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Reaction Paths between LiNH₂ and LiH with Effects of Nitrides

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The solid-state reaction between LiNH₂ and LiH potentially offers an effective route for hydrogen storage if it can be tailored to meet all the requirements for practical applications. To date, there still exists large uncertainty on the mechanism of the reaction—whether it is mediated by a transient NH₃ or directly between LiNH₂ and LiH. In an effort to clarify this issue and improve the reactivity, the effects of selected nitrides were investigated here by temperature-programmed desorption, X-ray diffraction, in-situ infrared analysis, and hydrogen titration. The results show that the reaction of LiNH₂ with LiH below 300 °C is a heterogeneous solid-state reaction controlled by Li⁺ diffusion from LiH to LiNH₂ across the interface. At the LiNH₂/LiH interface, an ammonium ion Li₂NH₂⁺ and a penta-coordinated nitrogen Li₂NH₃ could be the intermediate states leading to the production of hydrogen and the formation of lithium imide. In addition, it is identified that BN is an efficient "catalyst" that improves Li⁺ diffusion and hence the kinetics of the reaction between LiNH₂ and LiH. Hydrogen is fully released within 7 h at 200 °C with BN addition, rather than several days without the modification.

Introduction

Alkali amides are usually used as reagents in synthetic organic chemistry because of their ability to promote condensation reactions and introduce amino groups into a molecule.[1,2] Extensive research was devoted to the chemistry of alkali amides in the early part of the nineteenth century for their use in the commercial production of indigo, cyanides, and azides.[3] In particular, the reaction of LiNH₂ with LiH was investigated by Ruff and Goeres in 1910.[4,5] From their observations, it was postulated that lithium amide is converted to lithium imide and ammonia, and the latter reacts with lithium hydride to form lithium imide and hydrogen following reactions 1 and 2:

$$2LiNH_2 \rightarrow Li_2NH + NH_3 \tag{1}$$

$$NH_3 + LiH \rightarrow LiNH_2 + H_2 \tag{2}$$
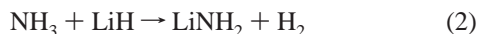
Hence the overall reaction 3 theoretically releases 6.48 wt % of hydrogen in a reversible manner:[5]

$$LiNH_2 + LiH \leftrightarrow Li_2NH + H_2 \tag{3}$$

Since the seminal report by Chen et al.,[6] there has been strong interest in recent years in lithium amide and more generally other metal amides as a hydrogen store.[6–11] The reaction of LiNH₂ with LiH provides a practically viable hydrogen storage path if hydrogen can be released around 100 °C and ideally reabsorbed at ambient temperature. Previous research shows that LiNH₂ mixed with LiH releases hydrogen from 200 to 450 °C.[12–14] By the addition of 1 mol % of nanosized Ti or TiCl₃ to the mixture, hydrogen can be desorbed in a narrow temperature range of 200–300 °C with increased kinetics.[10,15] The kinetics are further improved if LiH is substituted by MgH₂, but then the overall capacity is limited to 4.5 wt %.[11,16]

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SCHEME 1: Reaction between LiNH₂ and LiH with Formation of an Intermediate According to a Polar Mechanism by Chen et al.[12]
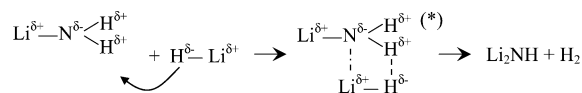
To lower the operating temperature and improve the hydrogen desorption kinetics, the reaction mechanism between LiNH₂ and LiH needs to be clearly understood. As the decomposition of LiNH₂ produces ammonia and lithium imide according to reaction 1, it is proposed that LiH reacts directly with ammonia to release hydrogen following reaction 2.[5,17] This hypothesis is supported by the fast reaction of LiH with ammonia at 400 °C as demonstrated by Hu and Ruckstein.[9] Isobe et al. also used isotopes of LiH and LiNH₂ to prove the validity of routes 2 and 3, and they proposed a multistep reaction mechanism in which LiNH₂ decomposition swings between reactions 1 and 2, with reaction 2 feeding reaction 1 after the release of hydrogen.[10,18] If such a mechanism is entirely responsible for the production of hydrogen, hydrogen desorption should occur in the range of 300–600 °C, corresponding to the release of ammonia from LiNH₂.[14] However, hydrogen desorption from (LiNH₂ + LiH) actually occurs at much lower temperatures from 200 to 450 °C.[13,14] This suggests that LiH "triggers" the decomposition of LiNH₂. A polar mechanism has since been proposed by Chen et al. to explain the effect of LiH (Scheme 1),[12] where an intermediate compound (noted *) is believed to form during the reaction.

