

Hydrogen Desorption/Absorption Properties of Li-Ca-N-H System

Kazuhiko Tokoyoda^a, Satoshi Hino^b, Takayuki Ichikawa^c*,

Keisuke Okamoto^a and Hironobu Fujii^c

^a*R&D Center, Taiheiyo Cement Corporation, 2-4-2 Osaku, Sakura 285-8655, Japan*

^b*Department of Quantum Matter, ADSM, Hiroshima University, 1-3-1 Kagamiyama,*

Higashi-Hiroshima 739-8530, Japan

^c*Institute for Advanced Materials Research, Hiroshima University, 1-3-1 Kagamiyama,*

Higashi-Hiroshima 739-8530, Japan

ABSTRACT

Hydrogen storage properties of two ball-milled composites of $\text{Ca}(\text{NH}_2)_2+2\text{LiH}$ and $\text{CaH}_2+2\text{LiNH}_2$ were investigated as a series of searching studies of high performance hydrogen storage materials. About 4.5 mass% hydrogen is desorbed from about 100 °C and the thermal desorption profiles show a peak around 200 and 220 °C for the composites of $\text{CaH}_2+2\text{LiNH}_2$ and $\text{Ca}(\text{NH}_2)_2+2\text{LiH}$, respectively, under a helium flow at 5 °C/min heating rate without any NH_3 emission within our experimental accuracy. The powder X-ray diffraction and infrared absorption spectroscopy indicated that the dehydrogenated states of both composites form “an unknown imide phase” after heating up to 400 °C, while the dehydrogenated states after heating up to 200 °C in vacuum are the mixed phases of Li_2NH and CaNH .

The rehydrogenated state for the ball-milled composite of $\text{CaH}_2+2\text{LiNH}_2$ is transformed into the composite of $\text{Ca}(\text{NH}_2)_2$ and 2LiH by repeating the dehydrogenation and rehydrogenation cycles at 180~200 °C.

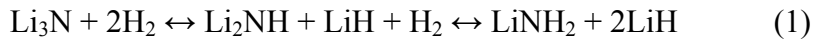
Keywords: Hydrogen storage materials, Gas-solid reactions, ball-milling, calcium amide

*Corresponding author: T. Ichikawa, fax: +81-82-424-5744, E-mail: tichi@hiroshima-u.ac.jp

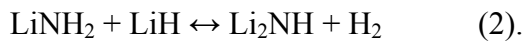
1. Introduction

The hydrogen storage technologies for realizing the hydrogen energy society in near future are currently under development all over the world. Particularly, hydrogen storage materials composed of light elements have been considered as one of the suitable candidates for on-board hydrogen tank application since its gravimetric hydrogen density can be expected to be high. For example, carbon based materials^[1], lithium borohydride^[2], complex aluminum hydrides^[3], imide-amide systems and so on, have attracted much attention in these years.

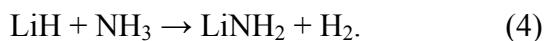
Recently, metal-N-H systems have been paid considerable attention as a new family of hydrogen storage materials since the Chen's report in 2002 that lithium nitride (Li_3N) reversibly absorbs/desorbs a large amount of hydrogen (~ 9.3 mass%), where the reaction is expressed by the following two-step reactions^[4]:



The large standard enthalpy change ($\Delta H \sim 148 \text{ kJ/mol H}_2$ ^[5]) of the first reaction indicates that a very high temperature over 430 °C needs for completing the hydrogen desorption from Li_2NH (lithium imide) to Li_3N ^[6]. However, the second step reaction has much lower $\Delta H \sim 45 \text{ kJ/mol H}_2$ and still a large amount of hydrogen capacity (6.5 mass%). Therefore, the second reaction can be suitable for on-board uses. In fact, Ichikawa *et al.*^[7] have examined the hydrogen storage properties of the ball-milled mixture of lithium hydride (LiH) and lithium amide (LiNH_2) with a small amount of titanium chloride (TiCl_3) as a catalyst, and the results obtained showed that a large amount of hydrogen (5.5-6.0 mass%) is reversibly desorbed/absorbed at 150~250 °C according to the following reaction:



Furthermore, they have experimentally demonstrated that the hydrogen desorption reaction (2) proceeds by the following two elementary reactions mediated by ammonia (NH_3)^[5],



Here, it is to be noted that the existence of the above two reactions has already been described in the previous reports.^[8,9]

