup>, Weijin Zhang<sup>1,2</sup>, Lin Liu<sup>1</sup> and Ping Chen<sup>1,3\*</sup>

Ammonia is a promising carbon-free energy carrier, but is currently synthesized industrially under harsh conditions. Synthesizing ammonia using lower temperatures and pressures could therefore improve its prospects as a chemical means to store and transport energy. Here we report that alkali and alkaline earth metal imides function as nitrogen carriers that mediate ammonia production via a two-step chemical looping process operating under mild conditions. Nitrogen is first fixed through the reduction of  $N_2$  by alkali or alkaline earth metal hydrides to form imides and, subsequently, the imides are hydrogenated to produce NH<sub>3</sub> and regenerate the metal hydrides. The oxidation state of hydrogen therefore switches between -1 (hydride), 0 (H<sub>2</sub>) and +1 (imide and NH<sub>3</sub>). Late 3d metals accelerate the reaction rates of both steps. The chemical loop mediated by BaNH and catalysed by Ni produces NH<sub>3</sub> at 100 °C and atmospheric pressure.

mmonia is a promising energy carrier to store and transport renewable energy because of its high energy density and facile storage and transportation<sup>1-3</sup>. To this end, photon-<sup>4-6</sup> and electron-driven7-10 routes for ammonia production from N2 and H<sub>2</sub>O (equation (R1)) have been actively explored in recent years. Along this line are research efforts targeted at decomposing reaction equation (R1) into sequential steps, allowing NH<sub>3</sub> synthesis via a chemical looping process (denoted as H<sub>2</sub>O-CL, see Fig. 1a)<sup>11-15</sup>. Chemical looping processes have been extensively studied in the field of conversion of carbonaceous feedstock into chemicals and/ or power, offering advantages in energy efficiency, product selectivity and separation<sup>16-18</sup>. Those advantages can add freedom for manipulating the process of NH<sub>3</sub> synthesis. A few successful H<sub>2</sub>O-CLs mediated by AlN/Al<sub>2</sub>O<sub>3</sub> (ref.<sup>11</sup>), Cr/Cr<sub>2</sub>N/Cr<sub>2</sub>O<sub>3</sub>(ref.<sup>12</sup>) and Li-Li<sub>3</sub>N-LiOH (ref.<sup>15</sup>), have been demonstrated, in which NH<sub>3</sub> production is via hydrolysis of metal nitrides, which also leads to the formation of stable oxides/hydroxides. The regeneration of metal nitrides or metal is energy consuming, with temperatures up to 1,500 °C required to convert Al<sub>2</sub>O<sub>3</sub> back to AlN (ref.<sup>11</sup>).

$$N_2 + 3H_2O \rightarrow 2NH_3 + 3/2O_2 \Delta_r H_{298K} = 765.6 \text{ kJ mol}^{-1} N_2$$
 (R1)

$$N_2 + 3H_2 \rightarrow 2NH_3 \Delta_r H_{298K} = -91.8 \text{ kJ mol}^{-1} N_2$$
 (R2)

Alternatively, NH<sub>3</sub> can be synthesized from N<sub>2</sub> and H<sub>2</sub> (equation (R2)) at renewable energy harvesting sites, where H<sub>2</sub> is produced from the electrolysis of H<sub>2</sub>O (ref. <sup>19</sup>). Unlike the highly endothermic nature of reaction equation (R1), reaction equation (R2) is an exergonic reaction. However, the traditional Haber–Bosch process is conducted under harsh conditions to overcome severe kinetic barriers in the dissociative activation and conversion of N<sub>2</sub> to NH<sub>3</sub> (refs <sup>20,21</sup>). A corresponding chemical looping process (denoted as

 $H_2$ -CL, see Fig. 1b) comprised of N fixation and hydrogenation steps is worth serious investigation<sup>22</sup>. Very limited efforts were given to such a CL even though its history dates back to the nineteenth century when the synthesis of NH<sub>3</sub> was attempted in a stepwise manner<sup>23</sup>. More recently a detailed investigation discussed the influences of metal–N bond strength and H<sub>2</sub> activation on the hydrogenation/ reduction of metal nitrides, and demonstrated experimentally<sup>24</sup> that the hydrogenation of Mn<sub>6</sub>N<sub>2.58</sub>, Ca<sub>3</sub>N<sub>2</sub> and Sr<sub>2</sub>N gave off NH<sub>3</sub> at 550 °C, respectively. A related work reported<sup>25</sup> that the hydrogenation of Mn nitrides to NH<sub>3</sub> was enhanced by the presence of Li at 400 °C.

As can be seen in Fig. 1, NH<sub>3</sub> formation from the H<sub>2</sub>O-CL or H<sub>2</sub>-CL process is mediated by metals that shift between different chemical states, where N<sub>2</sub> is reduced by metal. In this work, we report a chemical loop mediated by alkali or alkaline earth metal hydrides (denoted as AH) and imides (ANH). Such a CL features the reduction of dinitrogen by hydridic H in AH, and NH<sub>3</sub> production by the hydrogenation of ANH through the disproportionation of dihydrogen. Through this process, NH<sub>3</sub> can be synthesized at atmospheric pressure and 100 °C.