Polar mechanisms have been proven to occur between metal hydrides and metal amides in liquid media.[19] In the present case, the reaction proceeds in the solid state in the observed desorption temperature range. Therefore, it is difficult to envisage how such a mechanism could be sustained because the entire molecule of LiH or LiNH₂ would have to diffuse from the bulk to the interface for the reaction to continue.

TABLE 1: Particle Sizes of Different Additives (suppliers' data)

	Li_3N	BN	TiN	Fe_xN	B_4C
particle size (μm)	<180	~1	<3	<45	<75

To further clarify the reaction mechanism of $LiNH_2$ with LiH and improve the hydrogen desorption kinetics, the effects of selected nitride compounds (Li_3N, BN, TiN, Fe_xN with $x = 2-4$) on the ($LiNH_2 + LiH$) reaction were investigated here. Nitride compounds, particularly Fe_xN, are known to be effective catalysts for ammonia synthesis,[20-22] which is closed associated with the decomposition of $LiNH_2$, reaction 1. Therefore, an improvement of hydrogen desorption kinetics is expected from nitride additions, if the reaction between $LiNH_2$ and LiH is effectively mediated by ammonia. Indeed, we found that the hydrogen desorption kinetics of ($LiNH_2 + LiH$) are considerably improved by BN addition. The results support a hypothesis of a direct reaction between $LiNH_2$ and LiH, rather than an ammonia-mediated route. On the basis of this study, a mechanism is proposed to explain the solid-state reaction between $LiNH_2$ and LiH.

Materials and Methods

Li_3N and Fe_xN ($x = 2-4$) were purchased from Alfa Aesar; B_4C, BN, TiN, $LiNH_2$, and LiH were purchased from Sigma Aldrich; and MgH_2 was purchased from Th. Goldschmidt AG Chemical. The average particle sizes of the additives are given in Table 1. B_4C and MgH_2 were used here for comparison.

In order to achieve a homogeneous mixture, the as-received powders were milled in a SPEX 8000 mill under Ar atmosphere. Typically, a molar ratio of $LiNH_2/LiH = 1:1$ was milled with 40 mol % of a nitride or a carbide up to 20 h. The ball-to-powder ratio was 15:1, and each stainless steel grinding ball weighs 1 g. For comparison, $LiNH_2$ was also milled with MgH_2 and 40 mol % of B_4C for 20 h; however, in this case, a molar ratio of $LiNH_2/MgH_2 = 4:3$ was used. A relatively large amount of the additives was used purposefully to facilitate the release of NH_3 from $LiNH_2$ and therefore enhance the reaction of $LiNH_2$ with LiH, if it proceeds through the ammonia route.

Temperature-programmed desorption (TPD) of hydrogen was performed using a Setaram Setsys thermal analyzer coupled with a Pfeiffer Ommistar mass spectrometer. The experiments were performed at 10 °C min^{-1} under a 50 mL min^{-1} flow of high-purity Ar (99.999%). Hydrogen sorption kinetics were measured with a HyEnergy PCTpro Sievert apparatus at 300 °C with 1 MPa of hydrogen for absorption and 0.1 kPa for desorption. High-purity hydrogen was used (99.9995%), and the weight of the samples was 100 mg.

The evolution of $LiNH_2$ vibrational bands as a function of temperature was characterized using a Digilab Excalibur infrared spectrophotometer, equipped with an in-situ diffuse reflectance infrared Fourier transform (DRIFT) accessory. The sample was loaded in the DRIFT cell in a glove box under Ar atmosphere. A heating rate of 5 °C min^{-1} was used, and the experiment was performed under a 50 mL min^{-1} flow of high-purity Ar (99.999%), with a scan resolution of 4 cm^{-1}.

