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## Nitrogen fixation by alkali and alkaline earth metal hydrides assisted by plasma†

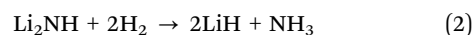
 Han Wu,<sup>‡,ab</sup> Kai Ma,<sup>‡,ab</sup> Jiaqi Wen,<sup>ab</sup> Liang Yang,<sup>c</sup> Ye qin Guan,<sup>ab</sup> Qianru Wang,<sup>ab</sup> Wenbo Gao,<sup>ab</sup> Jianping Guo<sup>ab\*</sup> and Ping Chen<sup>ab</sup>

**The chemical behaviors of alkali and alkaline earth metal hydrides including LiH, KH, MgH<sub>2</sub>, CaH<sub>2</sub>, and BaH<sub>2</sub> under nitrogen plasma differ significantly from one another, exhibiting an ammonia production trend that contrasts with that observed under thermal conditions. A prominent feature of KH is its ability to facilitate plasma-assisted N<sub>2</sub> fixation without generating H<sub>2</sub> byproduct, showing high atomic economy in utilization of hydride ions for N<sub>2</sub> reduction.**

Dinitrogen (N<sub>2</sub>) fixation is not only of scientific significance but also plays a paramount role in preparation of ammonia (NH<sub>3</sub>), which is a key raw molecule for producing nitrogen-based fertilizer and has been widely considered as an important energy or hydrogen carrier.<sup>1</sup> Currently, NH<sub>3</sub> is synthesized using the established and centralized Haber–Bosch process, which operates under harsh conditions (>673 K, >10 MPa) and is energy intensive. The reduction of energy loss and the development of medium for decentralized, distributed renewable energy storage have heightened the urgent need for sustainable ammonia synthesis approaches.<sup>2</sup> Significant efforts have been directed toward low-temperature thermal-catalytic, electro-chemical, photo-chemical, plasma-catalytic, and chemical looping ammonia synthesis methods.<sup>3–7</sup> And a number of new materials for nitrogen fixation have emerged.

Hydride (H<sup>−</sup>)-containing materials, such as alkali and alkaline earth metal hydrides, transition metal hydrides and oxyhydrides, nitride-hydrides, and composite hydrides have shown great promise for N<sub>2</sub> fixation to NH<sub>3</sub>.<sup>8–13</sup> For instance, alkali and alkaline earth hydrides such as LiH and BaH<sub>2</sub> can fix N<sub>2</sub> to form corresponding metal imides (Li<sub>2</sub>NH and BaNH) upon heating

to desired temperatures, accompanied by releasing H<sub>2</sub> (eqn (1)). The subsequent thermal hydrogenation of imides results in formation of NH<sub>3</sub> and regeneration of metal hydrides (eqn (2)).<sup>11,14</sup> NaH and KH, however, cannot fix N<sub>2</sub> under standard thermal conditions (Fig. S1, ESI†) due to the absence of thermodynamically stable imides.<sup>15</sup> We found unexpectedly, NaH is able to fix N<sub>2</sub> to form a surface NaNH<sub>2</sub> species with the assistance of plasma and the thermal hydrogenation of NaNH<sub>2</sub> to NH<sub>3</sub> occurs readily under low temperature, fulfilling a loop for ammonia production.<sup>16</sup> This plasma–thermal hybrid ammonia loop effectively prevents NH<sub>3</sub> from plasma-induced cracking, a challenging obstacle to overcome in plasma-catalytic ammonia synthesis.<sup>17</sup> Given the benefits of this hybrid chemical looping process for NH<sub>3</sub> synthesis, it is worthwhile to explore the potential of other alkali or alkaline earth hydrides, as well as those materials beyond hydrides. Herein, the interaction of a series of binary hydrides including LiH, KH, MgH<sub>2</sub>, CaH<sub>2</sub>, and BaH<sub>2</sub> with nitrogen plasma is investigated. Our findings reveal that their plasma-chemical responses under nitrogen plasma differ significantly from one another, exhibiting a trend that contrasts with that observed under normal thermal conditions. This study reveals the multi-facets of alkali and alkaline earth metal hydrides for N<sub>2</sub> fixation.



