

Hydrogen desorption properties of Ca-N-H system

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Abstract

After synthesizing calcium amide ($\text{Ca}(\text{NH}_2)_2$) through the reaction of calcium hydride (CaH_2) with ammonia (NH_3), the thermal decomposition properties have been examined. The results indicated that $\text{Ca}(\text{NH}_2)_2$ decomposed to calcium imide (CaNH) and NH_3 gas with increasing temperature, where the desorption of NH_3 started from about 60 °C and peaked around 300 °C in the thermal desorption mass spectra (TDMS). From the X-ray diffraction profiles, the product after heat treatment up to 350 °C was CaNH , but an unknown phase appeared in further heating up to 500 °C. Hydrogen (H_2) desorption properties of a mixture of $\text{Ca}(\text{NH}_2)_2$ and CaH_2 with 1:3 molar ratio were also examined. The H_2 gas of 3.5 wt.% in total was desorbed with two-peak structure in TDMS. The first peak corresponds to the reaction: $\text{Ca}(\text{NH}_2)_2 + \text{CaH}_2 \rightarrow 2\text{CaNH} + 2\text{H}_2$, and the second one originates in the reaction: $\text{CaNH} + \text{CaH}_2 \rightarrow \text{Ca}_2\text{NH} + \text{H}_2$. Simultaneously performed differential thermal analysis indicated that the former and the latter reactions were respectively exothermic and endothermic, so that the H_2 desorption corresponding to the first peak in TDMS disappeared after long time milling at room temperature.

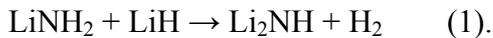
Keywords: Hydrogen storage materials (A), Gas-solid reactions (B), High-energy ball milling(B), Mechanochemical synthesis (B), Thermal analysis (D)

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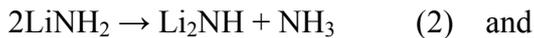
Introduction

It is necessary to improve the hydrogen storage (H-storage) technologies more and more for realizing hydrogen energy systems in near future. Especially the practical applications of H-storage for fuel cell vehicles are strongly expected as a key issue to be materialized. Therefore H-storage systems composed of light elements, such as carbon based materials [1], magnesium hydride [2], sodium alanate [3] and so on, have attracted attention all over the world.

Lithium nitride as new H-storage system, which can reversibly store a large amount of hydrogen (H_2), has recently been reported by Chen et al. [4]. After that, we investigated a ball-milled mixture of lithium amide ($LiNH_2$) and lithium hydride (LiH) doped with a small amount of $TiCl_3$. The results indicated that a large amount of H_2 (5.5-6.0 wt%) was absorbed and desorbed in the mixture in the temperature range from 150 to about 250 °C [5]. The H_2 desorption reaction of this Li-N-H system is expressed as follows:



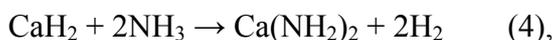
With respect to this H_2 desorption reaction, we experimentally confirmed that this reaction consists of following two elementary reactions mediated by ammonia (NH_3) [6]:



Furthermore, it was also clarified that the reaction (2) is a first order reaction and mainly controls the reaction (1) as rate-determining step[6,7]. Therefore, if the decomposition of any metal amides can take place at lower temperature than that of $LiNH_2$ and emit ammonia, the following H_2 desorption would proceed at lower temperature as well. In principle, the element Li in the Li-N-H system can be replaced with other elements in groups I and II. So, we have examined Li-Mg-N-H system as a H-storage system. Consequently, we designed the mixture of magnesium amide ($Mg(NH_2)_2$) and LiH in the 3:8 molar ratio, in which a large amount of H_2 (~7 wt %) was desorbed from 140 °C under a He flow atmosphere with zero partial pressure of H_2 , and the TDMS profile of hydrogen peaked at ~190 °C [8]. Actually, the electro-negativity of Mg is larger than

that of Li, which causes the decomposition of $\text{Mg}(\text{NH}_2)_2$ at lower temperature.

