



## Probing the reaction pathway of dehydrogenation of the $\text{LiNH}_2 + \text{LiH}$ mixture using *in situ* $^1\text{H}$ NMR spectroscopy

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### ABSTRACT

Using variable temperature *in situ*  $^1\text{H}$  NMR spectroscopy on a mixture of  $\text{LiNH}_2 + \text{LiH}$  that was mechanically activated using high-energy ball milling, the dehydrogenation of the  $\text{LiNH}_2 + \text{LiH}$  to  $\text{Li}_2\text{NH} + \text{H}_2$  was investigated. The analysis indicates  $\text{NH}_3$  release at a temperature as low as  $30^\circ\text{C}$  and rapid reaction between  $\text{NH}_3$  and  $\text{LiH}$  at  $\sim 150^\circ\text{C}$ . The transition from  $\text{NH}_3$  release to  $\text{H}_2$  appearance accompanied by disappearance of  $\text{NH}_3$  confirms unambiguously the two-step elementary reaction pathway proposed by other workers.

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### 1. Introduction

Since the first report by Chen et al. [1], Li–N–H system, particularly lithium amide ( $\text{LiNH}_2$ ), and lithium hydride ( $\text{LiH}$ ) mixture, has been investigated extensively as potential hydrogen storage materials [2–17]. It is generally agreed that the dehydrogenation reaction of the system can be generally expressed as



with a theoretical reversible hydrogen storage capacity of 6.5 wt.%, which makes it very attractive for on-board storage applications. It was suggested in the original report that  $\text{LiNH}_2$  might directly react with  $\text{LiH}$  to generate hydrogen as defined by Reaction (1) [1,2]. However, based on the results from a subsequent temperature-programmed mass spectrometry study using a two-layer materials consisting of  $\text{LiNH}_2$  and  $\text{LiH}$  powders, it has been proposed by Hu and Ruckenstein [3] that Reaction (1) proceeds with two elementary reactions, namely,



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As shown in Reactions (2) and (3), Reaction (1) proceeds by decomposition of  $\text{LiNH}_2$  to  $\text{Li}_2\text{NH}$  and  $\text{NH}_3$  first, followed by reaction of  $\text{LiH}$  with  $\text{NH}_3$  to form  $\text{H}_2$  and  $\text{LiNH}_2$ . The newly formed  $\text{LiNH}_2$  decomposes again and repeats the cycle of Reactions (2) and (3). Such successive reactions continue until all  $\text{LiNH}_2$  and  $\text{LiH}$  completely transform to  $\text{Li}_2\text{NH}$  and  $\text{H}_2$ . It has been shown that Reaction (3) takes place very fast in the order of less than 25 ms [3]. However, even with such high-reaction rates, escape of  $\text{NH}_3$  from the hydrogen storage system has been reported [2,6,15] and used as an indirect evidence to support the mechanism defined by Reactions (2) and (3) [11]. Several recent studies [5,16] have also provided evidence supporting the two-step elementary reaction mechanism. However, so far there is no direct evidence to support the two-step elementary reaction mechanism as all the previous investigations [3,5,11,16] have been based on detecting the eluted molecules from a reacted system where carrier gas such as Ar or He is used for carrying the molecules to the analyzer. Therefore, such kind of analysis is intrinsically an *ex situ* experiment. An *in situ* investigation would be required for gaining further insights into the reaction mechanism.

In this work, the reaction mechanisms are investigated using a recently established *in situ* variable temperature  $^1\text{H}$  MAS NMR [18] at a magnetic field of 7.05 T on a mixture of  $\text{LiNH}_2 + \text{LiH}$  that was mechanically activated using high-energy ball milling at room temperature. The result clearly confirms the proposed two-step elementary reactions.

