

Ca–Na–N–H system for reversible hydrogen storage

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Abstract

Ca–Na–N–H system was introduced and evaluated in this paper for reversible hydrogen storage. Similar to other amide–hydride systems already reported, interaction between $\text{Ca}(\text{NH}_2)_2$ –NaH (1/1) was observed in the temperature range of 120–270 °C with 1.1 wt% of hydrogen desorption, from which 0.96 wt% of hydrogen can be recharged. XRD and FTIR identified NaNH_2 and Ca–N–H solid solution as dehydrogenation products. Concurrent with hydrogen absorption/desorption transformation between –NH and –NH₂ units within solid solution was observed.

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1. Introduction

To protect our environment from harmful emissions of combusting fossil fuels new energy sources and technologies have to be developed imperatively, among which hydrogen powered fuel cell attracts the maximal attention, and in the next few decades it is believed to be the driving force for vehicles and portable devices. However, before fuel cell car can truly run on the road there is a big problem to be solved—highly efficient onboard hydrogen storage system [1]. So far several new systems, such as carbonaceous materials [2,3], alanates [4,5], B–N–H complex [6] and metal–N–H [7–17] have been developed and actively investigated worldwide. As the first studied metal–N–H system, Li–N–H system [7] was proposed for hydrogen storage on the basis of the discovery of hydriding Li_3N . Approximately 6.5 wt% of hydrogen can be reversibly stored at temperatures above 250 °C through the chemical reaction of $\text{Li}_2\text{NH} + \text{H}_2 \rightleftharpoons \text{LiNH}_2 + \text{LiH}$. Though this system was not suitable for practical hydrogen storage due to the unfavorable thermodynamics it brought an idea on hydrogen release from the mixtures of amide and hydride. Recently, new metal–N–H systems starting from LiNH_2 – MgH_2 [10,11],

LiNH_2 – CaH_2 [10], $\text{Mg}(\text{NH}_2)_2$ – LiH [12,13], $\text{Mg}(\text{NH}_2)_2$ – NaH [14], $\text{Mg}(\text{NH}_2)_2$ – CaH_2 [15] and $\text{Ca}(\text{NH}_2)_2$ – CaH_2 [16] have been explored and evaluated for hydrogen storage. All those amide–hydride mixtures showed hydrogen release upon heating to certain temperatures. After desorption, some of the dehydrogenated samples can be recharged with hydrogen and go back to the two starting chemicals, which enables metal–N–H new candidate for hydrogen storage. However, to meet the requirements of practical applications more amide–hydride combinations should be investigated and evaluated. In this paper, $\text{Ca}(\text{NH}_2)_2$ and NaH were employed as starting materials. Detailed investigations were performed to study the hydrogen absorption/desorption properties of their mixture.

2. Experiment

NaH powder with 95% purity was purchased from Aldrich. $\text{Ca}(\text{NH}_2)_2$ was synthesized by reacting metal Ca (98.5% purity, MERCK) with purified ammonia gas at room temperature for 1 day. At the end of reaction the sample weight increased 80% indicating that metallic Ca was completely converted to $\text{Ca}(\text{NH}_2)_2$. The following up XRD measurement also revealed the vanishment of metallic Ca and the development of $\text{Ca}(\text{NH}_2)_2$. Three $\text{Ca}(\text{NH}_2)_2$ –NaH samples with $\text{Ca}(\text{NH}_2)_2$ /NaH molar ration of 1/1, 1/1.5 and 1/2 were ball milled over a Fretsch planetary mill under inert atmosphere. The ball-to-sample weight ratio is about 30/1. No gaseous product(s) was detected after milling for 1 day.

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To avoid any moisture and oxygen contaminations all the material handlings were performed inside a MBRAUN glove-box filled with purified argon.

