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

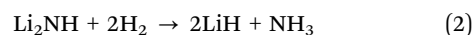
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The chemical behaviors of alkali and alkaline earth metal hydrides including LiH, KH, MgH₂, CaH₂, and BaH₂ under nitrogen plasma differ significantly from one another, exhibiting an ammonia production trend that contrasts with that observed under thermal conditions. A prominent feature of KH is its ability to facilitate plasma-assisted N₂ fixation without generating H₂ byproduct, showing high atomic economy in utilization of hydride ions for N₂ reduction.

Dinitrogen (N₂) fixation is not only of scientific significance but also plays a paramount role in preparation of ammonia (NH₃), which is a key raw molecule for producing nitrogen-based fertilizer and has been widely considered as an important energy or hydrogen carrier.¹ Currently, NH₃ 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.² Significant efforts have been directed toward low-temperature thermal-catalytic, electro-chemical, photo-chemical, plasma-catalytic, and chemical looping ammonia synthesis methods.^{3–7} And a number of new materials for nitrogen fixation have emerged.

Hydride (H[−])-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 N₂ fixation to NH₃.^{8–13} For instance, alkali and alkaline earth hydrides such as LiH and BaH₂ can fix N₂ to form corresponding metal imides (Li₂NH and BaNH) upon heating

to desired temperatures, accompanied by releasing H₂ (eqn (1)). The subsequent thermal hydrogenation of imides results in formation of NH₃ and regeneration of metal hydrides (eqn (2)).^{11,14} NaH and KH, however, cannot fix N₂ under standard thermal conditions (Fig. S1, ESI†) due to the absence of thermodynamically stable imides.¹⁵ We found unexpectedly, NaH is able to fix N₂ to form a surface NaNH₂ species with the assistance of plasma and the thermal hydrogenation of NaNH₂ to NH₃ occurs readily under low temperature, fulfilling a loop for ammonia production.¹⁶ This plasma-thermal hybrid ammonia loop effectively prevents NH₃ from plasma-induced cracking, a challenging obstacle to overcome in plasma-catalytic ammonia synthesis.¹⁷ Given the benefits of this hybrid chemical looping process for NH₃ 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, MgH₂, CaH₂, and BaH₂ 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 N₂ 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 H₂ upon exposure to argon plasma, indicating the occurrence of dehydriding. Fig. 1a displays the time course of H₂ signals detected during the nitrogen plasma process. H₂ signals are also observed in LiH, CaH₂, and BaH₂ under nitrogen plasma. Taking LiH as an example, the intensity of the H₂ signal initially showed slow growth over the first 10 min and then gradually decreased over time. The H₂ signals declined quickly with the turn-off of the plasma. Differing significantly

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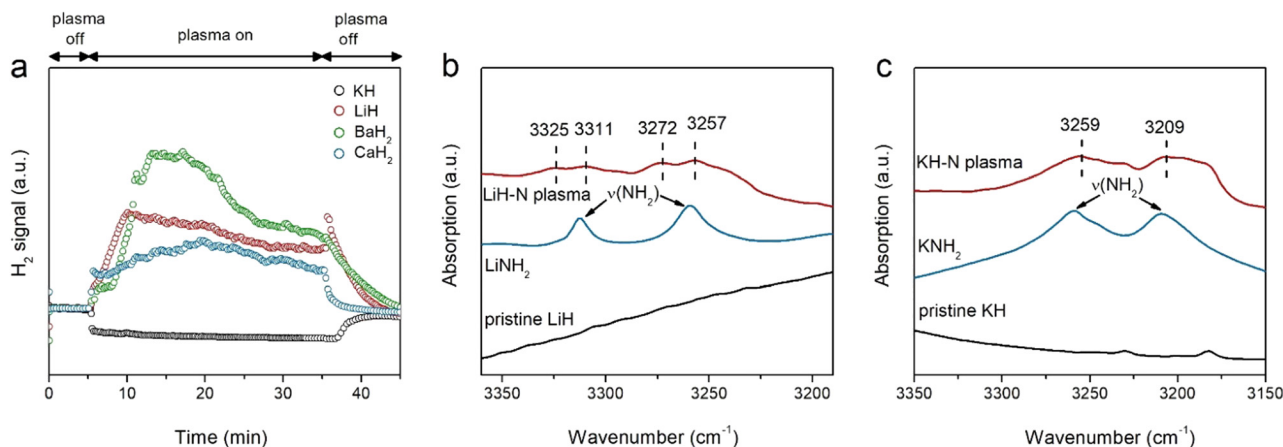


Fig. 1 (a) Time courses of H₂ MS signals ($m/z = 2$) for LiH, KH, CaH₂, and BaH₂ under nitrogen plasma. Voltage is 12 kV. Plasma power is ca. 8 W. FTIR spectra of LiH (b) and KH (c) collected after nitrogen plasma treatment and reference LiH, KH, LiNH₂, and KNH₂ samples.

from these hydrides, although dehydrogenating of KH also takes place under argon plasma (Fig. S2, ESI[†]), there is essentially no H₂ formation from the KH sample under nitrogen plasma (Fig. 1a). The differing behaviors of KH under Ar and nitrogen plasmas suggest that N₂ fixation by KH is fundamentally different from that of other alkali or alkaline earth metal hydrides.