Results and Discussion

Effect of Nitride Additives. Figure 1 shows the effect of the nitride additives on the hydrogen release from the reaction of $LiNH_2$ with LiH. All the nitrides seem to enhance the initial hydrogen desorption from 200 °C, but their effects differ subsequently. Li_3N, Fe_xN, and TiN extend the range of temperatures for hydrogen desorption from 200–450 °C to
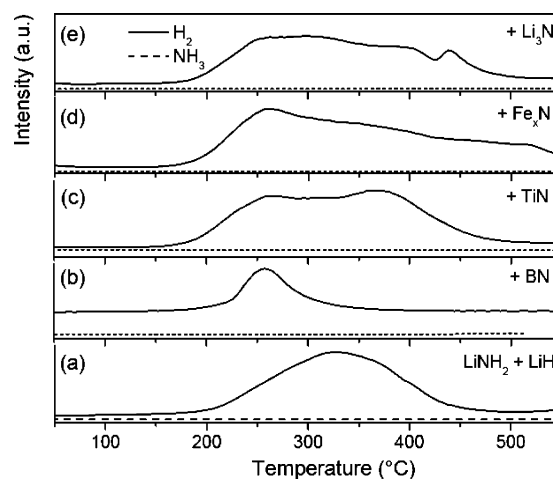

Figure 1. TPD curves of ($LiNH_2 + LiH$) milled for 20 h: (a) alone and with various additives: (b) BN, (c) TiN, (d) Fe_xN, and (e) Li_3N.

200–600 °C, whereas BN addition reduces this range to 210–300 °C. Results from X-ray diffraction do not show any new phases (see Supporting Information, Figure S1), and further analysis by IR spectroscopy does not reveal any shift of ν(NH) or formation of new bonds between the nitrides and $LiNH_2$ or LiH (Supporting Information, Figure S2). Therefore, the hydrogen release from 200 °C should not be due to any structural changes or new compounds as a result of mechanical milling.

In the case of the Li_3N addition, hydrogen desorption observed above 450 °C could be due to the hydrogenation of Li_3N into Li_2NH (reaction 4), because hydrogen is released during the TPD measurement and the plateau pressure for the hydrogenation of Li_3N is low (<0.1 bar of H_2).[6]

$$Li_3N + H_2 \leftrightarrow Li_2NH + LiH \qquad (4)$$
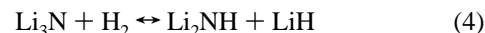
The formation of Li_2NH can result in hydrogen release above 400 °C.

The effect of Fe_xN is rather surprising. Iron nitrides were suggested to be responsible for the high activity of iron catalysts in the synthesis of ammonia.[21,22] In addition, it has been reported that for hydrazine decomposition, similar to $LiNH_2$, iron nitrides are very efficient catalysts.[20] Therefore, it is expected that Fe_xN should enhance the reaction between $LiNH_2$ and LiH. On the contrary, Fe_xN considerably slows down most of the reaction and the hydrogen desorption continues after 400 °C (Figure 1). The reaction between $LiNH_2$ and LiH may proceed at the solid–solid ($LiNH_2$–LiH) and/or the solid–gas (LiH–NH_3) interfaces. Therefore, at least one of these reaction paths is inhibited by Fe_xN. Moreover, it is noted that Fe_xN does not accelerate the decomposition of $LiNH_2$ (Figure 2), though it enhances ammonia decomposition into hydrogen. Consequently, Fe_xN is unlikely to inhibit the diffusion of ammonia from $LiNH_2$ to LiH. Nevertheless, Fe_xN may physically impede the diffusion of the Li^+ ions in the solid–solid reaction of $LiNH_2$ and LiH. To a certain extent, the results support the hypothesis that the reaction of $LiNH_2$ with LiH is not controlled by ammonia release, but by the diffusion of ions in the $LiNH_2$–LiH solid-state reaction. Depending on the distribution of Fe_xN within the powder, LiH particles in direct contact with $LiNH_2$ could react according to a heterogeneous solid-state reaction while other LiH particles, shielded by Fe_xN, will not react with $LiNH_2$ prior to ammonia release from $LiNH_2$. Therefore, the solid–gas reaction due to NH_3 may occur at relatively high temperatures, compared to the solid–solid reaction.
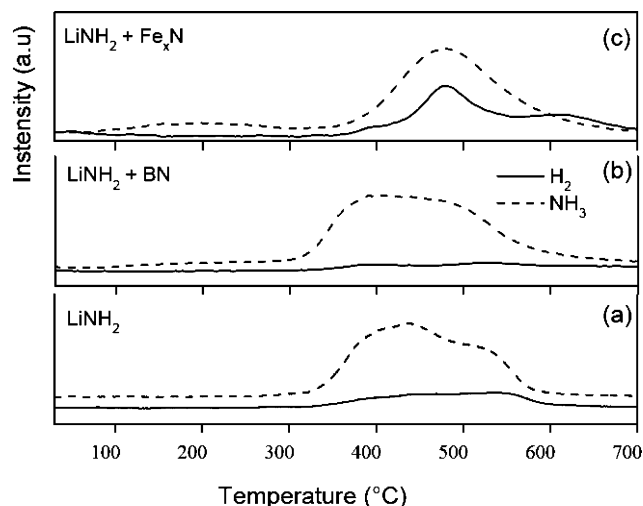
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Figure 2. TPD curves of LiNH₂ milled for 20 h: (a) alone, (b) with BN, and (c) with Fe$_x$N.