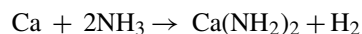
Thermal desorption properties of post-milled samples were first investigated by temperature-programmed-desorption (TPD). Detailed operation procedure was mentioned elsewhere [8]. Tail gas was conducted to a GC–MS combined system and an ammonia sensitive reagent for analysis. Temperature programmed decomposition (TPDC) testing was performed on the TPD system with same testing conditions applied. The heat-of-desorption was measured by a Netzsch HP DSC 204 with the dynamic mode applied. Purified He was used as carrier gas and the heating rate set at 2 °C/min. Thermal gravimetric (TG) measurement was carried out over Ca(NH₂)₂ sample in a Setaram TG-DTA/DSC system with heating rate of 2 °C/min under a flow of argon gas. Hydrogen desorption and absorption over Ca(NH₂)₂–NaH system was quantitatively measured by a commercial pressure–composition–isotherm unit provide by Advanced Material Corporation with release and soak modes applied. Static P–C isotherms were recorded at three temperature points. Delay time was set at 300 s. Four hundred milligrams sample were tested each time.

Structural/compositional changes were identified by a Bruker D8-advance X-ray diffraction (XRD) with Cu K α radiation. N–H vibration in samples was detected by a Perkin-Elmer FTIR-3000.

3. Results

3.1. Decomposition of Ca(NH₂)₂

As starting material, Ca(NH₂)₂ was synthesized on-site by reacting commercial Ca particles with NH₃ gas at room temperature according to the reaction:



XRD patterns of the product (see Fig. 2a) exhibit characteristic peaks of Ca(NH₂)₂ at 19.24°, 34.83° and 50.11°, respectively. No patterns assigned to other species can be identified, indicating the complete conversion of Ca to Ca(NH₂)₂ by this method. Temperature programmed decomposition of Ca(NH₂)₂ was monitored by a mass spectrometer with H₂, NH₃, N₂ signals recorded at *M/e* = 2, 15, 28, respectively. As shown in Fig. 1, NH₃ was the major gaseous product at temperatures below 370 °C. It was detected at temperature around 150 °C and peaked at 347 and 428 °C, respectively. Slight amount of H₂ and N₂ were generated at temperatures above 300 °C, which might be due to the decomposition of NH₃ at high temperatures. To understand the phase and compositional changes involved in this thermal process samples collected at 374 and 500 °C, respectively, were subject to XRD and FTIR analysis. Thermal gravimetric measurement showed that the weight loss at above two stopping points were 15.7 and 23.5 wt%, which is consistent with results from literature [16]. XRD profiles of thermally treated Ca(NH₂)₂ samples (illustrated in Fig. 2b and c) revealed that a CaNH-like (NaCl structure with *a* = 5.155 Å) and an unknown structures are the dominant species after heated to

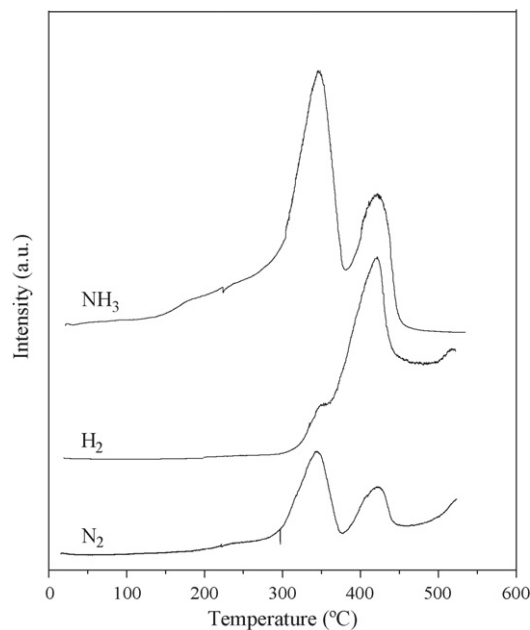


Fig. 1. TPDC spectra of freshly prepared Ca(NH₂)₂.