Although they show different time courses of H₂ signals under argon or nitrogen plasma, it is difficult to ascertain whether N₂ fixation occurs based solely on the phenomenon of H₂ formation. Therefore, the solid products after nitrogen plasma treatment were subjected to XRD and FTIR characterization. As shown in Fig. S3 (ESI[†]), the phase structures of LiH and CaH₂ become amorphous after nitrogen plasma treatment, while the structure of KH remains largely unchanged although the intensity of the diffraction peaks significantly weaken. SEM images (Fig. S4, ESI[†]) 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 N₂ fixation process. Fig. 1b, c and Fig. S5 (ESI[†]) 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 CaH₂ and BaH₂. 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 NH₂⁻ species ($\nu_{\text{NH}_2^-}$) of LiNH₂, respectively. For KH, two observable bands centered around 3255 and 3206 cm⁻¹ are clearly seen, which can be attributed to the surface KNH₂ 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 NH₃ produced when heated in a H₂ flow. Fig. 2a presents the temperature-programmed hydrogenation (TPH) profile for the KH powder pretreated under nitrogen plasma at 12 kV. The formation of NH₃ was monitored by using an on-line mass spectrometer and quantified by using a conductivity meter. It is clearly seen that NH₃ 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 μmol and the conversion of KH could

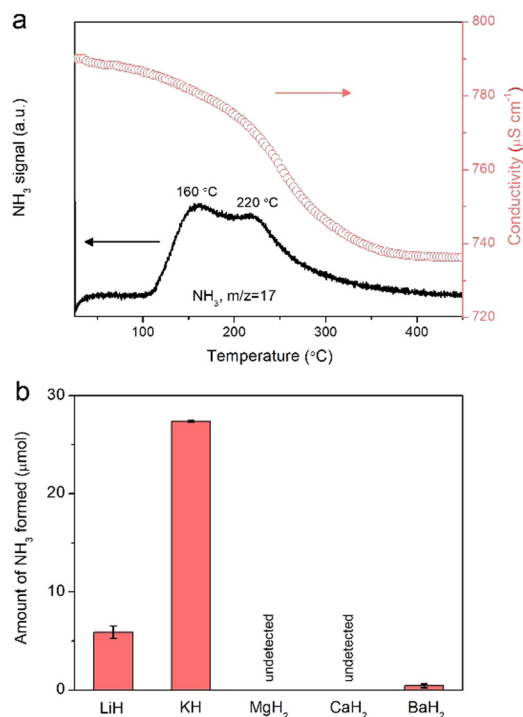


Fig. 2 (a) Temperature-programmed hydrogenation (TPH) profiles of NH₃ signal ($m/z = 17$) and conductivity decrease during the hydrogenation of the nitrogen plasma-treated KH sample. Sample mass is 30 mg. P_{H_2} is 1 bar. H₂ flow rate is 30 mL min⁻¹. (b) The amounts of fixed N in metal hydrides determined 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 N₂ 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[†]). H₂-TPR profiles for LiH and BaH₂ samples are shown in Fig. S7 (ESI[†]) and the amounts of produced ammonia are shown in Fig. 2b. The amounts of fixed N in LiH and BaH₂ are 5.9 and 0.45 μmol, respectively, while negligible amounts of NH₃ were obtained from the hydrogenation of plasma-treated



MgH₂ and CaH₂ samples. Since some nitrogen species may not react with H₂ below 450 °C, an alternative method for NH₃ measurement, *i.e.*, hydrolysis of these samples using water vapor was also studied under room temperature. The hydrolysis of the MgH₂, CaH₂, and BaH₂ samples after nitrogen plasma treatment produces a measurable amount of NH₃. 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, MgH₂, CaH₂, and BaH₂ are able to fix N₂ 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,¹⁸ which may facilitate the dehydriding and accommodation of nitrogen in hydrides.