In this work, we focus on the chemical properties of a Ca-N-H system from the analogy of the Li-N-H and Mg-N-H systems. From a viewpoint of electro-negativity, we can presume that calcium amide ($\text{Ca}(\text{NH}_2)_2$) decomposes to calcium imide (CaNH) and emits NH_3 at higher temperature than the case of $\text{Mg}(\text{NH}_2)_2$, because the electro-negativities of Ca, Mg and Li are, respectively, 1.0, 1.3 and 1.0 [9]. Therefore, the decomposition properties of $\text{Ca}(\text{NH}_2)_2$ can be expected to be similar to LiNH_2 . For this purpose, we mechanochemically synthesized $\text{Ca}(\text{NH}_2)_2$ by ball milling of calcium hydride (CaH_2) in NH_3 atmosphere at room temperature. The reaction is expressed as follows;



where this reaction was deduced from the analogy of reaction (3). Furthermore, we examined the decomposition properties of $\text{Ca}(\text{NH}_2)_2$ and the H_2 desorption properties of the ball-milled mixture of $\text{Ca}(\text{NH}_2)_2$ and CaH_2 as well.

2. Experimental

As a starting material, CaH_2 powder with 99.99% purity was purchased from Sigma-Aldrich Co. Ltd. To synthesize $\text{Ca}(\text{NH}_2)_2$, CaH_2 was loaded into a Cr-steel pot (25 ml volume) together with 20 Cr-steel balls (7 mm in diameter). After introduction of pure NH_3 gas of 0.5 MPa into the pot, the sample was mechanically milled for 18 hrs in total using a rocking mill (SEIWA GIKEN Co., Ltd., RM-10) with a frequency of 10 Hz. In order to avoid an increase in temperature during milling, the milling process was interrupted every 15 min and rested 15 min. The atmosphere was replaced to pure NH_3 every 2 hrs milling so as to realize the gas-solid reaction (4) completely.

A mixture of $\text{Ca}(\text{NH}_2)_2$ and CaH_2 with a molar ratio of 1:3 was mechanically milled under a H_2 atmosphere of 1MPa using a planetary ball mill (Fritsch, P7) at 400 rpm for 2 hrs. The samples were handled in a glovebox filled with purified argon to avoid being exposed to air and moisture.

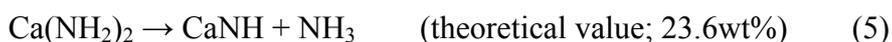
The thermal gas desorption properties were examined by thermal desorption mass spectroscopy (TDMS) (Anelva, M-QA200TS) combined with thermogravimetry (TG) and differential thermal analysis (DTA) (Rigaku, TG8120). This equipment was specially set inside the glovebox, so that the measurements of TG, DTA and TDMS could simultaneously be achieved without exposing the samples to air. In the thermal analysis measurement, high-purity helium (purity > 99.9999%) was flowed as a carrier gas, and the heating rate was fixed at 5 °C/min. The identification of phases in the products was carried out by X-ray powder diffraction (XRD) with $\text{Cu K}\alpha$ radiation (Rigaku, RINT-2500).

3. Results and Discussion

As is described in Introduction, $\text{Ca}(\text{NH}_2)_2$ was synthesized by ball milling of CaH_2 with an NH_3 atmosphere of 0.5 MPa using a rocking mill equipment with a frequency of 10 Hz. After 18 hrs milling at room temperature, the X-ray diffraction (XRD) profile of the product was assigned as almost a single phase of $\text{Ca}(\text{NH}_2)_2$ as shown in Fig.1 (a), indicating that the reaction (4) was almost completely progressed by ball milling method at room temperature. However, a small amount of non-reacting CaH_2 coexisting as an impurity. The details of sample preparation will be described in elsewhere [10].

Fig. 2a shows thermal desorption mass spectra (TDMS) of NH_3 and H_2 gases and corresponding weight loss (TG) for the $\text{Ca}(\text{NH}_2)_2$ decomposition in heating process. The NH_3 desorption from the product starts around 60 °C and peaks at 300 °C and 400 °C. For comparison, the TDMS result for $\text{Mg}(\text{NH}_2)_2$ is also shown in Fig. 2b [8], where the NH_3 desorption starts around 180 °C and peaks at 340 °C. Against our expectation from the consideration of the electro-negativity, the decomposition of $\text{Ca}(\text{NH}_2)_2$ seems to be easier than that of $\text{Mg}(\text{NH}_2)_2$, because the starting temperature of $\text{Ca}(\text{NH}_2)_2$ decomposition was much lower than that of $\text{Mg}(\text{NH}_2)_2$.