The above reaction (4) suggests that it is possible to synthesize LiNH_2 by

ball-milling LiH under a gaseous NH₃ atmosphere at room temperature.^[5] Indeed, since the reaction (4) is an exothermic^[5] and ultra-fast^[8] reaction, the LiNH₂ product can be easily synthesized by the above reactive ball-milling method. Furthermore, other alkali or alkaline earth metal amides M(NH₂)_x (such as NaNH₂, Mg(NH₂)₂ and Ca(NH₂)₂) were also synthesized by ball-milling their hydrides MH_x (such as NaH, MgH₂ and CaH₂) under the NH₃ atmosphere. Their decomposition properties were investigated in detail.^[10-12] Those properties were useful for designing new metal-N-H systems for the hydrogen storage, because LiNH₂ or LiH in reaction (2) can be replaced with other metal hydrides or amides, respectively. Actually, Leng *et al.* have reported the ball-milled mixture of magnesium amide (Mg(NH₂)₂) and LiH with the 3:8 molar ratio as a novel H-storage system. In this composite system, a large amount of H₂ (> 6 mass%) was reversibly absorbed/desorbed at 150~200 °C^[13].

In addition, Xiong *et al.*^[14] have reported that the mixture of LiNH₂ and calcium hydride (CaH₂) with the 2:1 molar ratio desorbs hydrogen from 70 °C and takes a hydrogen desorption peak at 206 °C at the heating rate of 2 °C/min in the temperature-programmed desorption (TPD) profile. Furthermore, Hino *et al.*^[12] have examined the thermal desorption mass spectra (TDMS) of the calcium amide (Ca(NH₂)₂) in details and clarified that Ca(NH₂)₂ decomposes into the calcium imide (CaNH) and emits NH₃ at lower temperatures than any of LiNH₂ and Mg(NH₂)₂ decompositions.

In this paper, we examined the hydrogen storage properties of Li-Ca-N-H systems

by analogy with the Li-N-H and Li-Mg-N-H systems. For that, two kinds of the ball-milled mixtures of $\text{Ca}(\text{NH}_2)_2$ and 2LiH ($\text{Ca}(\text{NH}_2)_2\text{-}2\text{LiH}$), and CaH_2 and 2LiNH_2 ($\text{CaH}_2\text{-}2\text{LiNH}_2$) were prepared and examined the hydrogen desorption and absorption characteristics.

2. Experimental details

The starting materials, LiH (95 mass% purity), CaH_2 (99.99 mass% purity) and LiNH_2 (95 mass% purity) were purchased from Sigma-Aldrich Co. In this work, $\text{Ca}(\text{NH}_2)_2$ was mechanochemically synthesized by ball-milling CaH_2 in a pure NH_3 atmosphere of 0.6 MPa.^[10] The mechanical milling was performed for 10 hrs at room temperature by using a planetary ball-mill apparatus (Fritsch P5) at 250 rpm. Each mixture of $\text{Ca}(\text{NH}_2)_2\text{-}2\text{LiH}$ and $\text{CaH}_2\text{-}2\text{LiNH}_2$ without any catalyst was mechanically ball-milled under 1 MPa argon (Ar) atmosphere using the planetary ball-mill apparatus at 250 rpm for 2 hrs.

The gas-desorption properties were examined by a thermal desorption mass spectroscopy (TDMS, PFEIFFER, QME200) combined with thermogravimetry (TG) and differential thermal analysis (DTA, Seiko NanoTechnology Inc., TG/DTA6300) at a heating rate of 5 °C/min up to 400 °C under a highly pure helium (purity > 99.9999 %) flow. The reversibility of the composites was tested by repeating dehydrogenation at 200 °C under vacuum for 8 h and rehydrogenation at 180 °C under 3 MPa H_2 for 8 h.

The identification of phases in the samples was carried out by X-ray powder diffraction (XRD) with Cu-K α radiation (Rigaku, RINT2500). Infrared absorption spectra (IR) were collected by Fourier transform infrared spectrometer (PerkinElmer, Inc., Spectrum One) with the diffuse reflectance accessory (PIKE Technologies Inc., DiffuseIR). The sample was diluted to 10 mass% in KBr (99+%, Sigma-Aldrich Co.).

In this work, all the experimental processes from the sample preparation to the examinations of hydrogen storage properties were performed in a glovebox filled with a purified Ar gas without exposing the sample to air at all.