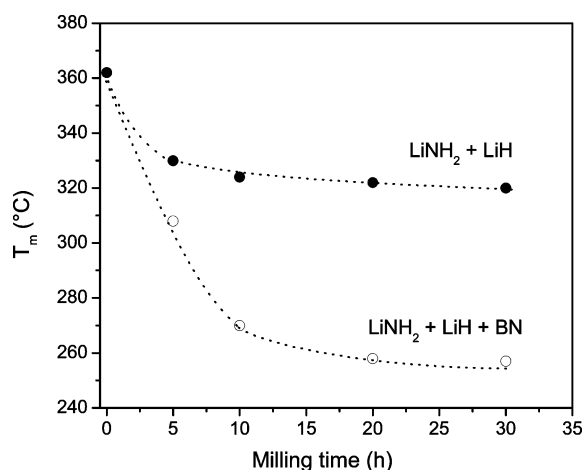**Figure 3.** Effect of milling time on the decomposition temperature (T_m) of (LiNH₂ + LiH + BN). T_m corresponds to the maximum peak temperature of the hydrogen profile obtained from TPD measurements.

Figure 4. Hydrogen titration curves obtained at 200 °C for (LiNH₂ + LiH) (full circle) and (LiNH₂ + LiH + BN) (open circle): (a) absorption, and (b) desorption.

Despite a less significant effect, TiN may have an impact on the reaction of LiNH₂ with LiH similar to that of Fe$_x$N. The difference may be due to different particle sizes of TiN and Fe$_x$N after milling and hence, different extents of "shielding" around LiH or LiNH₂ particles.

In the case of BN, such a delay in hydrogen desorption does not occur, and all the hydrogen is released between 200 and 300 °C. This result is akin to that obtained by Ichikawa et al. with the addition of TiCl₃ and a nanosized Ti.[10] The positive effect of the microsized BN particles also indicates that "nanosize" of additives is not a prerequisite to achieve rapid kinetics and the chemistry of the additives is of more importance. The effect of BN is further investigated as follows.

The Role of Boron Nitride. As shown in Figure 3, at least 10 h of milling is necessary to release hydrogen from the mixture of LiNH₂ with LiH below 300 °C, and an optimum of 260 °C is reached after 20 h of milling. On first observation, it seems that BN, being a hard material, assists the refinement of LiNH₂ and LiH particles during milling, and thus increases the number of interfaces between LiNH₂ and LiH particles. However, as shown in Figure 1, the other nitrides, which are of similar hardness, do not enhance the hydrogen desorption of (LiNH₂ + LiH) as much as BN does. Furthermore, the addition of BN to LiNH₂ shows that BN does not affect the decomposition and the production of ammonia from LiNH₂ (Figure 2). Hence, it
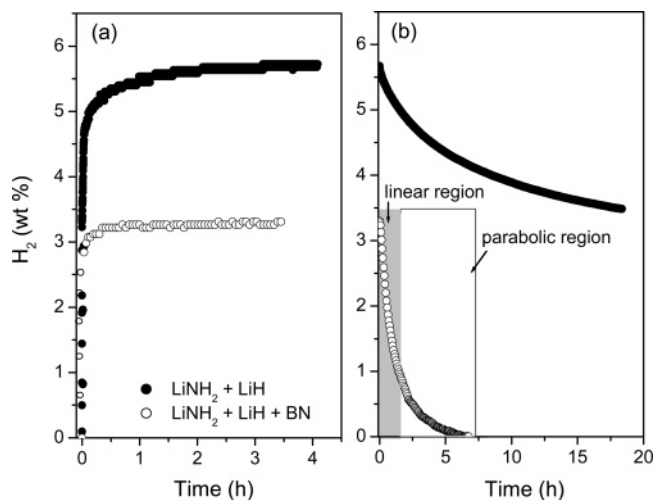
is unlikely that BN would enhance the solid−gas reaction between LiH and NH₃, if the reaction between LiNH₂ and LiH did proceed this way. Therefore, BN must be involved in another reaction mechanism.