Fig. 1 shows XRD profile of $\text{Ca}(\text{NH}_2)_2$ before and after heat treatment up to 500 °C. Weight loss after the heat treatment was about 23.5 wt.% (Fig. 2a), suggesting that the decomposition of $\text{Ca}(\text{NH}_2)_2$ is expressed by the following reaction:



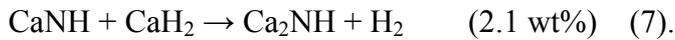
As shown in Fig. 1b, the XRD patterns of the product after heat treatment up to 350 °C agree with the phase of a cubic CaNH in the PDF-2 of the JCPDS-ICDD, and the corresponding weight loss was 16 wt.%. However, an unknown phase appears after heat treatment up to 500 °C corresponding to the weight loss of 23.5 wt% (Fig. 1c). In 1963, the thermal decomposing properties of $\text{Ca}(\text{NH}_2)_2$ to CaNH were investigated by Juza and Schumacher [11] as well. They showed the XRD pattern of $\text{Ca}(\text{NH}_2)_2$ after performing partial decompositions up to 67.7%, and the decomposed phase of 67.7 % was regarded as the cubic CaNH phase. This decomposing percentage of 67.7 % just corresponds to the weight loss of 16.0 wt%, which is consistent with our result.

Here, it is notable that the H_2 desorption are additionally observed as shown in Fig.

2a. From only the reaction (5), the H₂ desorption could not be expected. However, we can notice that there are two kinds of H₂ desorption peaks in Fig. 2a. The H₂ desorption corresponding to the peak at lower temperatures synchronized with the NH₃ desorption. Therefore, two possibilities to explain this H₂ desorption can be taken into account as follows; one is the decomposition of NH₃ to H₂ and N₂, and another is the reaction of a small amount of non-reacting CaH₂ in produced amide and NH₃ emitted by the decomposition reaction of Ca(NH₂)₂. In this work, we only focused on the latter possibility, and we expect that H₂ desorption at low temperatures corresponds to the following reaction:



On the other hand, the H₂ desorption corresponding to the peak at higher temperatures did not synchronize with the NH₃ desorption profile. Therefore, we guess that the H₂ desorption come from the direct solid-solid reaction[4] between CaNH and CaH₂, where CaH₂ still remains in the core part of Ca(NH₂)₂ after the reaction (4) (Fig.3), as follows:

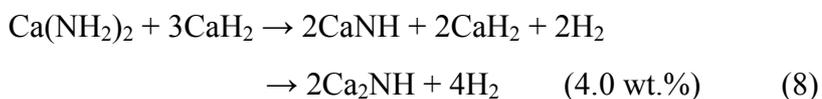


To confirm whether the reactions (6) and (7) are realized or not, we prepared a mixture of Ca(NH₂)₂ and CaH₂ in 1:1 molar ratio and a mixture of CaNH and CaH₂ in 1:1 molar ratio by mechanical milling under 1MPa H₂ pressure for 2h, where the CaNH product was prepared from Ca(NH₂)₂ by heat treatment at 400 °C in vacuum. Figs. 4a and 4b show the TDMS profiles of the H₂ and NH₃ gas desorption from the above mixtures. The result indicates that only the H₂ gas is desorbed in heating process up to 500 °C for both the reactions. From those TDMS profiles, we conclude that the H₂ desorption properties in Fig. 2a could be explained by the reactions (6) and (7) corresponding to the lower and higher peaks, respectively.

The structural properties of the products after the above thermal analyses were examined indicate that the products obtained after the TDMS experiments are, respectively, CaNH and Ca₂NH as shown in Figs. 5a and 5b. Thus, the XRD results also suggest that the reactions (6) and (7) actually progress at high temperatures. In details, the XRD pattern of the product obtained by the reaction between Ca(NH₂)₂ and CaH₂ in Fig. 5a is “CaNH-like” phase, that is, it seems to be intermediate between CaNH and

the unknown phase described in Fig. 2c.