#### Alkali and alkaline earth metal imides as nitrogen carriers

Alkali and alkaline earth metal hydrides (AH) and imides (ANH) have been extensively studied as hydrogen storage materials in the past few decades<sup>26–29</sup>. Hydrogen in AH bears a negative charge and is highly reductive. Our previous investigations reveal that N<sub>2</sub> can be reduced by some AHs, forming imides and hydrogen<sup>30</sup>. Imides, on the other hand, react with H<sub>2</sub>, forming amides and NH<sub>3</sub> in a stepwise manner<sup>26,31</sup>. Such an understanding inspired us to propose a chemical looping process for NH<sub>3</sub> production comprising two sequential steps. In Step I, N<sub>2</sub> is reduced by the hydridic H of AH, forming ANH, then in Step II, hydrogenation of ANH via disproportionation of dihydrogen produces NH<sub>3</sub> and regenerates AH (as shown in Fig. 1c, denoted as AH-CL). It should be noted that

<sup>&</sup>lt;sup>1</sup>Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, China. <sup>2</sup>University of Chinese Academy of Sciences, Beijing, China. <sup>3</sup>Collaborative Innovation Center of Chemistry for Energy Materials, Dalian, China. \*e-mail: guojianping@dicp.ac.cn; pchen@dicp.ac.cn



**Fig. 1** [Chemical looping processes for ammonia synthesis.  $\mathbf{a}$ - $\mathbf{c}$ ,  $H_2$ O-CL (refs<sup>11,12</sup>) ( $\mathbf{a}$ ) and  $H_2$ -CL (ref.<sup>24</sup>) ( $\mathbf{b}$ ) denote chemical looping processes for ammonia production that have been reported previously. AH-CL ( $\mathbf{c}$ ) is the loop presented in this work. M, M–N and M–O denote metal, the corresponding metal nitride and oxide, respectively; A–H and A–N–H denote alkali or alkaline earth metal hydride and imide, respectively. Electron flow is indicated.



**Fig. 2 | Thermodynamic analyses of steps I and II in AH-CL.** The solid lines are the temperature dependences of  $\Delta G$  for nitridation of hydrides (BaH<sub>2</sub>, LiH, CaH<sub>2</sub> and MgH<sub>2</sub>). The dashed lines are the temperature dependences of  $\Delta G$  for hydrogenation of imides (BaNH, Li<sub>2</sub>NH, MgNH and CaNH), nitride (Mg<sub>3</sub>N<sub>2</sub>) and amides (KNH<sub>2</sub> and NaNH<sub>2</sub>). The entropies of solids are not considered. The thermodynamic data used to prepare this plot are given in Supplementary Tables 1 and 2.

ANH may convert to nitride, amide, nitride hydride, or nonstoichiometric compounds under certain reaction conditions<sup>28,32,33</sup>.

The energy efficiency of the AH-CL depends on the thermodynamic properties of steps I and II. Based on the known thermodynamic data (Supplementary Tables 1 and 2), we calculated the Gibbs free energy changes of steps I and II mediated by different AH/ANH pairs (A = Li, Na, K, Mg, Ca or Ba) (shown in Fig. 2) in the temperature range 0–450 °C and 1.0 bar pressure of  $N_2$  or  $H_2$ . Neither Na nor K have an imide form, so they can hardly fix N under the present scheme, although the hydrogenation of NaNH<sub>2</sub> or KNH<sub>2</sub> to NH<sub>3</sub> is thermodynamically favourable at lower temperatures. In contrast, Mg has an imide form (MgNH); however, Mg<sub>3</sub>N<sub>2</sub> is thermodynamically more stable, making it difficult to hydrogenate to NH<sub>3</sub> under moderate conditions-that is, the energy gap between steps I and II is wide for the MgH<sub>2</sub>/Mg<sub>3</sub>N<sub>2</sub> pair. As shown in Fig. 2, the thermodynamic feasibility of the AH/ANH pair in mediating AH-CL is in the order  $LiH/Li_2NH \approx BaH_2/BaNH > CaH_2/CaNH > MgH_2/$ MgNH (Mg<sub>3</sub>N<sub>2</sub>).

We then validated the N fixation and hydrogenation steps experimentally. Fig. 3a shows that H<sub>2</sub> is produced from the reaction of N<sub>2</sub> and  $\overline{AH}$  ( $\overline{AH}$  = LiH, CaH<sub>2</sub> or BaH<sub>2</sub>) in the temperature range of 300 to 500 °C. The formation of H<sub>2</sub> can be regarded as an indication of the reduction of N<sub>2</sub> by the hydridic H of AH. It should be noted that the self-decomposition of these AHs occurs at much higher temperatures, as shown in the Ar-temperature programmed decomposition (Ar-TPD) profiles (Fig. 3a)<sup>34</sup>. In comparison, alkaline earth metal hydrides react with N2 at lower temperatures (onset temperature at approximately 260 °C) than LiH (at approximately 350 °C). Correspondingly, BaH<sub>2</sub> and CaH<sub>2</sub> have faster rates of weight gain than LiH in a N<sub>2</sub> atmosphere, as shown in the N<sub>2</sub>-thermogravimetric (N<sub>2</sub>-TG) profiles (Fig. 3b). The postnitridized solid residues were collected for characterization. As shown in Fig. 3d and Supplementary Fig. 1, the bulk phase diffractions and N-H vibrations of BaNH, CaNH and Li<sub>2</sub>NH were detected by X-ray diffraction (XRD) and Fourier transform infrared (FTIR) analysis, respectively, which confirm the fixation of N by these alkali and alkaline earth metal hydrides via reaction equation (R3).