3. Results and Discussion

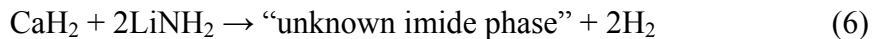
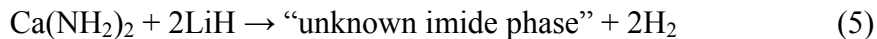
As described in the Introduction, we found that the hydrogen desorption reaction between LiNH₂ and LiH was controlled by the two-step elementary reactions mediated by NH₃. Similarly, it can be expected that the reaction between Ca(NH₂)₂ and LiH, or CaH₂ and LiNH₂ proceeds by a molecule-solid reaction mediated NH₃ as well.

Then, both the mixtures of Ca(NH₂)₂ + 2LiH, and CaH₂ + 2LiNH₂ were mechanically ball-milled under an Ar atmosphere of 1 MPa for 2 hrs and their hydrogen desorption properties were examined. In Figure 1, the TDMS and TG profiles for both the composites are shown. As reference, the profiles for the ball-milled mixture of LiH and LiNH₂ with a TiCl₃ catalyst are also given in Fig. 1. The results indicate that both the Ca(NH₂)₂-2LiH and CaH₂-2LiNH₂ composites desorb ~4.5 mass% hydrogen from

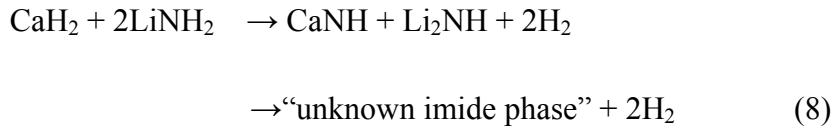
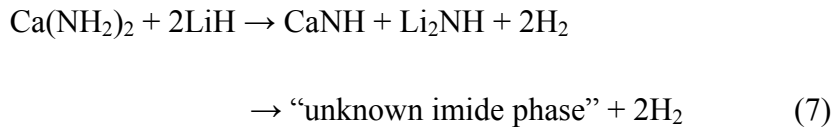
~100 °C and the peak temperatures of hydrogen desorption are 200, 220 and 230 °C for the $\text{CaH}_2\text{-2LiNH}_2$, $\text{Ca(NH}_2)_2\text{-2LiH}$ and LiH-LiNH_2 composites, respectively. Here, it should be noted that any NH_3 emission for all the products could not be detected in the TDMS profiles within our experimental accuracy. Expectedly, we notice that the starting temperature of hydrogen desorption for $\text{Ca(NH}_2)_2\text{-2LiH}$ is much lower than that for LiH-LiNH_2 because the decomposition temperature of $\text{Ca(NH}_2)_2$ is much lower than that of LiNH_2 . Unexpectedly, however, the $\text{CaH}_2\text{-2LiNH}_2$ composite showed much lower peak temperature of hydrogen desorption than $\text{Ca(NH}_2)_2\text{-2LiH}$ although both the TG curves around 150 °C exhibited quite similar behavior. Nevertheless, it can be concluded that the H_2 desorption temperature of the Li-Ca-N-H systems is lower than that of the catalyzed Li-N-H system.

Figure 2 shows the powder XRD profiles for the ball-milled composites of $\text{Ca(NH}_2)_2\text{-2LiH}$, and $\text{CaH}_2\text{-2LiNH}_2$ before and after performing the TDMS and TG measurements up to 400 °C. In the XRD profiles for the as-milled composites of $\text{Ca(NH}_2)_2\text{-2LiH}$, and $\text{CaH}_2\text{-2LiNH}_2$, the phases of original materials are somehow recognized to exist. However, they were transformed into the similar unknown phase, which might be of $\text{Li}_2\text{Ca(NH)}_2$ composition, after heating up to 400 °C irrespective of the starting materials as is shown in Fig. 2(II-a) and (II-b). This phase is analogous to the unknown phase observed by Xiong *et al.*^[14] for the Li-Ca-N-H system. This indicates that the hydrogen desorption reactions of $\text{Ca(NH}_2)_2\text{-2LiH}$, and $\text{CaH}_2\text{-2LiNH}_2$

are respectively expressed as follows;