Finally, we examined the H₂ desorbing properties of a mixture of Ca(NH₂)₂ and CaH₂ with 1:3 molar ratio, from which we expect the following reaction:



In our previous results concerning the mixture of LiH and LiNH₂ [6], we have confirmed that the NH₃ molecule plays a great role for the above reaction. So, we guess that the first step of reaction (8) could be mediated by NH₃ emitted from Ca(NH₂)₂.

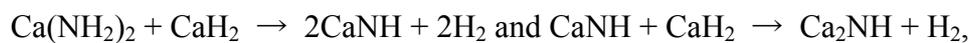
Fig. 4c shows the TDMS result of the above 1:3 mixture milled for 2 h. We can find the two-peak structure in the TDMS profile of the H₂ desorption. The first and second peak should respectively correspond to the first and second steps of the reaction (8). Obviously, the first and second peaks originate in the reactions (6) and (7), respectively, because both the peak temperatures and the corresponding weight losses are almost the same as the reactions (6) and (7), respectively, shown in Figs. 4a and 4b. Actually, the XRD profiles shown in Figs. 5c and 5d indicate that the products are cubic CaNH after heating up to 300 °C and Ca₂NH after heating up to 500 °C. Simultaneously measured DTA result for the mixture of Ca(NH₂)₂ and 3CaH₂ shows that only the second peak in the TDMS profile is endothermic. This suggests that only the second step of reaction (8), that is, the reaction (7) is reversible for H₂ storage [4]. In Fig. 4d, the TDMS profile of the mixture milled for 20 h is shown. We notice that the first peak which existed in the TDMS profile for 2 h milling sample disappears by longer milling for 20 h. This suggests that the first step of reaction (8) is exothermic because the H₂ desorption could spontaneously proceed in an activated condition by ball milling.

We believe that the detailed clarification of the chemical reaction in Ca-N-H system is important as a basic concept for designing a new high-performance hydrogen storage material of M-N-H systems.

4. Conclusion

In conclusion, the calcium amide Ca(NH₂)₂ were easily synthesized from CaH₂ by ball milling in the NH₃ atmosphere at room temperature. The TDMS profile indicates

that $\text{Ca}(\text{NH}_2)_2$ decomposes to CaNH in heating process up to $500\text{ }^\circ\text{C}$. The starting temperature of the decomposition is about $60\text{ }^\circ\text{C}$, which is lower than that of $\text{Mg}(\text{NH}_2)_2$. The XRD profile shows that CaNH produced agrees with the cubic CaNH phase up to $350\text{ }^\circ\text{C}$, but changes to an unknown phase up to $500\text{ }^\circ\text{C}$. The H_2 desorption process from the mixture of $\text{Ca}(\text{NH}_2)_2$ and CaH_2 with 1:3 molar ratio was carefully examined. The results indicate that the H_2 desorption reaction can be described by the following 2 reactions:



where the former and the latter reactions are exothermic and endothermic, respectively.