The chemical responses of a series of alkali and alkaline earth hydrides under argon or nitrogen plasma were investigated. Fig. S2 (ESI†) shows that, similar to NaH, all of the hydrides produce H<sub>2</sub> upon exposure to argon plasma, indicating the occurrence of dehydriding. Fig. 1a displays the time course of H<sub>2</sub> signals detected during the nitrogen plasma process. H<sub>2</sub> signals are also observed in LiH, CaH<sub>2</sub>, and BaH<sub>2</sub> under nitrogen plasma. Taking LiH as an example, the intensity of the H<sub>2</sub> signal initially showed slow growth over the first 10 min and then gradually decreased over time. The H<sub>2</sub> signals declined quickly with the turn-off of the plasma. Differing significantly

<sup>a</sup> State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China. E-mail: guojianping@dicmp.ac.cn

<sup>b</sup> Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, China

<sup>c</sup> Key Laboratory of Chemical Lasers, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

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‡ These two authors contribute equally to this work.



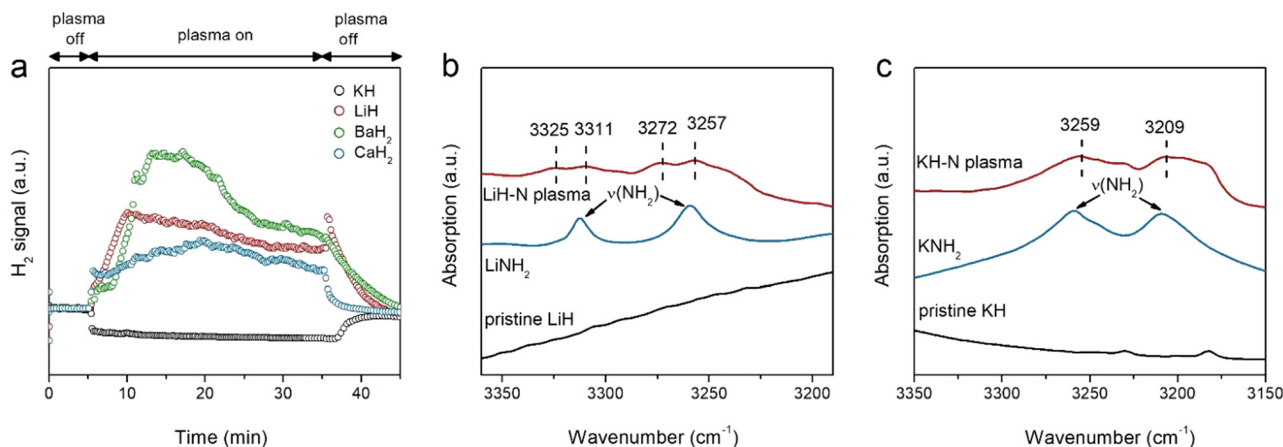


Fig. 1 (a) Time courses of  $H_2$  MS signals ( $m/z = 2$ ) for LiH, KH,  $CaH_2$ , and  $BaH_2$  under nitrogen plasma. Voltage is 12 kV. Plasma power is ca. 8 W. FTIR spectra of LiH (b) and KH (c) collected after nitrogen plasma treatment and reference LiH, KH,  $LiNH_2$ , and  $KNH_2$  samples.

from these hydrides, although dehydrogenating of KH also takes place under argon plasma (Fig. S2, ESI<sup>†</sup>), there is essentially no  $H_2$  formation from the KH sample under nitrogen plasma (Fig. 1a). The differing behaviors of KH under Ar and nitrogen plasmas suggest that  $N_2$  fixation by KH is fundamentally different from that of other alkali or alkaline earth metal hydrides.

Although they show different time courses of  $H_2$  signals under argon or nitrogen plasma, it is difficult to ascertain whether  $N_2$  fixation occurs based solely on the phenomenon of  $H_2$  formation. Therefore, the solid products after nitrogen plasma treatment were subjected to XRD and FTIR characterization. As shown in Fig. S3 (ESI<sup>†</sup>), the phase structures of LiH and  $CaH_2$  become amorphous after nitrogen plasma treatment, while the structure of KH remains largely unchanged although the intensity of the diffraction peaks significantly weakened. SEM images (Fig. S4, ESI<sup>†</sup>) show that the morphology of samples collected after nitrogen plasma treatments remained unchanged, suggesting it is only the (sub)surface of hydrides that is involved in the  $N_2$  fixation process. Fig. 1b, c and Fig. S5 (ESI<sup>†</sup>) show the FTIR spectra of different hydride samples after nitrogen plasma. LiH and KH exhibit prominent N–H vibrations, while there are no significant N–H vibrations on  $CaH_2$  and  $BaH_2$ . Specifically, several bands centered around 3325, 3311, 3272, and 3257  $cm^{-1}$  are observed for the LiH sample, which could be assigned as the asymmetric and symmetric stretch vibrations of  $NH_2^-$  species ( $\nu_{NH_2}$ ) of  $LiNH_2$ , respectively. For KH, two observable bands centered around 3255 and 3206  $cm^{-1}$  are clearly seen, which can be attributed to the surface  $KNH_2$  species (3259 and 3209  $cm^{-1}$ ).