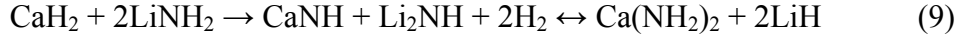
Next, we examined the reversibility of hydrogenation reaction for both the $\text{CaH}_2\text{-2LiNH}_2$ and $\text{Ca}(\text{NH}_2)_2\text{-2LiH}$ composites. The dehydrogenation and rehydrogenation were performed at 200 °C under vacuum for 8 h and at 180 °C for 8 h under 3 MPa H_2 , respectively. Figures 3(I-a) and (I-b) respectively show the XRD profiles after performing the dehydrogenation for both the $\text{CaH}_2\text{-2LiNH}_2$ and $\text{Ca}(\text{NH}_2)_2\text{-2LiH}$ composites. We notice that each composite is partially transformed into the mixed phases of both imides Li_2NH and CaNH , which is in contrast with the XRD profiles after performing the TDMS and TG examinations up to 400 °C, where the unknown imide phase is developed. The composite of $\text{CaH}_2\text{-2LiNH}_2$ rather than $\text{Ca}(\text{NH}_2)_2\text{-2LiH}$ shows that the structural characteristics after the dehydrogenation of the $\text{CaH}_2\text{-2LiNH}_2$ composite at 200 °C under vacuum are closer to those obtained at 400 °C compared to the case for the $\text{Ca}(\text{NH}_2)_2\text{-2LiH}$ composite, indicating that $\text{CaH}_2\text{-2LiNH}_2$ reveals much faster dehydrogenating reaction than $\text{Ca}(\text{NH}_2)_2\text{-2LiH}$. This may be due to that the $\text{CaH}_2\text{-2LiNH}_2$ composite has brought much better nano-scale contact between the amide and hydride phases rather than the $\text{Ca}(\text{NH}_2)_2\text{-2LiH}$ composite by ball-milling. From the above results, the hydrogen desorption reactions from both the ball-milled composites of $\text{Ca}(\text{NH}_2)_2\text{-2LiH}$ and $\text{CaH}_2\text{-2LiNH}_2$ are respectively expressed as follows:



where the mixture of Li-imide and Ca-imide phases can be gradually transformed into the unknown imide phase with increase in the temperature up to 400 °C. The theoretically expected weight loss due to hydrogen release was deduced to be 4.5 mass%, which is in good agreement with the experimental weight loss value due to the TG measurement in Fig. 1.

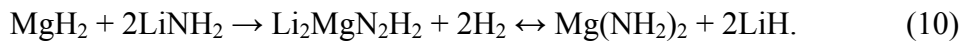
After the dehydrogenation of both the $\text{CaH}_2\text{-}2\text{LiNH}_2$ and $\text{Ca}(\text{NH}_2)_2\text{-}2\text{LiH}$ composite at 200 °C, the rehydrogenation of the samples was performed at 180 °C under the 3 MPa H_2 atmosphere for 8 h, and their XRD profiles are shown in Fig. 3(II). In both the profiles, the LiH phase can be assigned to exist though the intensities are quite weak. However, it is difficult to claim that the $\text{Ca}(\text{NH}_2)_2$ phase exists in the profiles since $\text{Ca}(\text{NH}_2)_2$ shows quite similar diffraction patterns to CaNH. Then, the experiment for further phase identification was performed by the IR spectroscopy. As shown in Figure 4, the IR absorption peaks corresponding to $\text{Ca}(\text{NH}_2)_2$ are detected in the both rehydrogenated samples. Therefore, we conclude that both the composites are transformed into the same mixture of $\text{Ca}(\text{NH}_2)_2$ and 2LiH after rehydrogenation. Consequently, the reversible reaction in the Li-Ca-N-H systems can be expressed as

follows;



Both the composites rehydrogenated under 3 MPa H₂ atmosphere at 180 °C for 8 h only desorbed ~2.5 mass%, indicating that the composites are not fully rehydrogenated under the above experimental condition. Taking into account smaller ΔH speculated from relatively low hydrogen desorbing temperature^[15], much higher pressure and lower temperature may be required for complete rehydrogenation.