Step I–N fixation:  

$$4AH_x + xN_2 \rightarrow 2xA_{2/x}NH + xH_2$$
 (x: valence of A) (R3)

Step II-Hydrogenation:  

$$xA_{2/x}NH + 2xH_2 \rightarrow 2AH_x + xNH_3$$
(R4)

The overall reaction is  $N_2 + 3H_2 \rightarrow 2NH_3$ 

The formation of NH<sub>3</sub> from the hydrogenation of ANH was tested by H<sub>2</sub>-temperature-programmed-reaction (H<sub>2</sub>-TPR). As shown in Fig. 3c, an ammonia signal was detected on the nitridized LiH and BaH<sub>2</sub> samples at temperatures above 200 °C, whereas little NH3 was formed from CaNH under the conditions applied in this work (probably due to kinetic or thermodynamic reasons). In comparison, BaNH hydrogenates to NH<sub>3</sub> at lower temperatures. The solid product collected after the H2-TPR measurement contains bulk phase LiH or BaH<sub>2</sub>, respectively (Fig. 3d), evidencing that ANH (A = Ba and Li) can be hydrogenated to  $NH_3$  and AH following reaction equation (R4). We further conducted a hydrogen isotopic exchange experiment over a BaNH sample. As shown in Supplementary Fig. 5, ammonia isotopomer-related species with signals at m/z = 17 (NH<sub>3</sub> or NDH), 18 (NH<sub>2</sub>D or ND<sub>2</sub>), 19 (ND<sub>2</sub>H) and 20 (ND<sub>3</sub>) were all detected. The intensities of H-containing species weaken with time, whereas ND3 enhances with time. These data



**Fig. 3** | Nitridation of hydride samples and hydrogenation of post-nitridized samples. a, N<sub>2</sub>-TPR (solid lines) and Ar-TPD (dashed lines) profiles of hydride samples. **b**, N<sub>2</sub>-TG profiles of hydride samples. **c**, H<sub>2</sub>-TPR profiles of post-nitridized samples. **d**, XRD patterns of nitridized (black lines) and hydrogenated (red lines) samples. a.u., arbitrary units.

show that H in BaNH combines with N to form  $NH_3$  in the hydrogenation process. We thus conclude that, under the conditions applied in this study, that is, atmospheric pressure and 100–500 °C, the BaH<sub>2</sub>/BaNH and LiH/Li<sub>2</sub>NH pairs can mediate ammonia production via the AH-CL proposed in Fig. 1c.

Kinetic optimization of N fixation and hydrogenation steps

From the thermodynamic point of view (Fig. 2), the nitridation of LiH and BaH<sub>2</sub> (reaction equation (R3)) can take place at temperatures below 250 °C. We thus introduced late 3d transition metals (denoted as TM), such as Fe, Co and Ni, to catalyse step I of AH-CL. BaH<sub>2</sub> and LiH were then ball milled with Fe, Co or Ni particles with sizes of approximately 5-9µm, 30 nm and 20-100 nm, respectively. The nitridation of those samples was monitored by N<sub>2</sub>-TPR and N<sub>2</sub>-TG at atmospheric pressure (shown in Figs 4a,b and Supplementary Fig. 2a). The addition of TM can greatly reduce the onset temperature by more than 100 °C. In comparison, Ni and Co performed better than Fe in promoting N fixation in LiH; Ni is slightly better than Co and Fe for BaH<sub>2</sub>. The postnitridized TM-BaH<sub>2</sub> samples contain metallic TM and BaNH phases (Supplementary Fig. 3). The degree of nitridation of the Ni-BaH<sub>2</sub> sample reached approximately 40% within 30 min at 265 °C (Fig. 4c). Approximately 60% of the fixed N converted to NH<sub>3</sub> within 10 min of hydrogenation at 265 °C (Fig. 4d). Only Ni and BaH<sub>2</sub> phases were observed by XRD in the post-hydrogenated sample (Supplementary Fig. 4).

We thus focused on Ni-BaH<sub>2</sub> in the following study. Quantitative kinetic analyses of the nitridation of BaH<sub>2</sub> and Ni-BaH<sub>2</sub> were performed based on N<sub>2</sub>-TG measurements. The rate of nitridation was calculated on the basis of the sample weight gain within the first 10 min at preset temperatures. As shown in Fig. 5a,

the neat BaH<sub>2</sub> sample undergoes nitridation at approximately 190  $\mu$ mol N g<sup>-1</sup>BaH<sub>2</sub>h<sup>-1</sup> and 3,230  $\mu$ mol N g<sup>-1</sup>BaH<sub>2</sub>h<sup>-1</sup> at 265 °C and 338 °C, respectively. The 50% Ni-BaH<sub>2</sub> sample, on the other hand, exhibits much higher rates at lower temperatures; approximately 1,100  $\mu$ mol N g<sup>-1</sup>BaH<sub>2</sub>h<sup>-1</sup> at 192 °C and 5,720  $\mu$ mol N g<sup>-1</sup>BaH<sub>2</sub>h<sup>-1</sup> at 265 °C. The apparent activation energy (*E*<sub>a</sub>) of nitridation was thus calculated based on the data measured at different temperatures (Fig. 5b). The addition of Ni markedly reduces the kinetic barrier from 109.3 ± 11.6 kJ mol<sup>-1</sup> to 46.4 ± 4.8 kJ mol<sup>-1</sup>, manifesting the strong catalytic role of Ni in promoting the N fixation step.