It has been reported that N₂ fixation by LiH, CaH₂, and BaH₂ produces H₂ and the corresponding metal imides under thermal conditions (eqn (1)). Under nitrogen plasma, NaH can also fix N₂ to form NaNH₂ and H₂.¹⁶ The phenomenon of H₂ formation has also been observed in the nitrogen fixation processes mediated by some molecular transition metal hydrido complexes and nitrogenase enzymes, increasing energy consumption.^{19–21} The pathways of reductive elimination of H₂ (2H[−] leading to H₂ and 2e, which then reduce N₂), and reductive protonation (H[−] leading to H⁺ and 2e) have been proposed to account for the formation of H₂ by-product and N–H bond during nitrogen fixation process, respectively. The interaction of KH with nitrogen plasma is, however, fundamentally different: KH fixes N₂ to form NH₂ species without releasing H₂ under plasma conditions. Therefore, majority of hydride ions in KH can be used for N₂ reduction and N–H bond formation, which is virtually more efficient for utilization of hydride than those of LiH, NaH, CaH₂, and BaH₂. There are two possible routes for N–H bond formation. For one thing, the hydrides act as electron sources for N₂ reduction through the reductive elimination of H atoms (H[−] leading to H and e), which then undergo further reductive protonation to form NH₂ species instead of generating H₂ (eqn (3)). On the other hand, the impact of energetic particles in plasma leads to the dehydriding of KH to form K and H₂ as demonstrated by H₂ formation under argon plasma (Fig. S2, ESI†) and a strong and symmetrical EPR signal (Fig. S9, ESI†). H₂ then easily reacts with reactive N species in plasma forming gaseous NH₃. NH₃ may react with K through two possible pathways, *i.e.*, to form KNH₂ and H₂ (eqn (4)), or to form KNH₂ and KH (eqn (5)). Noted there is no H₂ 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 NH₃ to form KNH₂ and KH is thermodynamically more favorable than the formation of KNH₂ and H₂ under room temperature. It is known that KNH₂ and KH can form an amide-hydride K(NH₂)_x(H)_{1−x} solid solution,²² which will further promote the reaction (4). While for the reaction of Na and NH₃, the formation of NaNH₂ and H₂ is more favorable under room temperature (Fig. S10, ESI†).

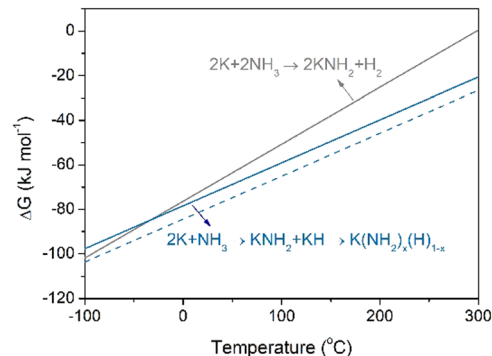
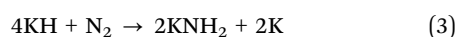
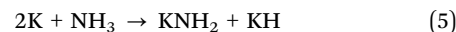
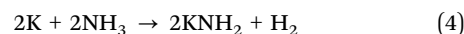


Fig. 3 Temperature dependences of ΔG for reactions of K and NH₃ to form different products. The enthalpies of KH and KNH₂ are taken from the literature.¹⁵ The entropies of solids are not considered. The dashed line serves as a guide, illustrating that the formation of K(NH₂)_x(H)_{1−x} solid solution is thermodynamically more favorable.



As demonstrated in previous sections, the synergy of plasma and alkali and alkaline earth metal hydrides enables N₂ fixation, and the following thermal hydrogenation of fixed N produces NH₃. 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 NH₃ 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 > BaH₂, while MgH₂ and CaH₂ produce negligible amounts of NH₃ under the same reaction condition. The NH₃

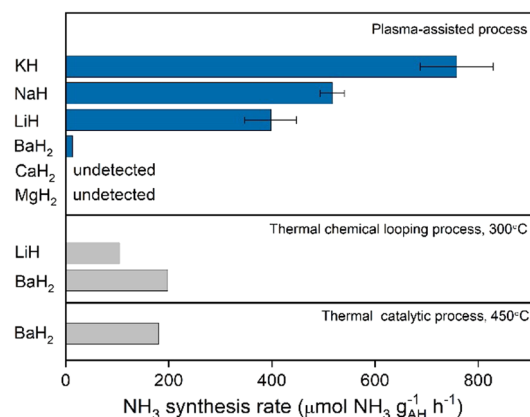


Fig. 4 Chemical looping ammonia production rates of a series of AH samples. The voltage is 12 kV. Error bars represent the standard deviation from three independent measurements. The data of thermal looping and catalytic rates are taken from ref. 11 and 23 and the data of NaH is taken from ref. 16.

production rate increases with the increasing of the applied voltage (Fig. S11, ESI†). 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 BaH₂ are 758, 398, and 13 μmol g⁻¹ h⁻¹, respectively. And the NH₃ production rate of KH is slightly higher than that reported on NaH (ca. 550 μmol g⁻¹ h⁻¹). This trend is inversely proportional to their lattice energies as shown in Table S1 (ESI†). 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 NH₃ at a rate that is ca. 3–7 times of the thermal-CL mediated by LiH and BaH₂ samples conducted at 300 °C and the thermal-catalytic rate of BaH₂ at 450 °C.

In summary, the interaction of a series of alkali and alkaline earth hydrides including LiH, KH, MgH₂, CaH₂, and BaH₂ 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 NH₃, 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 NH₃ is easier at low temperatures. MgH₂, CaH₂, and BaH₂ can all fix N₂ 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 H₂ during N₂ 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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