From kinetic measurements, BN does not seem to have much effect on the hydrogen absorption kinetics of Li₂NH, the decomposition product of (LiNH₂ + LiH) (Figure 4). However, the hydrogen desorption kinetics are much enhanced by BN addition. It takes only 7 h to complete the desorption from the (LiNH₂ + LiH) mixture with BN, but more than 20 h to release half of the hydrogen without BN. It is also noted in Figure 4 that the hydrogen desorption curves display both a linear and a nonlinear region. In general, a solid-state reaction between two compounds A and B proceeds through the formation of an interfacial chemical compound A$_x$B$_y$. At the beginning of the reaction, the kinetics of the reaction are usually controlled by the chemical reaction of A and B at the interface (reaction-controlled regime), and as the layer A$_x$B$_y$ grows, the kinetics may be controlled by the diffusion of A or B through the interface layer (diffusion-controlled regime).[23] Typically, in a reaction-controlled regime, the evolution of the reacted volume as a function of time is linear, while for a diffusion-controlled regime, it is parabolic. In the present case, the desorption curve of (LiNH₂ + LiH) mainly shows a parabolic behavior, identical to the one observed by Chen et al., for the reaction of LiNH₂ and MgH₂.[24] Therefore, even from the early stages, the reaction between LiNH₂ and LiH is likely to be controlled by diffusion across the interface. In contrast, the desorption of the (LiNH₂ + LiH + BN) mixture clearly shows two regions: a linear region during the first stages of desorption and then a parabolic region at the later stages of desorption. Hence, it seems that the addition of BN considerably improves both the initial reaction and, more importantly, diffusion between the two reactants and thus enhances overall hydrogen desorption kinetics in the "heterogeneous" solid-state reaction between LiNH₂ and LiH. An improvement in diffusion would mean that the particle sizes of LiNH₂ and LiH are fine and the surface contacts between the particles of LiNH₂ and LiH are frequent, and/or the diffusions of Li⁺, NH₂⁻, and/or H⁻ have been improved.

As previously discussed, BN does not show much "extra" effect on the particle refinement or improving the contact between LiNH₂ and LiH particles, compared with other nitrides. To further confirm this point and clarify the process of diffusion, that is, the diffusion of Li⁺ and NH₂⁻ from LiNH₂ and/or Li⁺

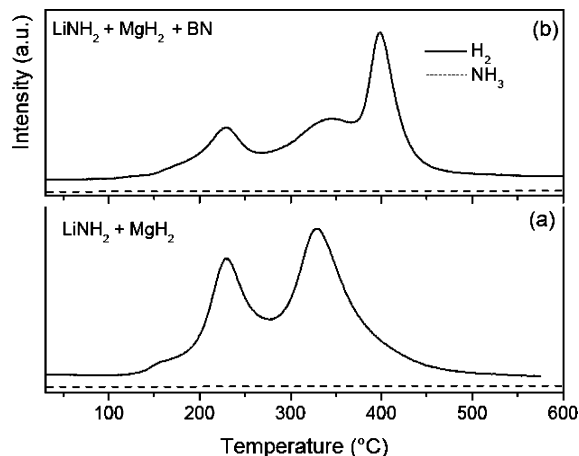**Figure 5.** TPD of (4LiNH$_2$ + 3MgH$_2$) milled for 20 h: (a) without BN, and (b) with BN.

Figure 6. TPD of (LiNH$_2$ + LiH) milled with B$_4$C for 20 h.

and H$^-$ from LiH, MgH$_2$ was milled with LiNH$_2$ and BN for 20 h, and the result of the TPD is shown in Figure 5. Here, hydrogen desorption seems to be delayed by the BN addition. The (LiNH$_2$ + MgH$_2$ + BN) mixture is still releasing hydrogen above 400 °C, while the milled (LiNH$_2$ + MgH$_2$) releases all the hydrogen before 400 °C. Therefore, it is clear that the effect of BN is due neither to particle size reduction nor an improved contact between the particles. The effect of BN in the (LiNH$_2$ + MgH$_2$) mixture is similar to that of Fe$_x$N in the (LiNH$_2$ + LiH) mixture, mainly of a physical nature. Assuming that the reaction between LiNH$_2$ and MgH$_2$ is a solid-state reaction,[24] BN physically impedes the diffusion of the ions in the (LiNH$_2$ + MgH$_2$) mixture. Since the only difference between (LiNH$_2$ + MgH$_2$ + BN) and (LiNH$_2$ + LiH + BN) is the metal hydride used, the effect of BN must be on the diffusion of the cations. BN may slow down the diffusion of Mg^{2+} in the reaction of LiNH$_2$ with MgH$_2$, but speed up the Li$^+$ in the (LiNH$_2$ + LiH) couple. The above observation also indicates that the reaction of LiNH$_2$ with LiH is mainly controlled by the diffusion of Li$^+$ into the LiNH$_2$ phase. Therefore, in the heterogeneous solid-state reaction of LiNH$_2$ with LiH, the growth of the lithium imide phase would proceed at the expense of the diffusion of Li$^+$ from LiH to LiNH$_2$.