Finally, we discuss the mechanism of hydrogen absorption reaction for the Li-Ca-N-H system by analogy with the Li-Mg-N-H system. With respect to reaction (9), similar results were obtained with the Li-Mg-N-H system. Luo and Sickafoose^[16] prepared the ball-milled composite of 2LiNH₂ and MgH₂ as starting material and revealed that the mixture converted to the composite of Mg(NH₂)₂ and 2LiH after repeating a dehydrogenation and rehydrogenation cycle. After fully dehydrogenation at 220 °C, it has been found that the composite is transformed into the new Li₂MgN₂H₂ phase. Therefore, they claimed that the following reaction equations are realized in sorption process:



On the basis of appearance of the single ternary imide, the hydrogen absorption reaction could be understood by a single solid-phase reaction as one of the disproportionation reactions, while Leng *et al.* reported that the composite phase of 4Li₂NH and Mg₃N₂

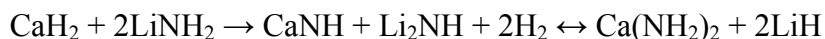
was transformed into the mixed phase of $8\text{LiH} + 3\text{Mg}(\text{NH}_2)_2$ by hydrogen uptake, which was explained by the NH_3 mediated reaction model.^[17] Based on this reaction model, we can smoothly deduce the rehydrogenating reaction of the reaction (9) as follows: (i) At the first step, $2\text{Li}_2\text{NH}$ is hydrogenated into 2LiH and 2LiNH_2 . (ii) Secondly, 2LiNH_2 decomposes to Li_2NH and NH_3 . (the net result of steps *i* and *ii* is: $\text{Li}_2\text{NH} + 2\text{H}_2 \rightarrow 2\text{LiH} + \text{NH}_3$.) (iii) Then, CaNH reacts with the generated NH_3 and is transformed into $\text{Ca}(\text{NH}_2)_2$. (iv) Finally, all of the Li_2NH and CaNH absorb H_2 and are transformed into $\text{Ca}(\text{NH}_2)_2$ and LiH . Thus, we notice that the nitrogen atom in the Li_2NH phase transfers to the $\text{Ca}(\text{NH}_2)_2$ phase through the NH_3 mediated reaction and the LiH phase is formed. Actually, we were not able to obtain the $\text{Ca}(\text{NH}_2)_2$ phase only by the same hydrogenating treatment for the CaNH phase^[12] and the detected reaction enthalpy change corresponding to the dehydrogenation from $\text{Ca}(\text{NH}_2)_2 + \text{CaH}_2$ to $2\text{CaNH} + 2\text{H}_2$ was quite small value^[12]. Further detailed investigation on the hydrogenation reaction in the Li-Ca-N-H system is necessary to understand the mechanism of the hydrogen storage reactions in the amide-imide systems.

4. Summary

The H-storage properties for both the ball-milled composites of $\text{Ca}(\text{NH}_2)_2$ and 2LiH , and 2LiNH_2 and CaH_2 were examined. The results obtained are summarized as follows:

- (1) Both the dehydrogenated states were confirmed to form the mixture of Li_2NH and CaNH phases after dehydrogenation at $200\text{ }^\circ\text{C}$ under vacuum for 8 h, which were transformed into an “unknown imide phase” after heating up to $400\text{ }^\circ\text{C}$.
- (2) The TDMS profiles indicated that the peak temperatures due to hydrogen desorption are 200 and $220\text{ }^\circ\text{C}$ for the $\text{CaH}_2\text{-}2\text{LiNH}_2$ and $\text{Ca}(\text{NH}_2)_2\text{-}2\text{LiH}$ composites, respectively, though the starting temperatures due to hydrogen desorption are almost the same for both the composites.
- (3) After rehydrogenation, both the composites were transformed into the mixture of $\text{Ca}(\text{NH}_2)_2$ and 2LiH .

Therefore, we conclude that the reversible hydrogen storage reaction in the Li-Ca-N-H system can be expressed as follows:



According to this reaction equation, we can theoretically expect a hydrogen capacity of 4.5 mass \% for the hydrogen storage.

Acknowledgement

This work was supported by the project “Development for Safe Utilization and Infrastructure of Hydrogen Industrial Technology” of NEDO, Japan.