374 and 500 °C, respectively. FTIR results (see Fig. 3) showed that the N–H vibration of the post-TPD-374 °C Ca(NH₂)₂ sample exhibit two peaks at 3220 and 3147 cm⁻¹, respectively, which are clearly different from the pristine Ca(NH₂)₂; Heating to higher temperature resulted in continuous change in N–H vibration. Finally, an imide-like absorbance positioned at 3174 cm⁻¹ was observed after decomposition at 500 °C. Juza and Schumacher [18] investigated decomposition of Ca(NH₂)₂ to CaNH in 1962. They found that such reaction yields a solid solution of Ca(NH₂)₂ and CaNH with a defect NaCl structure, NH₂ and NH ions occupy anionic positions, Ca ions and lattice defects occupy the cationic positions. Similar solid solution was

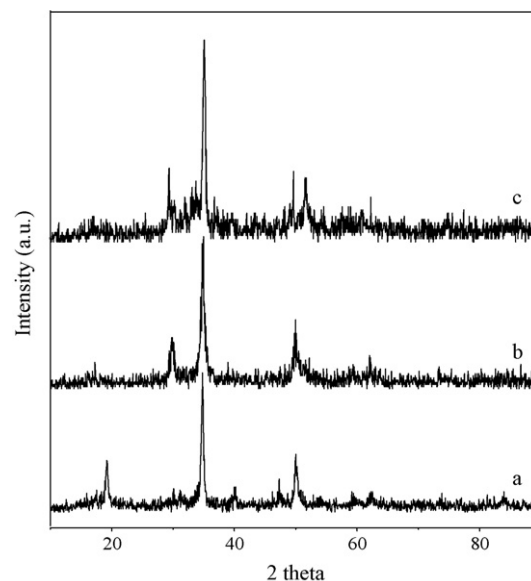


Fig. 2. XRD patterns of Ca(NH₂)₂: (a) pristine Ca(NH₂)₂; (b) after TPDC test to 374 °C; (c) after TPDC test to 500 °C.

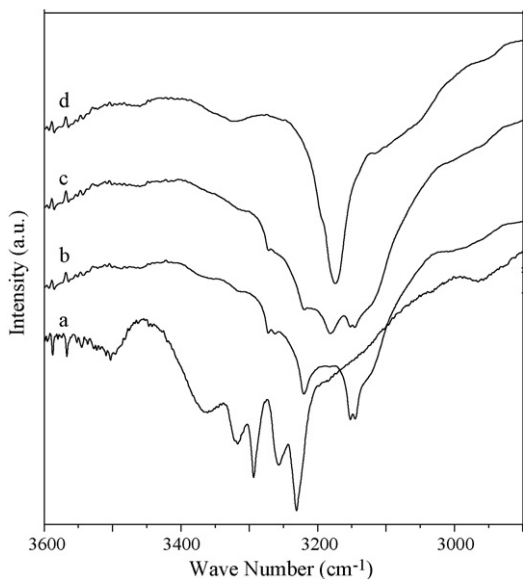
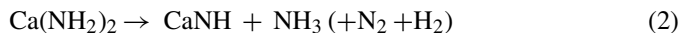
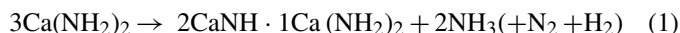


Fig. 3. FTIR spectra of Ca(NH₂)₂: (a) pristine Ca(NH₂)₂; (b) after TPDC test to 374 °C; (c) after TPDC test to 400 °C; (d) after TPDC test to 500 °C.

also identified by G. Jean and L. Jean [19] in their investigation of chemical reaction between Ca₃N₂ and NH₃. The composition of the solid solution was confirmed to be 2CaNH–1Ca(NH₂)₂. Taking into consideration of the TG, XRD and FTIR measurements and the previously reported results, the decomposition process of Ca(NH₂)₂ may be interpreted as follows:



The weight loss of reactions (1) and (2) were calculated to be 15.74 and 23.6 wt%, quite close to our experimental results. Referring to our previous studies on hydrogenation of Ca₃N₂ [8], it should be noted that pure Ca–N–H phases like CaNH are difficult to be reached by solid reactions. N or H atom numbers within the chemical composition may change slightly; as a result, distinct N–H vibrations and XRD patterns may be presented. Detailed structural identification is necessary in future investigations.