The ability of BN to ensure Li$^+$ conduction across the interface between LiNH$_2$ and LiH depends on the adsorption energy of lithium on BN. According to Zhou et al., lithium adsorption is very weak and partially ionic on BN because the B$-$N bond is electron-sufficient.[25] This fact lends further support that BN may facilitate the diffusion of Li$^+$. Zhou et al. also reported that lithium adsorption on boron carbide nanotubes is very strong and stable, and hence B$_4$C would be expected to slow down Li$^+$ diffusion or retard hydrogen release in the (LiNH$_2$ + LiH) mixture. To further verify the proposed effect of BN on the (LiNH$_2$ + LiH) mixture, 4 mol % of B$_4$C was milled with LiNH$_2$ and LiH for 20 h. As noted from Figure 6, B$_4$C shows an adverse effect on the (LiNH$_2$ + LiH) decomposition. A considerable amount of ammonia is released from 100 to 200 °C, and then hydrogen evolves from 200 to 600 °C. Thus, Li$^+$ at the surfaces of LiNH$_2$ particles may strongly bind to B$_4$C at the beginning of the reaction, which results in the release of ammonia observed at the low temperatures (100$-$200 °C). In fact, the ammonia released below 200 °C does not react with LiH to produce hydrogen. Neither can it self-decompose into hydrogen and nitrogen.[26] Hence, it would be difficult to improve hydrogen desorption from (LiNH$_2$ + LiH) by releasing ammonia from LiNH$_2$ at a low temperature. Above 200 °C, the reaction

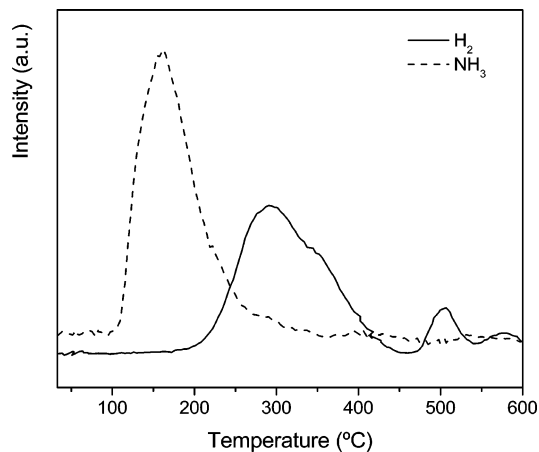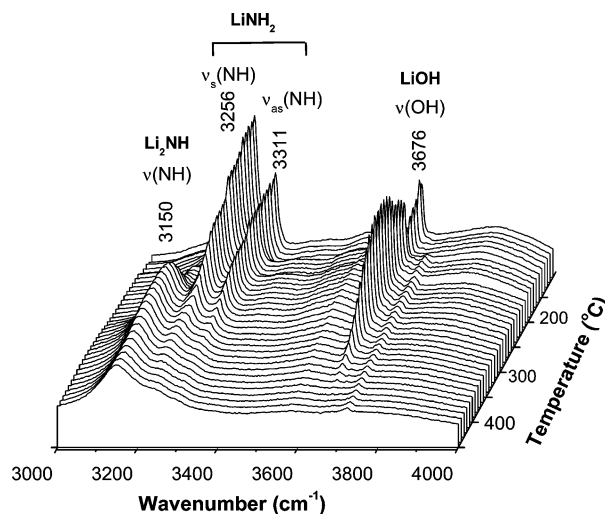**Figure 7.** Evolution of the FTIR spectra of (LiNH$_2$ + LiH + BN) milled for 20 h as a function of temperature.

proceeds as usual, but hydrogen is still released above 500 °C. The observed desorption behavior clearly indicates that B$_4$C strongly binds Li$^+$ and so retards Li$^+$ diffusion.