The addition of Ni particles also benefits the hydrogenation step, as evidenced by the reduced onset temperature and higher NH<sub>3</sub> intensity at lower temperatures of the corresponding H2-TPR curves (Supplementary Fig. 2b). The rate of hydrogenation was quantified according to the amount of ammonia produced within the first 30 min of hydrogenation at preset temperatures. As shown in Fig. 5c, the hydrogenation of the BaNH sample occurred immediately above 100 °C with a rate of approximately  $160 \,\mu\text{mol}\,\text{NH}_3\text{g}^{-1}\text{BaH}_2\text{h}^{-1}$  at 100 °C and 9,600 µmol NH<sub>3</sub>g<sup>-1</sup>BaH<sub>2</sub>h<sup>-1</sup> at 275 °C. In general, the nitridized Ni-BaH<sub>2</sub> sample underwent hydrogenation at much faster rates; approximately  $960\,\mu mol\,NH_3\,g^{-1}\,BaH_2\,h^{-1}$  at 100 °C and 28,800  $\mu$ mol  $\dot{NH}_3g^{-1}BaH_2h^{-1}$  at 275 °C. Accordingly, the apparent activation energy of hydrogenation is  $33.5 \pm 2.3$  kJ mol<sup>-1</sup> for Ni–BaNH and  $41.6 \pm 3.1$  kJ mol<sup>-1</sup> for BaNH; neither value is noticeably high, so the hydrogenation can take place at a temperatures as low as 100 °C.

### Performance of AH-CL

The stoichiometric reactions of steps I and II of AH-CL show that one or half an equivalent N can be fixed and converted to  $NH_3$ per cycle of the loop mediated by  $BaH_2/BaNH$  or  $LiH/Li_2NH$ ,



**Fig. 4 | Nitridation and hydrogenation of TM-AH samples. a**, N<sub>2</sub>-TG profiles of BaH<sub>2</sub> and TM-BaH<sub>2</sub> samples. **b**, N<sub>2</sub>-TG profiles of LiH and TM-LiH samples. **c**, Nitridation of the 50% Ni-BaH<sub>2</sub> sample at 265 °C based on TG measurements. **d**, Hydrogenation of the post-nitridized 50% Ni-BaH<sub>2</sub> sample at 265 °C.



**Fig. 5** | **Kinetic measurements of N**<sub>2</sub> **fixation and hydrogenation of BaH**<sub>2</sub>-**CL. a**, Temperature-dependent N<sub>2</sub> fixation in BaH<sub>2</sub> and 50% Ni-BaH<sub>2</sub>. **b**, Arrhenius plots of **a**; *R* in the *y* axis refers to reaction rate. **c**, Temperature-dependent NH<sub>3</sub> production via hydrogenation of the post-nitridized BaH<sub>2</sub> and 50% Ni-BaH<sub>2</sub> samples. **d**, Arrhenius plots of **c**. Error bars in **a**-**d** represent the standard deviation from three independent measurements. The solid lines in **a** and **c** are guides to the eye. The lines in **b** and **d** are fitted linearly by the method of least squares approximation.



**Fig. 6 | Performances of Ni-BaH2 (LiH) for ammonia production. a**, Temperature-dependent ammonia production rates of Ni-AH samples in chemical looping (CL) and thermo-catalytic processes (Catal.), respectively. Error bars in **a** represent the standard deviation from three independent measurements. The lines are guides to the eye. **b**, SEM and elemental mapping images of the post-tested Ni-BaH<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> sample. **c**, Comparison of NH<sub>3</sub> production rates of Ni-catalysed AH-CL (1bar) and the conventional thermo-catalytic process (10 bar). The activities of Co<sub>3</sub>Mo<sub>3</sub>N and Fe-K<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub> were taken from ref. <sup>38</sup>. Error bars in **c** represent the standard deviation from three independent measurements. **d**, Cyclic tests of Ni-catalysed BaH<sub>2</sub>-CL at 250 °C, 1bar. The sample collected after 10 cycles was ball milled and re-tested, which is denoted as Reactivated.

<b>Table 1</b>   NH <sub>3</sub> production rates of TM-AH samples in chemical
looping and thermo-catalytic processes at 300 °C, 1bar. The
$NH_3$ production rate of LiH was measured at 350 °C and 1 bar

Samples	Chemical looping (µmol g <sup>-1</sup> h <sup>-1</sup> )	Catalytic process (µmol g <sup>−1</sup> h <sup>−1</sup> )
BaH <sub>2</sub>	198±11	Undetectable
20% Fe-BaH <sub>2</sub>	1,703±70	384±13
20% Co-BaH <sub>2</sub>	1,866±92	$576 \pm 20$
20% Ni-BaH <sub>2</sub>	2,033±50	48±5
50% Ni-BaH <sub>2</sub>	3,125 ± 80	20±3
LiH	105±8	Undetectable
50% Ni-LiH	1,533±50	Undetectable

respectively. Therefore, the atomic efficiency can in principle reach 100%, which is supported by the following experimental facts: first, there are phase transitions from  $BaH_2$  to BaNH in the N fixation step and from BaNH back to  $BaH_2$  in the hydrogenation step (see Fig. 3d); second, the degree of nitridation of  $BaH_2$  reached  $96 \pm 4\%$  after heating the 50% Ni–BaH<sub>2</sub> sample under a N<sub>2</sub> flow at 265 °C for 5 h (see Methods section); and third, nearly all the fixed N can be hydrogenated to NH<sub>3</sub> (as shown in Fig. 4d).