## 2. Experimental

### 2.1. Sample preparation

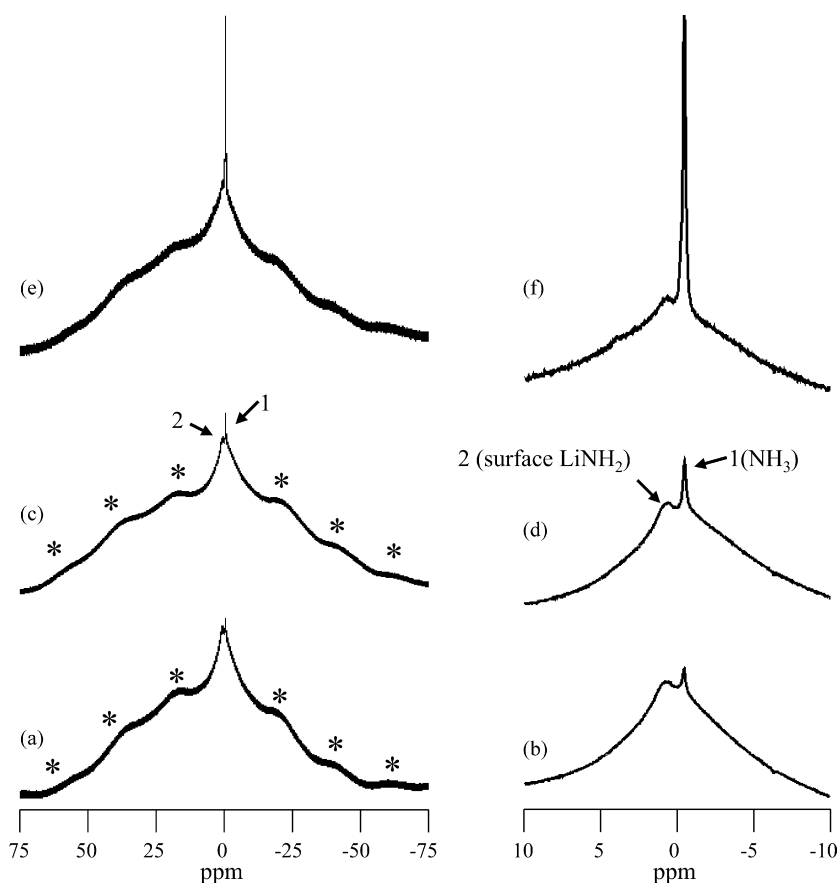
Lithium amide ( $\text{LiNH}_2$ ) with 95% purity was purchased from Alfa Aesar, while lithium hydride ( $\text{LiH}$ ) with 95% purity was purchased from Sigma–Aldrich. The  $\text{LiNH}_2$  and  $\text{LiH}$  mixture was prepared with a molar ratio of 1:1.1 according to Reaction (1). The 10% excess of  $\text{LiH}$  was added to minimize the loss of  $\text{NH}_3$  during the dehydrogenation process. High-energy ball milling was conducted using a modified Szegvari attritor which had been shown previously to be effective in preventing the formation of the dead zone and producing uniform milling products within the powder charge [19]. Furthermore, a previous study has demonstrated that the seal of the canister of the attritor is air-tight and there is no oxidation during ball milling of  $\text{LiH}$  [20]. The canister of the attritor and balls with 6.4 mm in diameter were both made of stainless steels. The loading of balls and the powder to the canister was performed in a glovebox filled with ultrahigh purity argon that contains  $\text{Ar}$  99.999%,  $\text{H}_2\text{O} < 1$  ppm,  $\text{O}_2 < 1$  ppm,  $\text{H}_2 < 3$  ppm, and  $\text{N}_2 < 5$  ppm (referred to as  $\text{Ar}$  of 99.999% purity hereafter). The ball-to-powder weight ratio was 60:1, the milling speed was 600 rpm, and the milling temperature was maintained at  $20^\circ\text{C}$ , achieved by water cooling circulated with a flowing rate of  $770\text{ ml min}^{-1}$ . Ball milling time in this study was 45 min. The samples were stored in a dry argon glovebox until NMR measurements and loaded into sealed NMR rotors inside an argon-filled glovebox to avoid exposing to air.