References

1. M. Hirscher, B. Panella, *J. Alloys Compd.* 2005, 404-406, 399.
2. S. Orimo, Y. Nakamori, G. Kitahara, K. Miwa, N. Ohba, S. Towata, A. Züttel, *J. Alloys Compd.*, 2005, 404-406, 427.
3. M. Fichtner, *Ann. Chim.-Sci. Mat.*, 2005, 30, 483.
4. P. Chen, Z. Xiong, J. Luo, J. Lin, K. L. Tan, *Nature*, 2002, 420, 302.
5. T. Ichikawa, N. Hanada, S. Isobe, H. Y. Leng, H. Fujii, *J. Phys. Chem. B*, 2004, 108, 7887.
6. Y. H. Hu, E. Ruckenstein, *Ind. Eng. Chem. Res.*, 2003, 42, 5135.
7. T. Ichikawa, S. Isobe, N. Hanada, H. Fujii, *J. Alloys Compd.*, 2004, 365, 271.
8. Y. H. Hu, E. Ruckenstein, *J. Phys. Chem. A* 2003, 107, 9737.
9. F. W. Bergstrom, W. C. Fernelius, *Chem Rev.* 1933, 12, 43.
10. H. Y. Leng, T. Ichikawa, S. Hino, N. Hanada, S. Isobe, H. Fujii, *J. Power Sour.*, 2006, 156, 166
11. H. Y. Leng, T. Ichikawa, S. Isobe, S. Hino, N. Hanada, H. Fujii, *J. Alloys Compd.*, 2005, 4404-406, 443.
12. S. Hino, T. Ichikawa, H. Y. Leng, H. Fujii, *J. Alloys Compd.* 2005, 62-66, 398.
13. H. Y. Leng, T. Ichikawa, S. Hino, N. Hanada, S. Isobe, H. Fujii, *J. Phys. Chem. B* 2004, 108, 8763.
14. Z. Xiong, G. Wu, J. Hu, P. Chen, *Adv. Mater.* 2004, 16, 1522.

15. W. Grochala, P. P. Edwards, *Chem. Rev.*, 2004, *104*, 1283
16. W. Luo, S. Sickafoose, *J. Alloys Compd.*, 2006, *407*, 274.
17. H. Leng, T. Ichikawa, S. Hino, T. Nakagawa, H. Fujii, *J. Phys. Chem. B*, 2005, *109*, 10744.

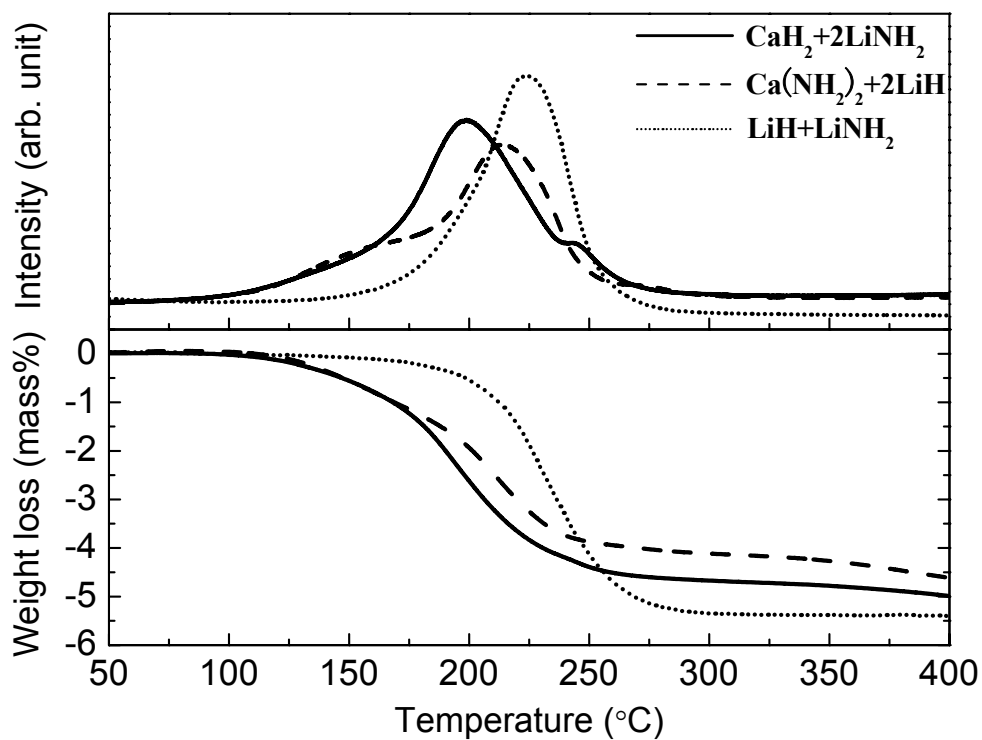


Fig. 1. Thermal desorption mass spectra (TDMS, top) for mass 2 and thermogravimetry (TG, bottom) profiles for the ball-milled composites of $\text{CaH}_2 + 2\text{LiNH}_2$ (solid line), $\text{Ca}(\text{NH}_2)_2 + 2\text{LiH}$ (dashed line) and $\text{LiH} + \text{LiNH}_2$ (dotted line) in the heating process up to 400 °C under a He gas flow atmosphere at a heating rate of 5 °C/min.