From the discussion above, it seems that the reaction of LiNH$_2$ with LiH proceeds through a heterogeneous solid-state reaction below 300 °C, controlled by the diffusion of Li$^+$. An appropriate additive, such as BN, facilitates Li$^+$ diffusion and hence enhances the kinetics of the reaction.

Proposed Reaction Mechanism for LiNH$_2$ and LiH. In a heterogeneous solid-state reaction, the reaction is initiated at the surface and therefore is controlled, at least, initially by the reactivity of the atoms at the particle$-$particle interface. As previously reported, the decomposition of LiNH$_2$ and LiH does not start before 300 and 600 °C, respectively.[14,27] Nevertheless, after 1 h of milling, the mixture (LiNH$_2$ + LiH) starts to decompose at 200 °C.[28] During mechanical milling, LiNH$_2$ and LiH particles are refined and homogeneously mixed. New surfaces with defects, free from oxides, are generated.[29] Therefore, after milling, the surface of the particles would be highly reactive and thus readily initiate a solid-state reaction between LiNH$_2$ and LiH.

To further understand the reaction mechanism of LiNH$_2$ and LiH, the evolution of the surface species of the mixture (LiNH$_2$ + LiH + BN) during heating was characterized by in-situ IR spectroscopy (Figure 7). As expected, LiNH$_2$ quickly decomposes to Li$_2$NH. In addition to the stretching vibrations ν(NH), there exists a band at 3676 cm^{-1}, corresponding to LiOH, which
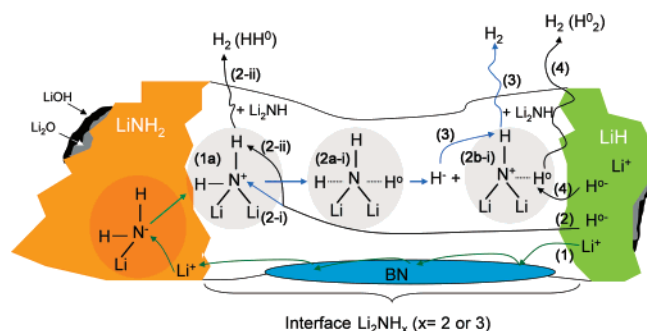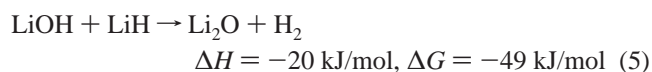
Figure 8. Schematic representation of the heterogeneous solid-state reaction paths of LiNH₂ and LiH. H^0 stands for hydrogen coming from LiH.

indicates a partial oxidation of LiH and/or LiNH₂. The presence of a thin oxide layer around the particles of LiNH₂ and LiH cannot be avoided because the reaction of LiH or LiNH₂ with water is exothermic and this reaction may occur during the handling of the powder despite extreme care. The intensity of this band decreases as the temperature increases to 150 °C, but surprisingly increases at 200 °C, before decreasing again to the end of the reaction 1. As previously reported, LiOH decomposes into Li₂O according to reactions 5 and 6:[30,31]

$$LiOH + LiH \rightarrow Li_2O + H_2$$
$$\Delta H = -20 \text{ kJ/mol}, \Delta G = -49 \text{ kJ/mol} \quad (5)$$

$$2LiOH \rightarrow Li_2O + H_2O$$
$$\Delta H = 136 \text{ kJ/mol}, \Delta G = 97 \text{ kJ/mol} \quad (6)$$

Reaction 5 occurs exothermically at room temperature and stops when all the LiOH is consumed. Hence, the decrease in intensity of $\nu(OH)$ below 150 °C is due to reaction 5. Above 150 °C, the reaction between LiNH₂ and LiH starts and part of the hydrogen ions released from LiH can react with the oxygen atoms at the surface of Li₂O to form LiOH. Thus, during the reaction of LiNH₂ with LiH, LiOH is formed again, which subsequently decomposes into Li₂O according to reactions 5 and 6. The increase and decrease of the $\nu(OH)$ intensity thus indicates that the reaction between LiNH₂ and LiH also involves hydrogen-ion diffusion. As the amount of oxygen residual is likely to be small, it is not expected to affect much of the sorption mechanism.