To evaluate the kinetic efficiency of the AH-CL in producing  $NH_{3}$ , we designed and set up a device that can run steps I and II in alternation by switching  $N_2$  and  $H_2$  streams to the TM-AH samples at preset temperatures. The ammonia production rate was calculated by dividing the amount of ammonia produced by the total time of nitridation and hydrogenation in a single loop,

Ammonia production rate ( $\mu$  mol g<sup>-1</sup> h<sup>-1</sup>) = amount of ammonia produced per gram of material

(time of nitridation + time of hydrogenation)

Table 1 and Fig. 6 summarize the ammonia production rates of the AH-CL with or without the addition of Fe, Co or Ni catalyst, respectively. The loop mediated by neat LiH/Li<sub>2</sub>NH produces NH<sub>3</sub> at a rate of approximately 100  $\mu$ mol NH<sub>3</sub>g<sup>-1</sup>LiH h<sup>-1</sup> at 350 °C, whereas the 50% Ni–LiH sample has a rate of approximately 1,530  $\mu$ mol NH<sub>3</sub>g<sup>-1</sup>LiH h<sup>-1</sup> at 300 °C. At 300 °C, the loop mediated by neat BaH<sub>2</sub>/BaNH produces NH<sub>3</sub> at a rate of approximately 200  $\mu$ mol NH<sub>3</sub>g<sup>-1</sup>BaH<sub>2</sub>h<sup>-1</sup>; a much higher value of approximately 3,120  $\mu$ mol NH<sub>3</sub>g<sup>-1</sup>Ni–BaH<sub>2</sub>h<sup>-1</sup> is achieved by the 50% Ni–BaH<sub>2</sub> sample. It is worth mentioning that the addition of 5% Ni can increase the rate of NH<sub>3</sub> production from BaH<sub>2</sub>-CL by a factor of six. The rate increases steadily with the Ni content until 50% (Supplementary Fig. 6), indicating the strong influence of the contact between Ni and AH particles on the reaction kinetics, which we will discuss in the following section.

To investigate whether a sample with Ni and AH dispersed on a high surface area support would have improved kinetics, we prepared an  $Al_2O_3$ -supported sample (Ni–BaH<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>). This material had improved performance, achieving a NH<sub>3</sub> production rate that is approximately twice that of the unsupported sample (Fig. 6 and Supplementary Table 3). The X-ray emission maps of the sample collected after reaction (Fig. 6b) reveal that Ba and Ni are evenly dispersed on  $Al_2O_3$ , evidencing a close contact between Ni and BaH<sub>2</sub>, and hence leading to improved kinetics in NH<sub>3</sub> production. To explore the capacity limit of the AH-CL, we reduced the operating temperature to 100 °C and then nitridized the Ni–BaH<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>



**Fig. 7 | Conceptual set-up for sustainable ammonia synthesis via AH-CL.** The proposed setup contains a fixed-bed reactor loaded with an Ni-BaH<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> sample, a hydrogen sorption unit (bottom left), an ammonia sorption unit (bottom right), an air separation unit (ASU) and an electrolyzer. An estimated mass balance is also indicated there, showing that 1 kg of Ni-BaH<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> converts approximately 81g of N<sub>2</sub> and 156g of H<sub>2</sub>O to 98g of NH<sub>3</sub> per hour at 300 °C and 1 bar.

sample for 40 h and hydrogenated for 0.5 h. A very low but still detectable NH<sub>3</sub> formation rate of approximately  $2.3 \,\mu$ mol NH<sub>3</sub> g<sup>-1</sup>Ni-BaH<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>h<sup>-1</sup> was obtained (see Supplementary Fig. 7).

For the purpose of comparison, we also measured the performances of Ni-AH samples in the thermo-catalytic process by co-feeding a mixed N<sub>2</sub>-3H<sub>2</sub> stream to the samples. The temperature-dependent NH<sub>3</sub> production rates of AH-CL and of the thermocatalytic process are shown in Fig. 6a. To achieve a similar NH<sub>3</sub> production rate, a temperature increase of approximately 150°C is needed for the thermo-catalytic process, which is consistent with the known fact that Ni hardly catalyses NH<sub>3</sub> synthesis<sup>35</sup>. We further compare the ammonia production rates of AH-CL with some known or derived activity data of conventional thermo-catalytic processes<sup>36</sup>. As shown in Fig. 6c, the AH-CL performs markedly well under milder conditions; for example, at 250 °C, the BaH<sub>2</sub>/ BaNH-mediated chemical looping process operated at atmospheric pressure produces NH<sub>3</sub> at a rate that is more than an order of magnitude higher than the thermo-catalytic process operated under 10 bar pressure.