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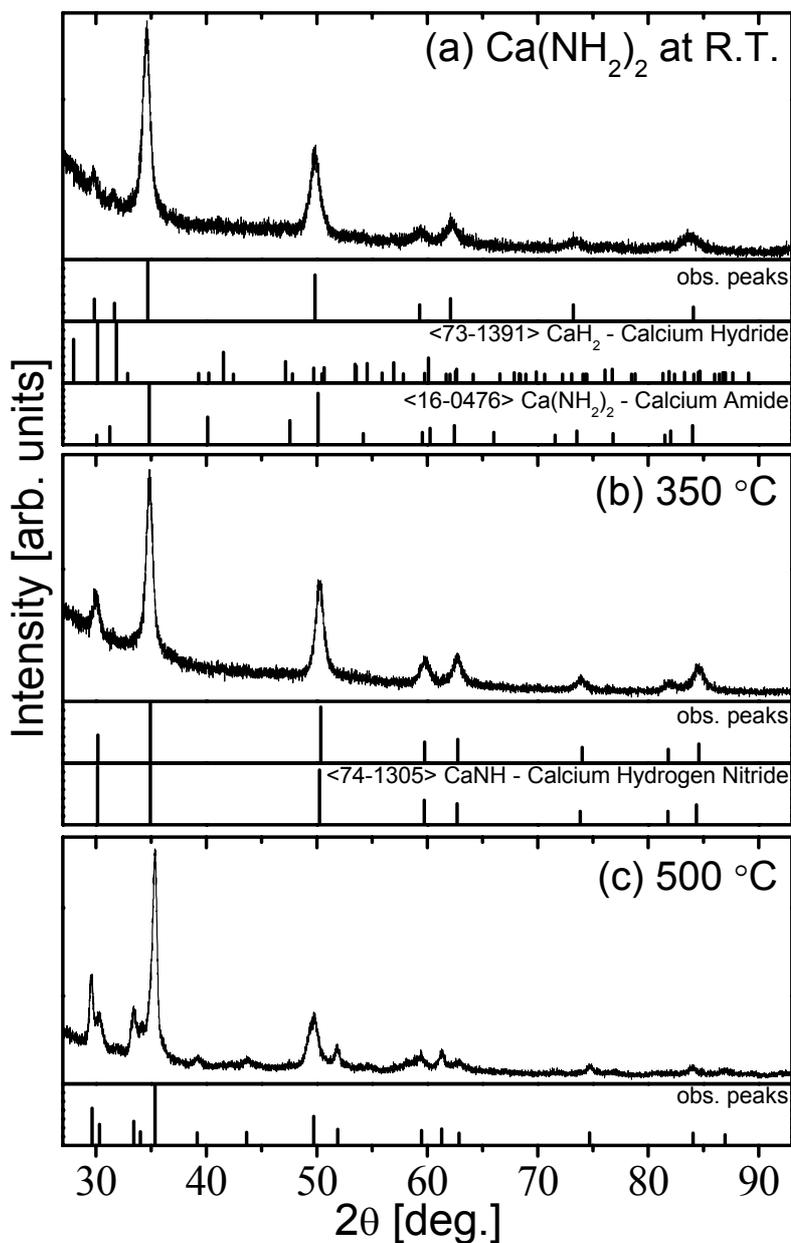


Fig.1 XRD profiles of $\text{Ca}(\text{NH}_2)_2$ produced by ball milling (a) before heat treatment, (b) after thermal decomposition at 350 °C and (c) after thermal decomposition at 500 °C. The positions of the observed peaks and typical patterns in the JCPDS diffraction database are included for comparison. The upturn of the back ground at low angle is due to grease used to fix the powder on the sample holder.