The presence of nitrogen species on the surfaces of alkali or alkaline earth metal hydrides after nitrogen plasma can be further verified and quantified by measuring the  $NH_3$  produced when heated in a  $H_2$  flow. Fig. 2a presents the temperature-programmed hydrogenation (TPH) profile for the KH powder pretreated under nitrogen plasma at 12 kV. The formation of  $NH_3$  was monitored by using an on-line mass spectrometer and quantified by using a conductivity meter. It is clearly seen that  $NH_3$  evolves in the temperature range of 100–350 °C with two peaks around 160 and 220 °C. The amount of fixed N is determined to be ca. 27.4  $\mu mol$  and the conversion of KH could

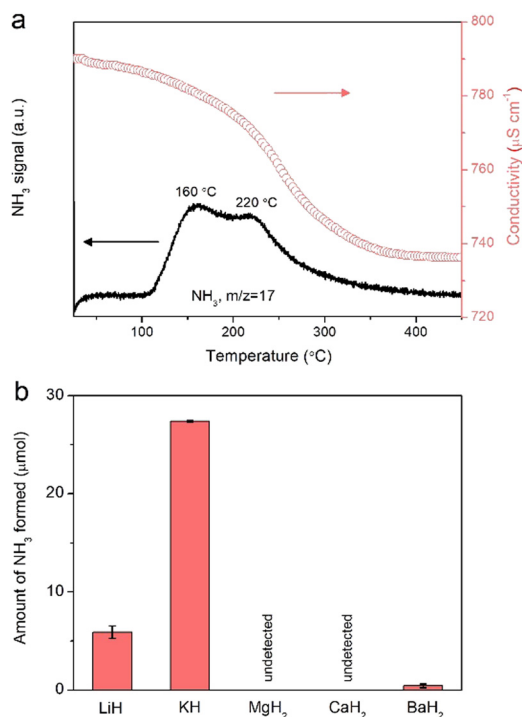


Fig. 2 (a) Temperature-programmed hydrogenation (TPH) profiles of  $NH_3$  signal ( $m/z = 17$ ) and conductivity decrease during the hydrogenation of the nitrogen plasma-treated KH sample. Sample mass is 30 mg.  $P_{H_2}$  is 1 bar.  $H_2$  flow rate is 30  $mL\ min^{-1}$ . (b) The amounts of fixed N in metal hydrides determined through TPH measurements. Voltage is 12 kV. Sample mass for LiH is 10 mg, and the others are 30 mg.

be estimated to 3.7%, suggesting that the  $N_2$  fixation occurs mainly at the (sub)surface of KH. XRD pattern shows that the phase structure of the KH sample was not changed (Fig. S6, ESI<sup>†</sup>).  $H_2$ -TPR profiles for LiH and  $BaH_2$  samples are shown in Fig. S7 (ESI<sup>†</sup>) and the amounts of produced ammonia are shown in Fig. 2b. The amounts of fixed N in LiH and  $BaH_2$  are 5.9 and 0.45  $\mu mol$ , respectively, while negligible amounts of  $NH_3$  were obtained from the hydrogenation of plasma-treated



MgH<sub>2</sub> and CaH<sub>2</sub> samples. Since some nitrogen species may not react with H<sub>2</sub> below 450 °C, an alternative method for NH<sub>3</sub> measurement, *i.e.*, hydrolysis of these samples using water vapor was also studied under room temperature. The hydrolysis of the MgH<sub>2</sub>, CaH<sub>2</sub>, and BaH<sub>2</sub> samples after nitrogen plasma treatment produces a measurable amount of NH<sub>3</sub>. The amounts of fixed nitrogen were determined to 1.1, 2.7, and 0.6 μmol by using hydrolysis method, respectively (Fig. S8, ESI†). Based on these results, it can be concluded that LiH, KH, MgH<sub>2</sub>, CaH<sub>2</sub>, and BaH<sub>2</sub> are able to fix N<sub>2</sub> under nitrogen plasma, but the amounts and fate of the fixed N vary significantly. We suppose the varying capacities of hydrides for plasma nitrogen fixation may be related to their different lattice energies. As shown in Table S1 (ESI†), alkali hydrides have much smaller lattice energies compared to their alkaline earth counterparts,<sup>18</sup> which may facilitate the dehydrating and accommodation of nitrogen in hydrides.