### 2.2. NMR experiment

All the  $^1\text{H}$  MAS experiments were performed on a Varian-Chemagnetics 300 MHz Infinity spectrometer, corresponding to  $^1\text{H}$  Larmor frequencies of 299.982 MHz. A commercial cross-polarization/MAS probe with a 7.5-mm outside diameter and 6 mm internal diameter pencil-type spinner system was used. The sample cell resembles the commercial cell except that two solid Teflon plugs were made in such a manner that they can only be fully inserted into the zirconium cylinder after pre-cooling using liquid nitrogen to seal  $\sim 0.1$  to  $0.2$  g of samples for variable temperature studies. The sample was first spun to the targeted spinning rate, i.e.,  $5.5\text{ kHz} \pm 2\text{ Hz}$  using a commercial Chemagnetics MAS speed controller prior to raising the temperature. Tetrakis(trimethylsilyl) silane (TKS),  $[(\text{CH}_3)_3\text{Si}]_4\text{Si}$ , was used as the reference, and spectra was acquired using a single  $20^\circ$  pulse excitation, a recycle delay time of 1 s and an acquisition time of 0.2 s.

## 3. Results and discussion

Fig. 1 illustrates  $^1\text{H}$  NMR spectra acquired at temperatures of 30, 50, and  $75^\circ\text{C}$ , respectively, and at a sample spinning rate of 5.5 kHz on 200 mg of  $\text{LiNH}_2$  sample that was ball milled for 45 min. Fig. 1a and its horizontal expanded spectrum (Fig. 1b) were acquired at  $30^\circ\text{C}$  using an experimental time of approximately 0.5 h. Three features are observed: (i) the presence of a sharp peak labeled as “1” at about  $-0.47$  ppm, (ii) a peak, labeled as “2”, centered



**Fig. 1.**  $^1\text{H}$  MAS NMR spectra of solid powder  $\text{LiNH}_2$  sample ( $\sim 200$  mg) that was ball milled for 45 min at room temperature. (a), (c), and (e) are full spectra, whereas (b), (d), and (f) are the corresponding horizontally expanded spectra, respectively. (a) and its horizontally expanded spectrum (b) were acquired at  $30^\circ\text{C}$  with 1500 accumulations for signal averaging, corresponding a total experimental time of 0.5 h. (c) and (d) were acquired at  $50^\circ\text{C}$  with 1500 accumulations (0.5 h experimental time). (e) and (f) were acquired at  $75^\circ\text{C}$  with 100 accumulations (2 min experimental time). The  $30^\circ\text{C}$  experiment was performed first. After the  $30^\circ\text{C}$  experiment, the temperature was increased to  $50^\circ\text{C}$  to acquire (c) and (d), and then to  $75^\circ\text{C}$  to acquire (e) and (f). Note that the sample was sealed in the rotor and the products continuously accumulate over the course of the experiment.

at about 1.0 ppm along with a few visible sample spinning sidebands (SSBs) (marked with “\*”) associated with the peak “2” that are spaced at the sample spinning rate of 5.5 kHz, and (iii) a very broad hump underneath both peaks “1” and “2”. The sharp peak at about  $-0.47$  ppm is assigned to the  $\text{NH}_3$  molecules based on a previous report [18]. The narrow linewidth (about 65 Hz, defined as the linewidth at half peak height) of the  $\text{NH}_3$  peak is a result of intense molecular motion. The ratio of the integral intensity of the  $\text{NH}_3$  peak to that of the overall spectrum is about 0.04%, which is accumulated over a time period of about 0.5 h. This result indicates that ammonia release in the  $\text{LiNH}_2$  system is slow at  $30^\circ\text{C}$ . However, it should be pointed out that this is the first time that ammonia release in the  $\text{LiNH}_2$  system is observed unambiguously at a temperature as low as  $30^\circ\text{C}$ .