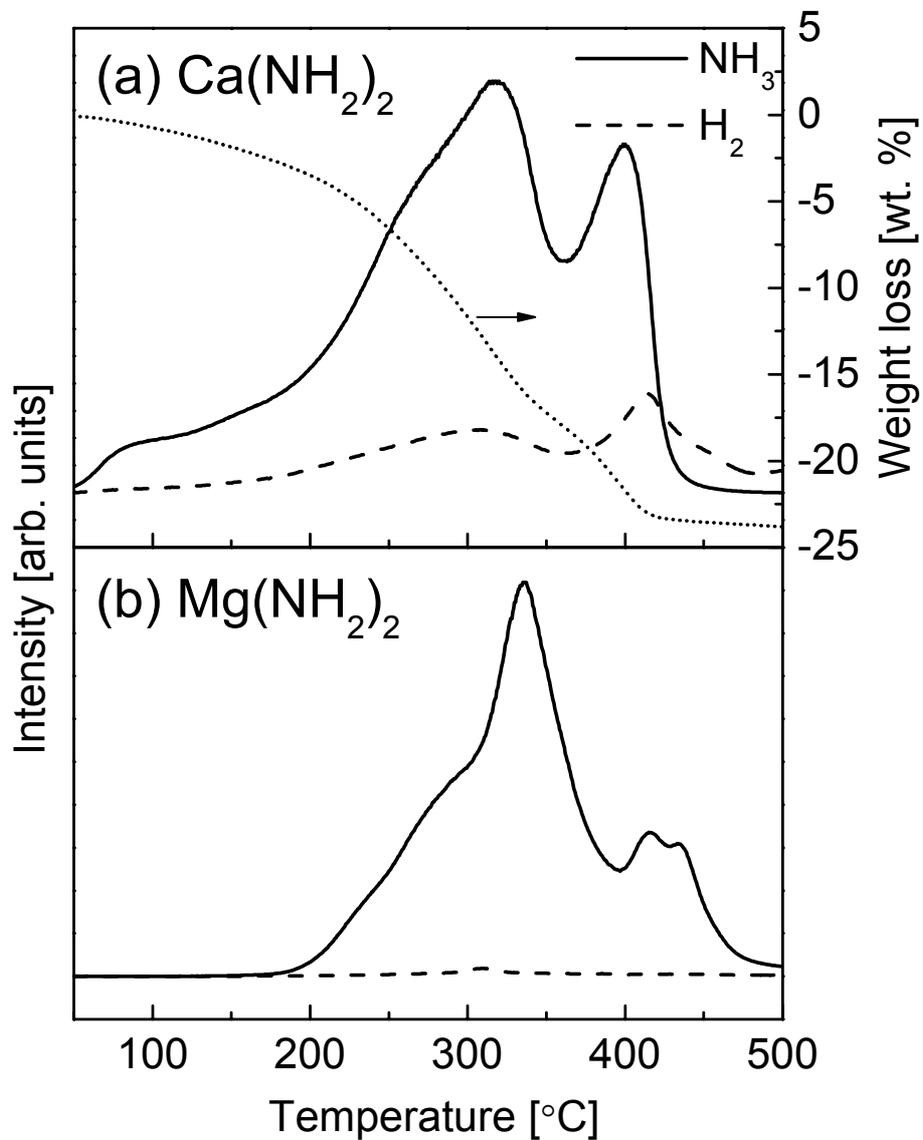


Fig.2 Thermal desorption mass spectra (TDMS) and Thermogravimetry (TG) analysis for (a) $\text{Ca}(\text{NH}_2)_2$ and (b) $\text{Mg}(\text{NH}_2)_2$ [8] in the heating process up to 500 °C under a He gas flow atmosphere at a heating rate of 5 °C/min. Here, the solid line indicates NH_3 desorption, the dashed line shows H_2 desorption and the dotted line shows weight loss.

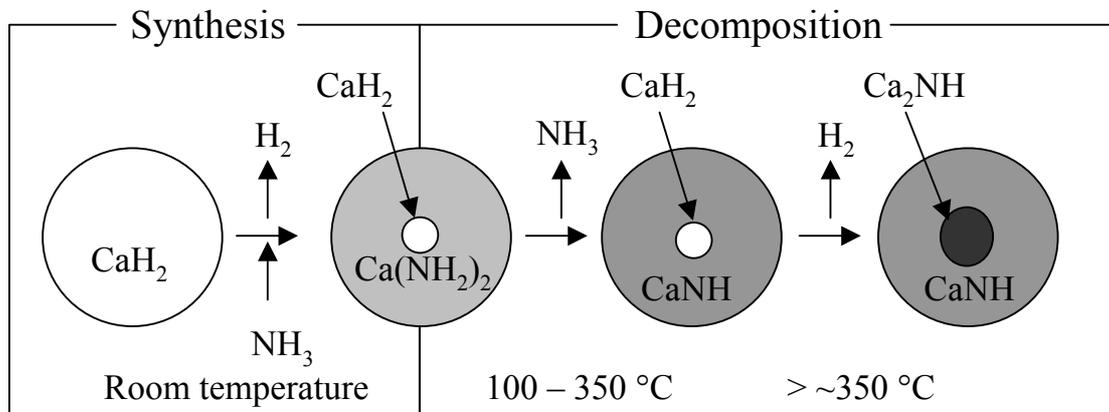


Fig.3 Schematic diagram for the synthesis and decomposition processes of $\text{Ca}(\text{NH}_2)_2$:
 Synthesis ; CaH_2 reacts with ammonia to produce $\text{Ca}(\text{NH}_2)_2$ during milling, but still exists in a core part. Decomposition ; $\text{Ca}(\text{NH}_2)_2$ decomposes to CaNH by heating, then CaNH reacts with CaH_2 in the core part at high temperatures and desorbs H_2 .