It has been reported that N<sub>2</sub> fixation by LiH, CaH<sub>2</sub>, and BaH<sub>2</sub> produces H<sub>2</sub> and the corresponding metal imides under thermal conditions (eqn (1)). Under nitrogen plasma, NaH can also fix N<sub>2</sub> to form NaNH<sub>2</sub> and H<sub>2</sub>.<sup>16</sup> The phenomenon of H<sub>2</sub> formation has also been observed in the nitrogen fixation processes mediated by some molecular transition metal hydrido complexes and nitrogenase enzymes, increasing energy consumption.<sup>19–21</sup> The pathways of reductive elimination of H<sub>2</sub> (2H<sup>-</sup> leading to H<sub>2</sub> and 2e, which then reduce N<sub>2</sub>), and reductive protonation (H<sup>-</sup> leading to H<sup>+</sup> and 2e) have been proposed to account for the formation of H<sub>2</sub> by-product and N–H bond during nitrogen fixation process, respectively. The interaction of KH with nitrogen plasma is, however, fundamentally different: KH fixes N<sub>2</sub> to form NH<sub>2</sub> species without releasing H<sub>2</sub> under plasma conditions. Therefore, majority of hydride ions in KH can be used for N<sub>2</sub> reduction and N–H bond formation, which is virtually more efficient for utilization of hydride than those of LiH, NaH, CaH<sub>2</sub>, and BaH<sub>2</sub>. There are two possible routes for N–H bond formation. For one thing, the hydrides act as electron sources for N<sub>2</sub> reduction through the reductive elimination of H atoms (H<sup>-</sup> leading to H and e), which then undergo further reductive protonation to form NH<sub>2</sub> species instead of generating H<sub>2</sub> (eqn (3)). On the other hand, the impact of energetic particles in plasma leads to the dehydrating of KH to form K and H<sub>2</sub> as demonstrated by H<sub>2</sub> formation under argon plasma (Fig. S2, ESI†) and a strong and symmetrical EPR signal (Fig. S9, ESI†). H<sub>2</sub> then easily reacts with reactive N species in plasma forming gaseous NH<sub>3</sub>. NH<sub>3</sub> may react with K through two possible pathways, *i.e.*, to form KNH<sub>2</sub> and H<sub>2</sub> (eqn (4)), or to form KNH<sub>2</sub> and KH (eqn (5)). Noted there is no H<sub>2</sub> formation in the latter pathway. Fig. 3 depicts the free energy changes (ΔG) of these two reaction pathways as a function of temperature. It is seen that the reaction between K and NH<sub>3</sub> to form KNH<sub>2</sub> and KH is thermodynamically more favorable than the formation of KNH<sub>2</sub> and H<sub>2</sub> under room temperature. It is known that KNH<sub>2</sub> and KH can form an amide-hydride K(NH<sub>2</sub>)<sub>x</sub>(H)<sub>1-x</sub> solid solution,<sup>22</sup> which will further promote the reaction (4). While for the reaction of Na and NH<sub>3</sub>, the formation of NaNH<sub>2</sub> and H<sub>2</sub> is more favorable under room temperature (Fig. S10, ESI†).

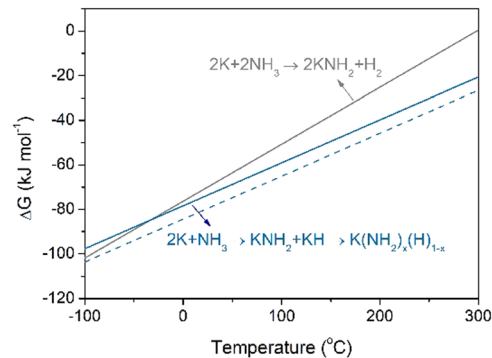
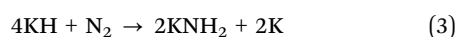
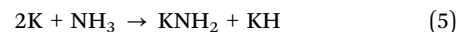
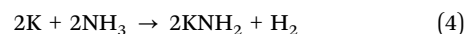


Fig. 3 Temperature dependences of ΔG for reactions of K and NH<sub>3</sub> to form different products. The enthalpies of KH and KNH<sub>2</sub> are taken from the literature.<sup>15</sup> The entropies of solids are not considered. The dashed line serves as a guide, illustrating that the formation of K(NH<sub>2</sub>)<sub>x</sub>(H)<sub>1-x</sub> solid solution is thermodynamically more favorable.