From the above observations, the following mechanism may be proposed for the reaction between LiNH₂ and LiH below 300 °C. The reaction proceeds in a heterogeneous solid-state manner if the reactants are uniformly mixed with fine particle sizes to ensure direct and frequent contacts. The reaction can be enhanced by the surface defects created during mechanical milling. Li⁺ diffusion from LiH to LiNH₂ takes place across the interface and is facilitated by BN particles (Path **1** in Figure 8). In LiNH₂, the negatively charged nitrogen is the "core" atom that interacts with Li and N: it bonds relatively weakly with Li and unequally with the two hydrogen atoms.[7] The nitrogen could directly react with Li⁺ from LiH to form an ammonium Li₂NH₂⁺ (**1a** in Figure 8). Thus the hydrogen from LiH, noted as H^{0-}, can directly react with the ammonium Li₂NH₂⁺ (**1a**) in a linear fashion to form a hydrogen molecule and lithium imide (Path **2-ii** in Figure 8). Alternatively, H^{0-} could also attack Li₂NH₂⁺ directly on the nitrogen in a nucleophile S_N2-type reaction (Path **2-i**), causing an exchange of hydrogen atoms via the pentacoordinated Li₂NH₂H⁰ (compound **2a-i** in Figure 8) and the formation of an ammonium Li₂NH⁰H⁺ (**2b-i**), which can further react with H⁻ (Path **3**) or H^{0-} (Path **4**) to produce hydrogen and lithium imide.

A precedent for such a mechanism exists in the study of pentacoordinated NH₅.[32] It has been observed that the reaction of ammonium salt with lithium deuteride, in addition to producing ammonia, also produces hydrogen with isotopic scrambling (66% HD, 21% H₂, and 13% D₂).[32] To explain such scrambling, it was proposed that the reaction of ammonium salt with LiD could follow two routes: (a) a linear-type displacement of the hydrogen atoms of NH₄⁺ to give HD and ammonia, and (b) a S_N2-type attack of D⁻ on the nitrogen provoking an isotopic exchange via pentacoordinated NH₄D, which results in the formation of H₂ and D₂. Similar hydrogen scrambling has been observed when LiNH₂ is reacted with LiD.[12,18] According to Isolbe et al., the hydrogen scrambling could be explained by the direct reaction of NH₃ with LiD and therefore supports the ammonia-mediated route for the reaction of LiNH₂ with LiH (reactions 1 and 2.[18] H and D atoms from NH₃ and LiD obey the law of probability, which results in the formation of HD, H₂, and D₂. Nevertheless, early reports show that only very limited exchange occurs between NH₃ and LiD or NH₃ and D₂.[32] In the latter case, no isotopic exchange is observed at all unless a catalyst is present or the temperature is above 500 °C.[33,34] This further indicates that the reaction between LiNH₂ and LiH is unlikely to follow the ammonia-mediated route at relatively low desorption temperatures.

According to the proposed mechanism (Figure 8) and with the support from the results of isotopic exchange,[12,18] the hydrogen from LiH (H^{0-}) will mainly react directly with LiNH₂ to form HH⁰. Nevertheless, the side reaction of H^{0-} nucleophile attack on the nitrogen will also occur, resulting in the formation of HH⁰, H₂, and H⁰₂. Hence, ammonia formation is not a necessary transient step for hydrogen desorption from (LiNH₂ + LiH).

Conclusions

We have demonstrated that the reaction of LiNH₂ with LiH below 300 °C is a heterogeneous solid-state reaction controlled by the diffusion of Li⁺ and H⁻ from LiH. Therefore, the kinetics of the reaction will be enhanced with suitable compounds that facilitate the diffusion of Li⁺ and/or H⁻ across the interface of LiNH₂ and LiH. We have identified that BN is one of such compounds, which greatly enhances the hydrogen desorption kinetics. Hydrogen can be fully desorbed from the mixture (LiNH₂ + LiH + BN) in less than 7 h, whereas the pristine (LiNH₂ + LiH) desorbs hydrogen in several days. Comparison of the observed effects of the different nitride additions to (LiNH₂ + LiH), a new reaction mechanism is proposed. It is suggested that the ammonium ion Li₂NH₂⁺ and the pentacoordinated nitrogen Li₂NH₃ are likely the intermediate states leading to the formation of hydrogen and lithium imide. Ammonia formation is not a necessary transient step for hydrogen desorption from (LiNH₂ + LiH).

Supporting Information Available: XRD patterns (Figure S1) and IR spectra (Figure S2) of (LiNH₂ + LiH) milled with the nitride additives. This material is available free of charge via the Internet at http://pubs.acs.org.

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