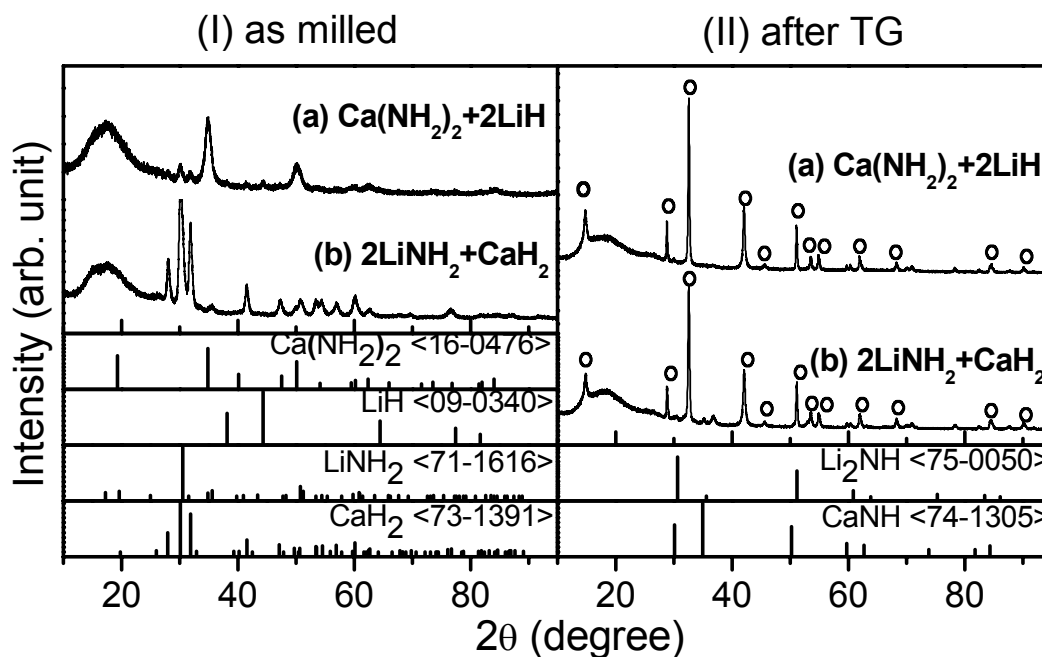


Fig. 2. Powder X-ray diffraction profiles for the ball-milled composites of (a) $\text{Ca}(\text{NH}_2)_2 + 2\text{LiH}$ and (b) $\text{CaH}_2 + 2\text{LiNH}_2$ (I: as milled, II: after heating up to 400 °C for the TDMS and TG measurements). The peak positions of the typical reflections in the ICDD powder diffraction files are included for comparison. The peaks for the unknown phase are marked by open circles. The upturn of the background at low angle is due to glue used to fix the powder on the sample holder.