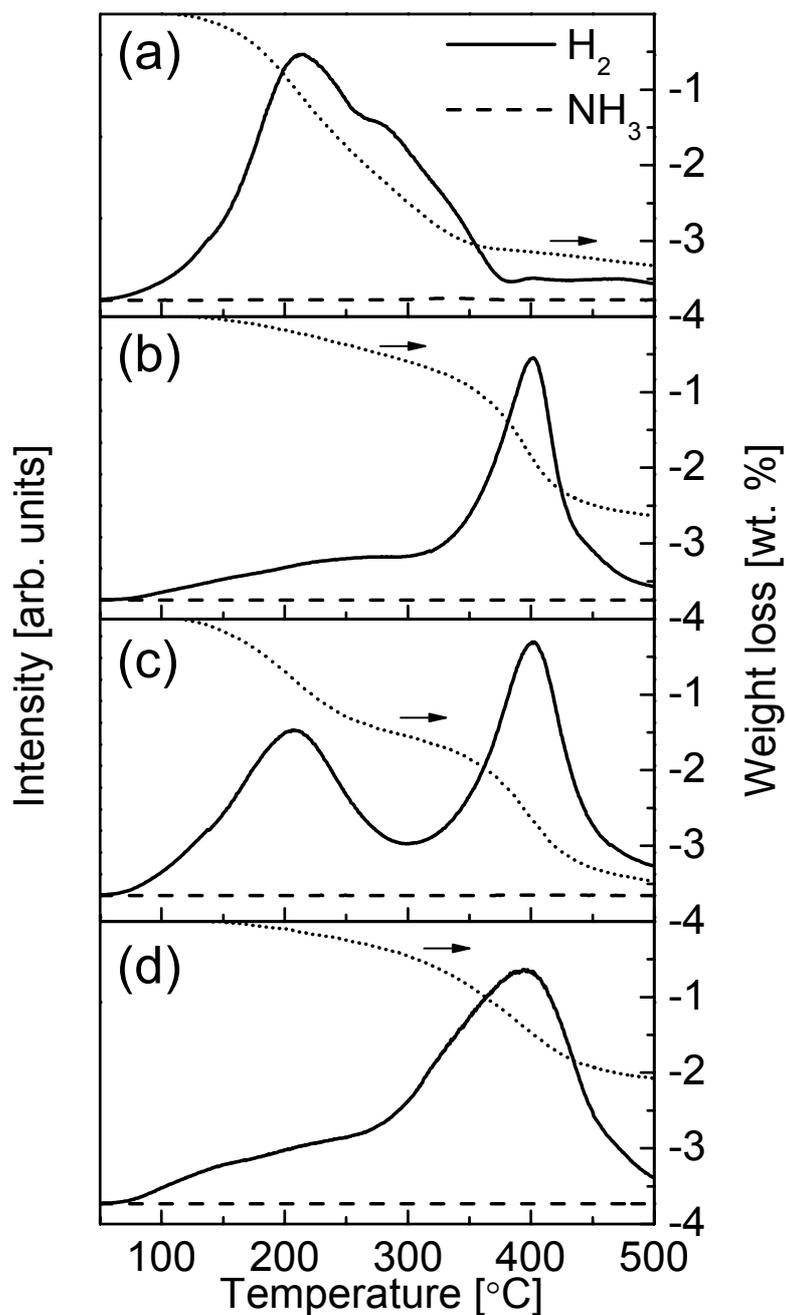


Fig.4 Thermal desorption mass spectra (TDMS) and Thermogravimetry (TG) analysis for the mixtures of (a) $\text{Ca}(\text{NH}_2)_2$ and CaH_2 (molar ratio 1:1), (b) CaNH and CaH_2 and (c) $\text{Ca}(\text{NH}_2)_2$ and CaH_2 (molar ratio 1:3) milled for 2 h. Sample (d) was milled the sample (c) for 20 hrs. The solid line indicates H_2 desorption, the dashed line shows NH_3 emission and the dotted line shows weight loss percent.