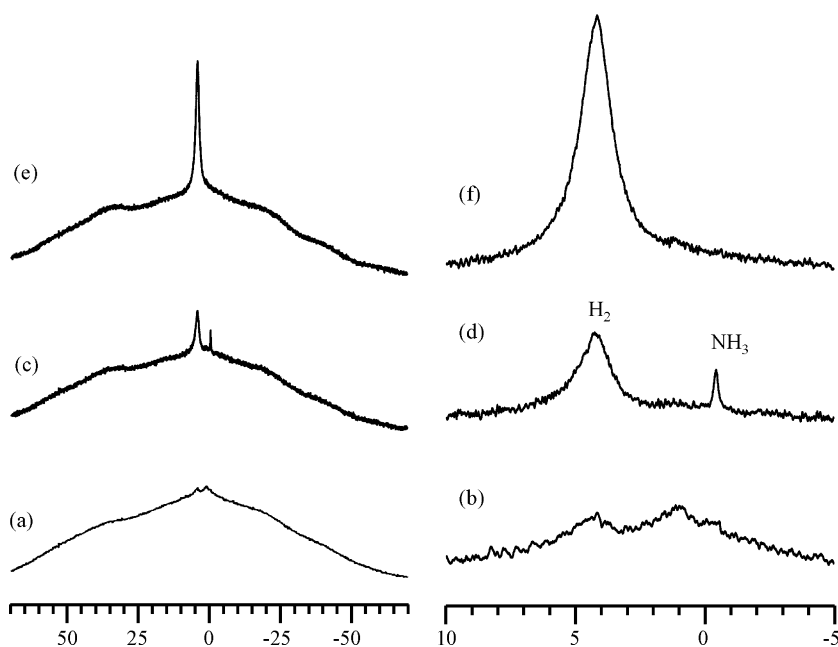
The peak at about 1.0 ppm, having a linewidth of about 2 kHz, is attributed to the mechanically activated  $\text{LiNH}_2$  molecules or the surface  $\text{LiNH}_2$  molecules, since considerable molecular motion is associated with these molecules. The molecular motion is evident by the appearance of the SSBs, labeled by “\*”, observed at a moderate sample spinning rate of 5.5 kHz. The integrated spectral intensity associated with this peak, including the SSBs, to the total spectral intensity is estimated to be about 10%.

The very broad hump has a linewidth of approximately 21 kHz and accounts for about 90% of the total spectral intensity. This broad peak is no doubt associated with the rigid lattice protons in the  $\text{LiNH}_2$  sample, where the homonuclear  $^1\text{H}$ – $^1\text{H}$  dipole–dipole interaction is so strong that a sample spinning rate of 5.5 kHz has no effect on the observed linewidth. This is because the linewidth in a  $^1\text{H}$  NMR spectrum is determined by the strength of the dipole–dipole interaction and line narrowing from MAS technique can only be effective if the sample spinning rate is comparable to or larger than the  $^1\text{H}$ – $^1\text{H}$  homonuclear dipolar interaction. It is well known [21] that the dipole–coupling constant between a pair of rigid  $^{13}\text{C}$ – $^1\text{H}$  that are separated by  $1.0\text{Å}$  is approximately 30 kHz. Given the fact that the gyromagnetic ratio of  $^1\text{H}$  is four times that of  $^{13}\text{C}$  and the dipolar coupling is proportional to the products of the gyromagnetic ratios, the dipolar coupling constant

between a pair of rigid  $^1\text{H}$ – $^1\text{H}$  that are spaced by  $1.0\text{Å}$  would be approximately 120 kHz. Since the dipolar coupling is inversely proportional to the distance to the cubic power, a linewidth of 21 kHz, taken as the approximate dipolar coupling constant, would correspond to a rigid proton–proton distance of approximately  $1.79\text{Å}$ . In principle, fast and random molecular motion such as those in liquids can completely eliminate the dipolar interaction so that a high-resolution spectrum is obtained. In solids, molecular motion, though restricted, can partially suppress dipolar interaction if the frequency of molecular motion is larger than or comparable to the static linewidth of  $^1\text{H}$  spectrum. That is why the surface  $\text{LiNH}_2$  molecules experience a reduced dipolar coupling and thus a narrow linewidth in the MAS spectrum compared with the linewidth of the rigid lattice protons.