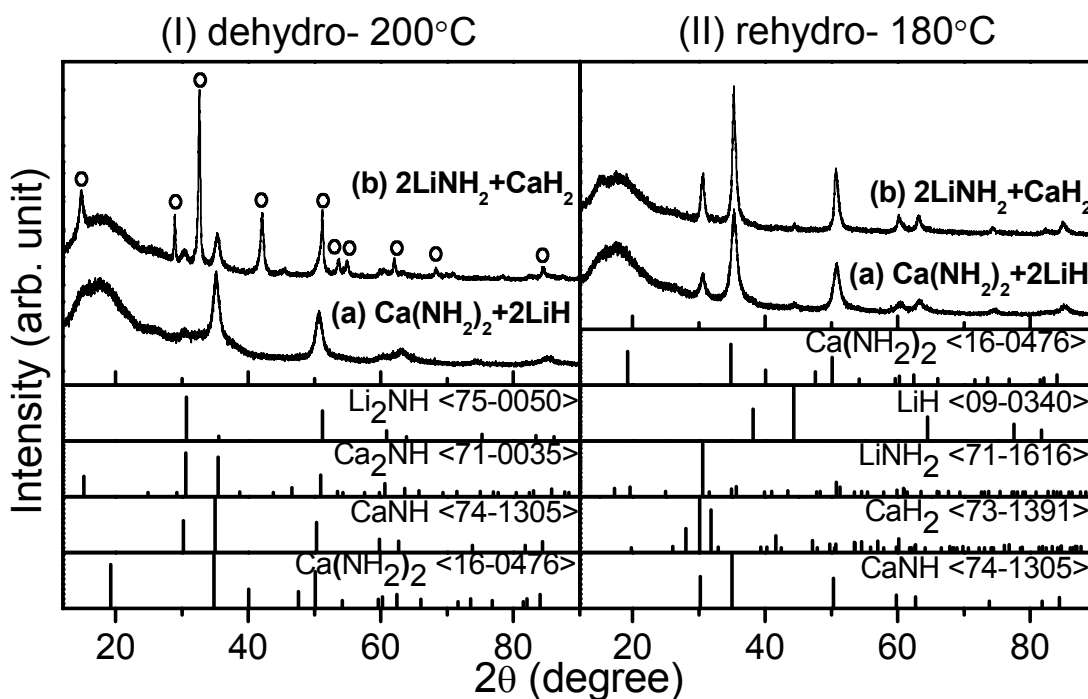


Figure 3. Powder X-ray diffraction profiles for the composites of (a) Ca(NH₂)₂ + 2LiH and (b) CaH₂ + 2LiNH₂ produced by ball-milling (I: after dehydrogenation at 200 °C in vacuum for 8 h, II: after rehydrogenation at 180 °C under 3 MPa H₂ atmosphere). The peak positions of the typical reflections in the ICDD powder diffraction files are included for comparison. The peaks for the unknown phase are marked by open circles. The upturn of the background at low angle is due to glue used to fix the powder on the sample holder.

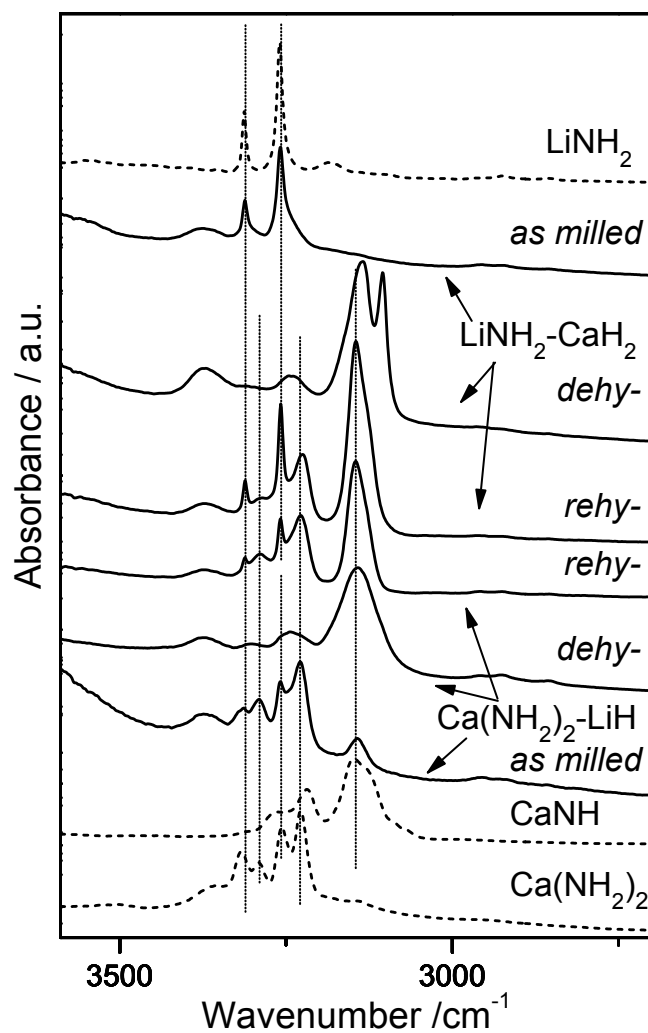


Fig. 4. Infrared (IR) spectra for the composites of $2\text{LiNH}_2\text{-CaH}_2$ (upper 3 solid lines) and $\text{Ca}(\text{NH}_2)_2\text{-2LiH}$ (lower 3 solid lines) for as milled, after dehydrogenation, and after rehydrogenation of . Dashed lines indicate IR spectra of the reference materials (LiNH_2 : top, CaNH and $\text{Ca}(\text{NH}_2)_2$: bottom).