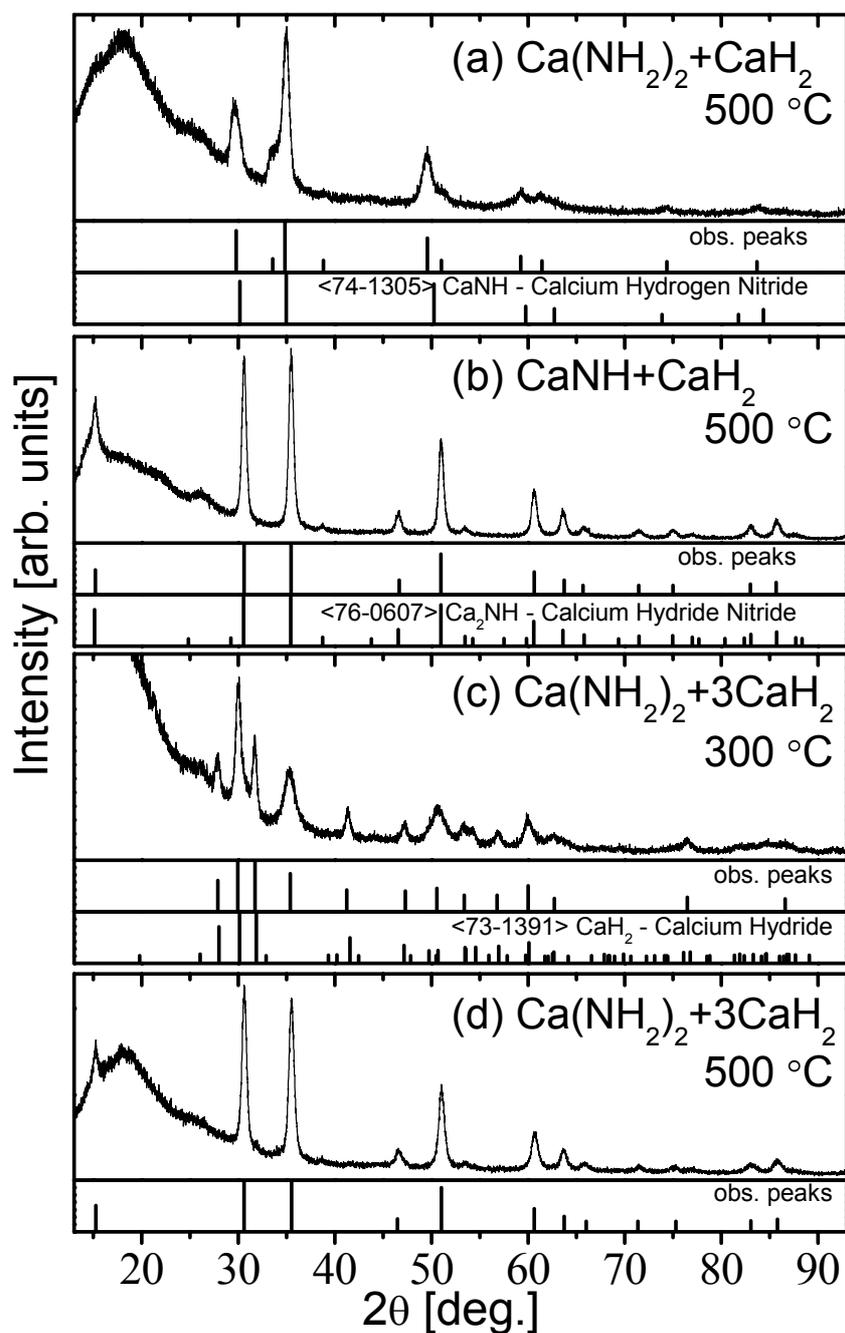


Fig. 5 XRD profiles of the mixtures of (a) $\text{Ca}(\text{NH}_2)_2$ and CaH_2 (molar ratio 1:1) after heating to 500 °C, (b) CaNH and CaH_2 (molar ratio 1:1) after heating up to 500 °C, (c) $\text{Ca}(\text{NH}_2)_2$ and CaH_2 (molar ratio 1:3) after heating to 300 °C and (d) $\text{Ca}(\text{NH}_2)_2$ and CaH_2 (molar ratio 1:3) after heating to 500 °C. All the mixtures were milled for 2 hrs at room temperature before heat treatment. The broad peak around 20° is due to grease used to fix the powder on the sample holder.