The stability of the Ni-catalysed BaH2-CL was evaluated at 250 °C and atmospheric pressure. Fig. 6d shows that the NH<sub>3</sub> production rate decreased from an initial rate of approximately 1,200  $\mu$ mol NH<sub>3</sub>g<sup>-1</sup>h<sup>-1</sup> to 900  $\mu$ mol NH<sub>3</sub>g<sup>-1</sup>h<sup>-1</sup> after eight cycles and stabilized at that level. XRD characterization of the cycled sample revealed the considerably increased peak intensities of Ni and BaH<sub>2</sub> (as shown in Supplementary Fig. 8 and Supplementary Table 4), indicating the occurrence of separation and aggregation of Ni and BaH<sub>2</sub> particles during the cycling treatment, which may explain the slowed reaction rate observed in Fig. 6d. We thus ball milled the sample collected after cycling 10 times and re-tested its performance. As shown in Fig. 6d the NH<sub>3</sub> production rate of the sample can be essentially recovered (at approximately 1,100 µmol  $NH_3g^{-1}h^{-1}$ ). Further materials engineering would be required to improve the morphological stability and to maximize the contact between TM and AH.

A simple diagram for ammonia production via the AH-CL powered by electricity and heat from renewable energy and with  $N_2$  and  $H_2O$  as feedstock is proposed and shown in Fig. 7. In this proposal,  $N_2$  from the air separation unit and three equivalent  $H_2$  from water electrolysis circulate in alternation within the reaction unit loaded with TM–AH material. NH<sub>3</sub> produced can be separated from the circulating stream by NH<sub>3</sub> absorbents such as halides<sup>37,38</sup>. We thus evaluated NH<sub>3</sub> absorption using CaI<sub>2</sub>, which has an equilibrium NH<sub>3</sub> pressure of 59 ppm at 25 °C when forming Ca(NH<sub>3</sub>)I<sub>2</sub>(ref. <sup>38</sup>). As shown in Supplementary Fig. 9a, a sorption unit filled with CaI<sub>2</sub> powder was placed between the vent of the reactor and the conductivity meter and the hydrogenation of nitridized Ni–BaH<sub>2</sub> was conducted at 275 °C. As clearly shown in Supplementary Fig. 9b, little NH<sub>3</sub> can be detected by the conductivity meter, evidencing efficient NH<sub>3</sub> absorption by CaI<sub>2</sub>. The absorbed NH<sub>3</sub> can be released by heating the sorbent to 300 °C (ref. <sup>38</sup>). The H<sub>2</sub> co-produced in the N fixation step can be stored in a solid hydrogen storage material<sup>39</sup> and re-used as feed gas upon thermal desorption.

The mass and energy balance analyses of the AH-CL are marked in Fig. 7 and Supplementary Fig. 10, respectively. Comparatively, the mild-condition AH-CL has a clear advantage over the Haber– Bosch process, which requires heavy energy input, especially for the gas compression and heat exchange. It is worth mentioning that smart management of the reaction heat from steps I and II and from  $NH_3/H_2$  sorption/desorption would probably improve the energy efficiency of the AH-CL.

#### Discussion

Most chemical looping processes reported to date make use of the reactivity of metals with  $O_2$ ,  $H_2O$ ,  $N_2$  and/or  $H_2$ , so that the corresponding M–O/N/H bond strength correlates with the thermodynamic and kinetic properties of the loops<sup>17,24</sup>. The work reported here highlights the role of hydrogen species in  $N_2$  activation and conversion. Bearing negative charge in H, AH is a strong reducing agent and has a chemical potential that drives the N fixation step (reaction equation (R3)) by providing electrons to  $N_2$  to break the N=N triple bond. The oxidative state of H in the N fixation step thus charges from -1 (AH) to 0 ( $H_2$ ) and +1 (ANH). The hydrogenation step also contains distinct features, especially in  $H_2$  conversion; that is,  $H_2$  undergoes disproportionation to hydridic and protic H atoms to bond with alkali (or alkaline earth) and N to form AH and NH<sub>3</sub>,

respectively. In this context, H shuttling among chemical states of -1 (AH), 0 (H<sub>2</sub>) and +1 (ANH and NH<sub>3</sub>) is the essence of the AH-CL (see Fig. 1).

The other interesting feature of the AH-CL is that both steps can be catalysed by late 3d metals, where Ni and Co have comparable if not superior performances to Fe. That is in striking contrast to the thermo-catalytic process, where Ni and Co are hardly active because they have relatively weak chemisorption to N and their surfaces would be preferentially covered with H, leaving few sites for N<sub>2</sub> activation<sup>40</sup>. The separation of N fixation and hydrogenation steps and the accommodation of activated N in imide in the AH-CL circumvent such a competitive situation commonly observed in the thermo-catalytic process. It would be intriguing to determine whether N<sub>2</sub> is activated directly on the surface of Ni (or Co) followed by N spilling over to AH nearby or through another mechanism in which AH takes part. Our previous investigation suggests that a ternary hydride species [Li-Fe-H] could form at the interface of LiH and Fe, which can dissociate N<sub>2</sub>, forming [Fe-NH<sub>2</sub>-Li] and [LiNH<sub>2</sub>] species<sup>41</sup>. Similarly, some hydride species containing both Ni (Co) and Ba (Li) are probably present at the interface (because the surface Ni (Co) and Ba (Li) are coordinatively unsaturated)<sup>42</sup> and play key roles in N<sub>2</sub> activation and/or N transfer. A follow-up mechanistic investigation is underway.