3.2. Hydrogen desorption and absorption over Ca(NH₂)₂–NaH system

Fig. 4 summarizes TPD results of Ca(NH₂)₂–NaH samples with molar ratio of Ca(NH₂)₂/NaH = 1/1, 1/1.5 and 1/2, respectively. Different from the TPDC features of Ca(NH₂)₂, H₂ instead of NH₃ appeared upon heating Ca(NH₂)₂–NaH (1/1) mixture at temperature above 100 °C, which is substantially lower than those of decomposition of two starting materials, revealing the absolute thermodynamic and kinetic changes. NH₃ was detected at temperatures above 300 °C, which is probably due to the continuous decomposition of intermediate product. Adding more NaH (Ca(NH₂)₂/NaH = 1/1.5 and 1/2) to the mixture seems of little help to enhance the hydrogen desorption at lower temperatures (below 250 °C) and depress NH₃ formation,

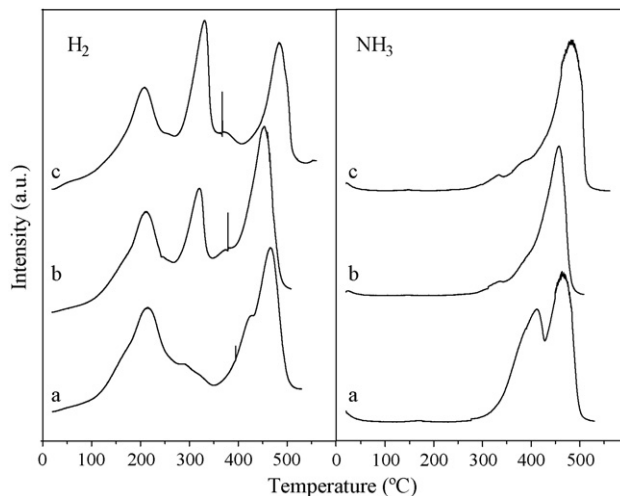


Fig. 4. TPD spectra of post-milled Ca(NH₂)₂–NaH samples: (a) Ca(NH₂)₂–NaH (1/1); (b) Ca(NH₂)₂–NaH (1/1.5); (c) Ca(NH₂)₂–NaH (1/2).

except the continuously increased hydrogen release at temperature around 320 °C, which is due to the thermo-decomposition of unreacted NaH. Therefore, we chose Ca(NH₂)₂–NaH (1/1) as our target sample. Desorption features of Ca(NH₂)₂–NaH (1/1) sample was also investigated by means of DSC and volumetric release and soak measurement. Results are illustrated in Fig. 5. DSC measurement shows an endothermic peak in the temperature range of 130–270 °C which is in accordance with that of hydrogen desorption (compare Figs. 4 and 5). The endothermic nature of dehydrogenation indicates that reversible hydrogen absorption/desorption could be achieved thermodynamically. Volumetric measurement shows that ~1.1 wt% of hydrogen is evolved in the temperature range from room temperature to 270 °C, which equals to 1H atom detached from

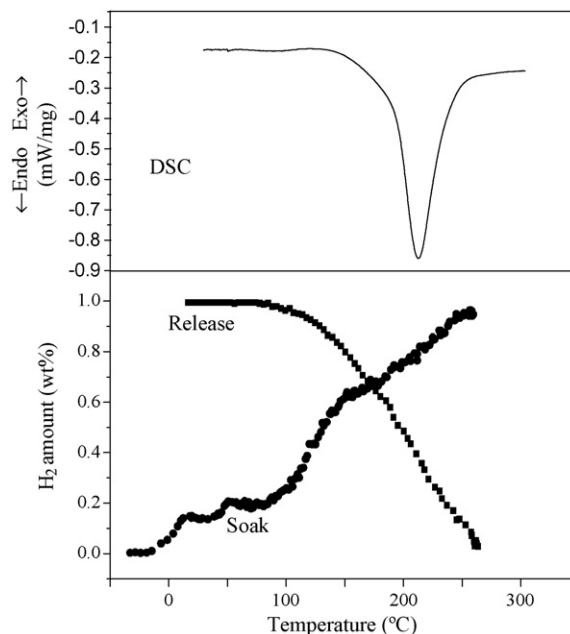


Fig. 5. Hydrogen desorption from sample Ca(NH₂)₂–NaH (1/1) investigated by DSC and volumetric measurement working at release and soak mode.