As demonstrated in previous sections, the synergy of plasma and alkali and alkaline earth metal hydrides enables N<sub>2</sub> fixation, and the following thermal hydrogenation of fixed N produces NH<sub>3</sub>. The performance of plasma-thermal hybrid chemical looping ammonia synthesis (PCLAS) for these metal hydrides was thus evaluated. The PCLAS process is basically composed of two steps, *i.e.*, step I—plasma-driven nitrogen fixation in alkali or alkaline earth hydrides, and step II—thermal hydrogenation of the fixed nitrogen to NH<sub>3</sub> which was operated in a temperature-programmed heating mode. The averaged ammonia production rates over a series of hydride samples are presented in Fig. 4. Generally, the chemical looping ammonia production rate follows the order: KH > NaH > LiH > BaH<sub>2</sub>, while MgH<sub>2</sub> and CaH<sub>2</sub> produce negligible amounts of NH<sub>3</sub> under the same reaction condition. The NH<sub>3</sub>

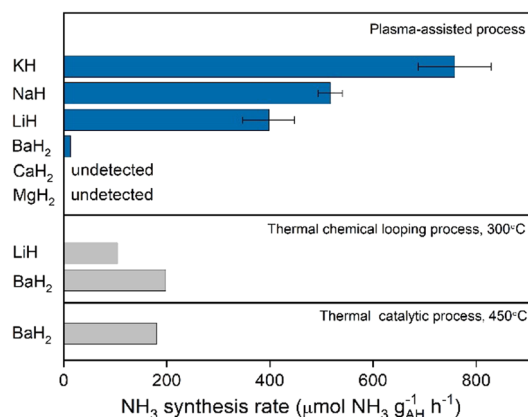


Fig. 4 Chemical looping ammonia production rates of a series of AH samples. The voltage is 12 kV. Error bars represent the standard deviation from three independent measurements. The data of thermal looping and catalytic rates are taken from ref. 11 and 23 and the data of NaH is taken from ref. 16.

production rate increases with the increasing of the applied voltage (Fig. S11, ESI<sup>†</sup>). The highest ammonia production rate was obtained over an applied voltage of 12 kV. Under a voltage of 12 kV, the rates of loops mediated by KH, LiH, and BaH<sub>2</sub> are 758, 398, and 13 μmol g<sup>-1</sup> h<sup>-1</sup>, respectively. And the NH<sub>3</sub> production rate of KH is slightly higher than that reported on NaH (ca. 550 μmol g<sup>-1</sup> h<sup>-1</sup>). This trend is inversely proportional to their lattice energies as shown in Table S1 (ESI<sup>†</sup>). The ammonia production rates of PCLAS are also compared with some reported data of conventional thermal chemical looping or thermal-catalytic process mediated by hydrides. As shown in Fig. 4, the KH-mediated PCLAS produces NH<sub>3</sub> at a rate that is ca. 3–7 times of the thermal-CL mediated by LiH and BaH<sub>2</sub> samples conducted at 300 °C and the thermal-catalytic rate of BaH<sub>2</sub> at 450 °C.

In summary, the interaction of a series of alkali and alkaline earth hydrides including LiH, KH, MgH<sub>2</sub>, CaH<sub>2</sub>, and BaH<sub>2</sub> with nitrogen plasma has been studied. They show quite different behaviors under nitrogen plasma or thermal conditions. Specifically, LiH can mediate both nitrogen fixation, whether through nitrogen plasma or heating, as well as the subsequent thermal hydrogenation to produce NH<sub>3</sub>, thus completing an ammonia loop. KH together with NaH can only facilitate nitrogen fixation under plasma conditions, while the thermal hydrogenation of fixed nitrogen to NH<sub>3</sub> is easier at low temperatures. MgH<sub>2</sub>, CaH<sub>2</sub>, and BaH<sub>2</sub> can all fix N<sub>2</sub> under thermal conditions; however, they do not effectively accommodate a significant amount of N atoms under nitrogen plasma conditions. Their different behaviors could be related to their different lattice energies. Among these binary hydrides, KH is very special because it does not release H<sub>2</sub> during N<sub>2</sub> fixation process. Searching for other ternary or multi-nary alkali or alkaline earth metal hydrides to manipulate their chemical properties under plasma is worthy of future studies.

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## Data availability

The data are available from the corresponding author on reasonable request.

## Conflicts of interest

There are no conflicts to declare.

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