As discussed previously<sup>24</sup>, separating the NH<sub>3</sub> synthesis into a stepwise chemical loop would possibly disturb the scaling relations that prevail in thermo-catalytic processes<sup>43</sup>. Such an effect can be clearly seen in this work by the comparable performance of Fe, Co and Ni in the N fixation step, and the additional freedom in tuning the kinetic/thermodynamic properties of each step; that is, the BaH<sub>2</sub>/BaNH pair exhibits different properties from the LiH/Li<sub>2</sub>NH pair in mediating the AH-CL. In the chemical looping processes of hydrocarbon oxidation, the thermodynamic and kinetic properties of oxygen carriers in reacting with hydrocarbons and oxygen are determining factors for high production/selectivity and exergy<sup>17,18</sup>. Similarly, N carriers in NH<sub>3</sub> synthesis loops should have suitable properties allowing N fixation and hydrogenation to be carried out efficiently. From the thermodynamic point of view, the relatively smaller energy gap between steps I and II mediated by the BaH<sub>2</sub>/ BaNH or LiH/Li2NH pair (shown in Fig. 2) is in favour of an energyefficient CL. Tremendous research efforts have been given to materials development for onboard hydrogen storage in the past two decades, where a wide variety of metal hydrides, complex hydrides and chemical hydrides have been synthesized and characterized<sup>27-29</sup>, providing plenty of scope for materials selection to mediate such an NH<sub>3</sub> synthesis loop.

### Conclusions

A looped ammonia synthesis process mediated by alkali or alkaline earth metal hydride/imide pairs is proposed and demonstrated in this work. Such a chemical loop mediated by BaNH and catalysed by Ni produces  $NH_3$  at 100 °C and atmospheric pressure, and has a  $NH_3$  production rate more than one order of magnitude higher than that of the Cs–Ru/MgO catalysed process at temperatures below 250 °C. This chemical looping process provides a promising solution to the efficient harvesting and storage of renewable energy and promotes  $NH_3$  as an energy vector for a clean and sustainable energy future.

### Methods

**Chemicals and materials.** Fe powder (Aldrich,  $5-9 \mu m$ , 99.5%), Co powder (Aladdin, 30 nm, 99.9%), Ni powder (Aladdin, 20-100 nm, 99.9%), Ba metal (Aldrich, 99%), LiH (Aladdin, 97%), CaH<sub>2</sub> (Alfa, 97%), urea (Sinopharm, 99%), Ni(NO<sub>3</sub>)<sub>2</sub>:6H<sub>2</sub>O (Kermel, 99.0%), CaI<sub>2</sub> (Aladdin, 99%),  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Aladdin, 10 nm, 99.9%), MgO (Macklin, 50 nm, 99.9%) were used as received. BaH<sub>2</sub> was synthesized by reacting Ba metal with H<sub>2</sub> at 20 bar and room temperature for 2 d followed by a heat treatment at  $400 \,^{\circ}$ C for 2 h. Ba(NH<sub>2</sub>)<sub>2</sub> was synthesized by

reacting Ba metal with purified NH<sub>3</sub> gas at room temperature for 7 d. BaNH was prepared by heating Ba(NH<sub>2</sub>)<sub>2</sub> at 300 °C for 5 h. The formations of BaH<sub>2</sub>, Ba(NH<sub>2</sub>)<sub>2</sub> and BaNH were confirmed by XRD characterization. All of the sample loadings were handled in a glove box filled with argon. N<sub>2</sub> (99.999%), H<sub>2</sub> (99.999%), Ar (99.999%), He (99.999%), N<sub>2</sub>/H<sub>2</sub> (1/3, 99.999%) and D<sub>2</sub> (99.999%) were purchased from JunFeng Gas Co.

Synthesis of transition metal(TM)-hydride mixtures. The mixtures of TM (Fe, Co or Ni) and alkali or alkaline earth hydride (AH) were prepared via ball milling the corresponding TM and AH powder, and were denoted as X%TM-AH, where X represents the weight percentage of TM in the sample. Typically, the 50% Ni-BaH<sub>2</sub> sample was prepared by ball milling BaH<sub>2</sub> (300 mg) and Ni powder (300 mg) in an Ar-filled stainless steel vessel on a Retsch planetary ball mill (PM 400, Germany) at 200 r.p.m. for 20h. Four stainless steel balls (i.d.=1 cm) were used. The ball-to-sample mass ratio is 100:1.

Synthesis of Al<sub>2</sub>O<sub>3</sub>- and MgO-supported Ni-BaH<sub>2</sub> sample. The supported Ni sample was prepared according to the reported method<sup>44</sup>. The mass ratio of Ni to (Ni+support) is 70%. The supported Ni-BaH<sub>2</sub> sample (denoted as Ni-BaH<sub>2</sub>/ support) was prepared by impregnating the 70% Ni/support sample in a barium– ammonia solution, where Ba metal converted to barium amide (Ba(NH<sub>2</sub>)<sub>2</sub>) in the presence of Ni. After removal of NH<sub>3</sub>, the solid residue was hydrogenated at 300 °C for 2 h to allow the complete conversion of Ba(NH<sub>2</sub>)<sub>2</sub> to BaH<sub>2</sub> according to the reaction Ba(NH<sub>2</sub>)<sub>2</sub> + 2H<sub>2</sub>  $\rightarrow$  BaH<sub>2</sub> + 2NH<sub>3</sub>.