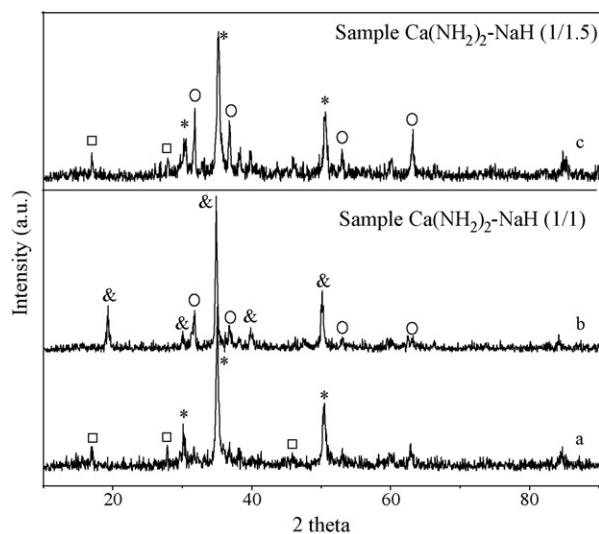


Fig. 6. XRD characterization of dehydrogenated (a) and hydrogenated (b) $\text{Ca}(\text{NH}_2)_2\text{-NaH}$ (1/1) sample; dehydrogenated (c) $\text{Ca}(\text{NH}_2)_2\text{-NaH}$ (1/1.5) sample. Peaks marked with (□) are the characteristic diffraction of NaNH_2 , (&) represents $\text{Ca}(\text{NH}_2)_2$, (○) represents NaH & (*) represents CaNH -like structure developed after dehydrogenation.

$\text{Ca}(\text{NH}_2)_2 + \text{NaH}$ (1 + 1) mixture molecules. Therefore, the heat of desorption was calculated to be ~ 55 kJ/mol- H_2 . Hydrogenation over the post-dehydrogenated $\text{Ca}(\text{NH}_2)_2\text{-NaH}$ (1/1) sample was carried out by using the volumetric soak measurement and testing with hydrogen pressure of 70 bar. As DSC measurement predicted almost same amount of hydrogen (0.96 wt%) was recharged, thus, evidencing reversibility in hydrogen storage over the Ca-Na-N-H system.

XRD was employed to identify phase changes during above hydrogen absorption/desorption processes. Variations in N–H bond stretch of samples at different hydrogenation stages were monitored by FTIR. XRD results showed that after dehydrogenation of $\text{Ca}(\text{NH}_2)_2\text{-NaH}$ (1/1) sample to 270°C NaNH_2 and a CaNH -like structure (NaCl structure with $a = 5.114 \text{ \AA}$) were developed (see Fig. 6). Simultaneously, diffraction patterns assignable to the two starting chemicals totally disappeared. As a comparison NaH signal can still be seen in the post-dehydrogenated (270°C) $\text{Ca}(\text{NH}_2)_2\text{-NaH}$ (1/1.5) sample revealing the excessive of NaH . Subsequent hydrogenation of the above mixture resulted in the regeneration of $\text{Ca}(\text{NH}_2)_2$ and NaH , further evidencing the reversibility of process. More details were revealed from FTIR results, it can be seen that N–H stretches at 3260 , 3210 and 3074 cm^{-1} , characteristic signals of NaNH_2 , were detected after hydrogen desorption from $\text{Ca}(\text{NH}_2)_2\text{-NaH}$ (1/1) sample (see Fig. 7). This result is in consistent with XRD observations. In addition, a broad absorbance was observed with two overlapped peaks located at 3149 and 3125 cm^{-1} , respectively. Considering those vibrations are within the energy scope of imide N–H stretch there should be $-\text{NH}$ unit in dehydrogenated sample. The subsequent hydrogenation leads N–H vibrations to 3230 and 3294 cm^{-1} , which are characteristic of N–H stretch in $\text{Ca}(\text{NH}_2)_2$. The vibration of imide is largely depressed with a relatively sharper peak at 3143 cm^{-1} . The existence of unconverted imide may