By increasing the temperature to  $50^\circ\text{C}$ , the amount of ammonia ( $-0.47$  ppm peak) is increased from 0.04% ( $30^\circ\text{C}$ ) to 0.1% ( $50^\circ\text{C}$ ). As in Fig. 1a and b, the spectra in Fig. 1c and d were also acquired using 0.5 h accumulation time. The speed of ammonia generation is considerably increased at  $75^\circ\text{C}$  (Fig. 1e and f), which were acquired using only 1/15 the time as those of the spectra at 30 and  $50^\circ\text{C}$ . Even during such a short time, the amount of ammonia increased to 0.65%. Based on these results, it is concluded that ammonia release in mechanically activated  $\text{LiNH}_2$  system occurs at a temperature as low as  $30^\circ\text{C}$ . The speed of ammonia release increases significantly at temperatures above approximately  $75^\circ\text{C}$ .

Fig. 2 shows variable temperature  $^1\text{H}$  MAS spectra obtained from the  $\text{LiNH}_2 + \text{LiH}$  mixture ball milled for 45 min. In order to observe the effects given in Fig. 2, the sample was prepared in the following way. About 64 mg of the sample was loaded into a sealed 7.5 mm MAS rotor using an argon glovebox. The sample rotor was then inserted into the MAS probe and spun at a constant speed of 5.5 kHz for 24 h at room temperature to ensure that all the samples will homogeneously distributed around the inner rotor wall and a hollow cylinder space was formed along the rotor axis. Note that the rotor is capable of holding about 180 mg of the mixture if the sample is tightly packed. The hollow space is important to allow the accumulation of the gaseous molecules during the experiment.



**Fig. 2.**  $^1\text{H}$  MAS spectra acquired at a sample spinning rate of 5.5 kHz on a mixture (64 mg) of  $\text{LiNH}_2 + \text{LiH}$  that was ball milled for 45 min. (a), (c), and (e) are full spectra, whereas (b), (d), and (f) are the corresponding horizontally expanded spectra, respectively. (a) and its horizontally expanded spectrum (b) were acquired at room temperature; (c) and (d) were acquired when the temperature was ramped from approximately  $40^\circ\text{C}$  to about  $150^\circ\text{C}$ ; (e) and (f) were acquired when the temperature was ramped from 150 to  $180^\circ\text{C}$ , where about 40 accumulations were acquired at  $180^\circ\text{C}$ . Each spectrum was acquired using 64 accumulations, corresponding to a data acquisition time of about 77 s.

After 24 h sample spinning at 5.5 kHz, the spinning was stopped and the sealed sample rotor was taken outside the magnet and kept at room temperature (25 °C) for about 2 weeks prior to the subsequent variable temperature  $^1\text{H}$  MAS experiments. The assumption is that some micrometer scale channels might be formed during this period, because the densely packed fine particle compact owing to the centrifugal force during the spinning can become slightly loosened during the 2-week holding. These micrometer channels can facilitate diffusion of the gaseous molecules to the hollow space of the rotor and thus increase the sensitivity of the NMR analysis. It should be emphasized that the  $\text{LiNH}_2 + \text{LiH}$  mixture was free from air during the entire experimental period owing to the tight seal of the Teflon plugs in the sample rotor.

Prior to increasing the temperature, a  $^1\text{H}$  MAS spectrum at a sample spinning rate of 5.5 kHz was acquired and the resultant spectrum is presented in Fig. 2a. The spectrum is dominated by a very broad resonance, corresponding to the rigid lattice protons inside the mixture. On top of the broad resonant peak, two peaks with low spectral intensities at about 1.0 and 4.1 ppm are visible. Fig. 2b, i.e., the horizontally expanded spectrum of Fig. 2a, highlights the spectral region between chemical shifts of  $-5$  to 10 ppm. A careful examination reveals a very low spectral feature centered at about  $-0.47$  ppm. Based on the results from Fig. 1, the 1.0 ppm peak is assigned to the surface  $\text{LiNH}_2$  molecules and the  $-0.47$  ppm peak is assigned to  $\text{NH}_3$  molecules. The 4.1 ppm peak is assigned to the  $\text{H}_2$  molecules based on a previous report [18].