**TPR measurements.** TPR measurements were performed on a quartz-lined stainless steel reactor, and the tail gases were analysed by an online mass spectrometer (MS, Hiden HPR20). Samples were heated in Ar (Ar-TPD), N<sub>2</sub> (N<sub>2</sub>-TPR) or H<sub>2</sub> (H<sub>2</sub>-TPR) flow (30 ml min<sup>-1</sup>) from room temperature to preset temperatures at a ramping rate of 5 °C min<sup>-1</sup>, and the signals of H<sub>2</sub> (m/z=2), N<sub>2</sub> (m/z=28), and NH<sub>3</sub> (m/z=17) were monitored.

 $N_2$  fixation in AH.  $N_2$  fixation in AH was measured quantitatively on a thermogravimeter (TG, Netzsch 449 C, Germany) or on a home-made reactor equipped with a detachable sample holder whose weight can be measured by a balance in a glovebox filled with argon. In both cases, AH samples were heated under a flow of purified  $N_2$  at ambient pressure. Approximately 10 mg (TG) or 50 mg (home-made reactor) sample was tested. The detection limit of TG and the balance are 0.1 µg and 0.1 mg, respectively. The degree of nitridation was calculated following the equation below:

Degree of nitridation(%) =  $\frac{\text{actual weight gain}}{\text{theoretical weight gain according to R3}}$ 

In a typical run, approximately 50 mg of 50% Ni–BaH<sub>2</sub> sample was loaded in the sample holder of the home-made reactor, heated under a flow of purified N<sub>2</sub> at 265 °C for 5 h and then cooled down to room temperature. The sample was then transferred to the glovebox and collected to measure the weight gain. Such an experiment was repeated three times. A degree of nitridation of 96 ± 4 % was obtained.

**NH**<sub>3</sub> **production from hydrogenation of ANH.** The hydrogenation was conducted by reacting the nitridized sample in a H<sub>2</sub> stream (30 ml min<sup>-1</sup>) at a given temperature or from room temperature to the desired temperature at a ramping rate of 5 °C min<sup>-1</sup>. The tail gas was introduced to a diluted H<sub>2</sub>SO<sub>4</sub> solution (1.0 mmoll<sup>-1</sup>, 100 ml at 25 °C) whose ion conductivity was monitored by a conductivity meter (Mettler Toledo SevenMulti)<sup>45-47</sup>. The principle of the NH<sub>3</sub> quantification method can be found in the Supplementary Methods.

The degree of hydrogenation (shown in Fig. 4d) was calculated following the equation

Degree of hydrogenation(%) = <u>amount of ammonia produced during hydrogenation process</u> <u>amount of fixed N in the nitridized TM-AH</u>

**Performance of chemical looping process.** NH<sub>3</sub> production from the AH-CL was via reacting the TM–AH sample (30 mg) with N<sub>2</sub> (30 ml min<sup>-1</sup>) for 30 min and subsequently H<sub>2</sub> (30 ml min<sup>-1</sup>) for 15 min at atmospheric pressure and the given temperature unless otherwise stated. The ammonia production rate was calculated by dividing the amount of ammonia produced by the total time of nitridation and hydrogenation in a single loop,

Ammonia production rate( $\mu$  mol g<sup>-1</sup> h<sup>-1</sup>) = amount of ammonia produced per gram of material (time of nitridation + time of hydrogenation)

### **NATURE ENERGY**

**Thermo-catalytic measurement.** The thermo-catalytic ammonia synthesis were conducted on a quartz-lined stainless steel fix-bed reactor under a continuous flow of syngas (N<sub>2</sub>–3H<sub>2</sub>, 30 ml min<sup>-1</sup>) at atmospheric pressure. Typically, 30 mg of catalyst was loaded in the reactor and heated at a ramping rate of 5 °C min<sup>-1</sup>. The amount of ammonia produced was measured with the aid of the conductivity meter. The decrease in conductivity of the diluted H<sub>2</sub>SO<sub>4</sub> solution with respect to the time can be correlated with the NH<sub>3</sub> production rate. This method has been widely employed in ammonia synthesis rate measurements<sup>45-47</sup>. The activity data at each temperature was recorded after a stable performance of catalyst was reached.

**Instrumentation.** SEM and EDX were conducted on a JSM-7800F ultrahighresolution thermal field emission scanning electron microscope; Powder XRD patterns were recorded on a PANalytical X'pert diffractometer using a home-made sample cell covered with KAPTON film to avoid air and moisture contamination; FTIR spectra were recorded on a Varian 3100 infrared spectrometer in diffuse reflectance FTIR (DRIFT) mode. The specific surface area of samples was determined by a QuadraSorb SI4 instrument. The mean particle size calculated by the Scherrer equation and specific surface area of some samples are shown in Supplementary Table 4.

### Data availability

The data that support the plots within this paper and other finding of this study are available from the corresponding author upon reasonable request.

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### Author contributions

P.C. conceived the research and wrote the paper. J.G. coordinated the experimental work. W.G. performed the synthesis, characterization and ammonia production rate measurements of the materials. All authors discussed the results and commented on the manuscript.

### **Competing interests**

The authors declare no competing interests.

### **Additional information**

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Correspondence and requests for materials should be addressed to J.G. or P.C.

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