Shortly after the acquisition of the spectra in Fig. 2a and b, the temperature control unit was turned on and the temperature started to ramp from room temperature to the targeted temperature of 180 °C. It was noticed that the spectrum shown in Fig. 2c and its horizontally expanded spectrum in Fig. 2d were acquired between the temperatures of 40 °C and 150 °C, whereas the spectra in Fig. 2e and f were acquired between about 150 and 180 °C, where the majority of the data acquisition time was at 180 °C. During the 64 scans of data accumulations for acquiring the spectra given in Fig. 2c and d, we observed that ammonia peak at  $-0.47$  ppm increases significantly prior to a noticeable increase in the intensity of  $\text{H}_2$  peak at about 4.1 ppm. Fig. 2c and d shows the final time averaged results for a total of 64 accumulation numbers, which corresponds to an experimental time of about 77 s. It is quite clear from Fig. 2c and d that both ammonia and  $\text{H}_2$  are present. In the spectra acquired at temperatures higher than 150 °C, i.e., Fig. 2e and f, no ammonia peak was observed. Many more spectra (data not shown) were continuously acquired after Fig. 2e and f at a stable temperature of 180 °C, but no ammonia peak was observed.

The results in Fig. 2 unambiguously show that for the  $\text{LiNH}_2 + \text{LiH}$  mixture ball milled for 45 min, ammonia was first generated according to Reaction (2) at temperatures below 150 °C. Although the exact temperature range at which ammonia is excessively produced is not explored in the current work, it can be inferred based on the results from Fig. 1 that the effective temperature range might be between 75 °C and a temperature that is lower than 150 °C. In the effective temperature range, gaseous  $\text{NH}_3$  molecules are produced in significant quantity by  $\text{LiNH}_2$  particles according to Reaction (2). A portion of these newly formed  $\text{NH}_3$  molecules react with  $\text{LiH}$  molecules and convert into  $\text{H}_2$  and  $\text{LiNH}_2$  according to Reaction (3), resulting in both the  $\text{H}_2$  and  $\text{NH}_3$  peaks in Figs. 2c and d. The ability to observe the  $\text{NH}_3$  peak indicates that Reaction (3) is not very fast at the so-called effective temperature range. However, at temperatures above approximately 150 °C, Reaction (3) is so fast that the  $\text{NH}_3$  molecules, once generated, react immediately with the surrounding  $\text{LiH}$  molecules to release  $\text{H}_2$ . Therefore, no net  $\text{NH}_3$  molecules are observed, as evident in Fig. 2e and f. The ultrafast reaction rate between  $\text{NH}_3$  and  $\text{LiH}$  at temperatures above 150 °C observed in this study is consistent with the previous stud-

ies showing that this reaction takes place in microseconds [3]. It is interesting to note that the results presented in Fig. 2e and f also indicate that the previously accumulated  $\text{NH}_3$  molecules (generated at temperatures below 150 °C as shown in Fig. 2c and d) in the central hollow space of the sample rotor react with the  $\text{LiH}$  molecules and completely convert into  $\text{H}_2$  at temperatures higher than 150 °C, suggesting high diffusion rates of  $\text{NH}_3$  within the sample rotor at temperatures above 150 °C.

#### 4. Conclusions

It is demonstrated that ammonia release in the  $\text{LiNH}_2$  sample mechanically activated using high-energy ball milling at room temperature for 45 min can be observed by *in situ*  $^1\text{H}$  MAS NMR spectroscopy at a temperature as low as 30 °C. The speed of ammonia release is dramatically increased at about 75 °C. The *in situ* variable temperature  $^1\text{H}$  NMR investigations between 25 and 180 °C on the  $\text{LiNH}_2 + \text{LiH}$  mixture mechanically activated using ball milling at room temperature for 45 min clearly confirm the previously proposed two elementary reaction steps, i.e.,  $\text{NH}_3$  is generated first by  $\text{LiNH}_2$  (see Reaction (2)) and then  $\text{NH}_3$  reacts with  $\text{LiH}$  to release  $\text{H}_2$  (Reaction (3)). The study further reveals that the minimum temperature for Reaction (3) to be effective in completely capturing all the  $\text{NH}_3$  molecules so that no net  $\text{NH}_3$  is observed is higher than the minimum temperature at which Reaction (2) is effective in releasing a large quantity of  $\text{NH}_3$  molecules.

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