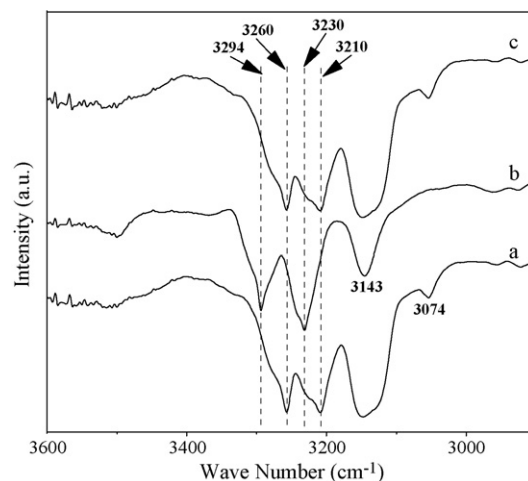


Fig. 7. FTIR spectra of $\text{Ca}(\text{NH}_2)_2\text{-NaH}$ (1/1) sample: after dehydrogenation (a), then hydrogenated with high pressure H_2 (b) and again dehydrogenated to 270°C (c).

be due to the slower absorption kinetics. Successive dehydrogenation of the hydrogenated mixture resulted in the regeneration of the same components as that of dehydrogenation from the fresh $\text{Ca}(\text{NH}_2)_2\text{-NaH}$ (1/1) sample (see Fig. 7c). To quantify the NaNH_2 in the product phase, we used Si as internal reference (Si is not reactive) for the XRD measurement. It was confirmed that NaNH_2 in the product phases exhibits the same quantity as that of NaH in reactant phases, revealing that Na component is limited in the transition process of $\text{NaH} \leftrightarrow \text{NaNH}_2$. As to Ca , things became more complicated. As

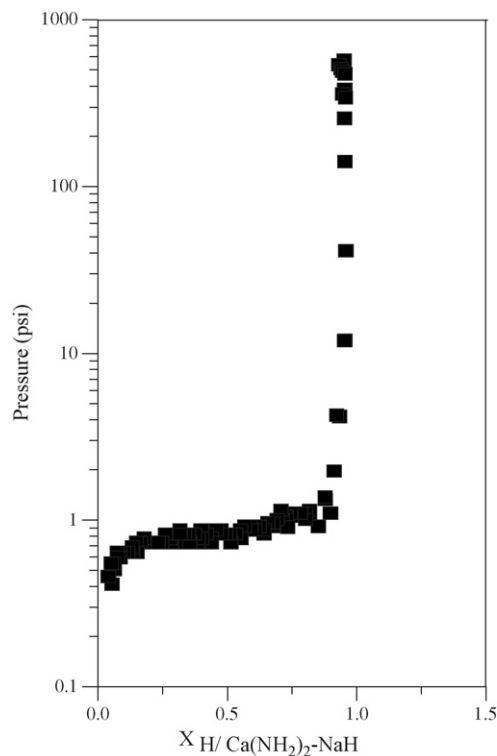


Fig. 8. Pressure–composition isotherm (only desorption) of 270°C -dehydrogenated $\text{Ca}(\text{NH}_2)_2\text{-NaH}$ (1/1) sample at 220°C .

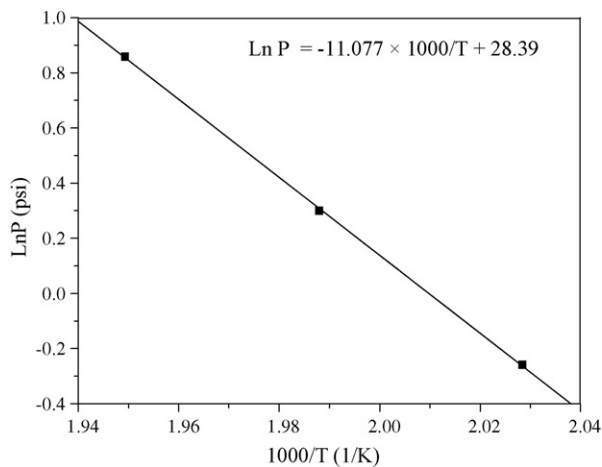
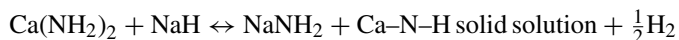


Fig. 9. Van't Hoff plot of $\text{Ca}(\text{NH}_2)_2\text{-NaH}$ (1/1) sample.

aforementioned, $\text{Ca}(\text{NH}_2)_2$ can easily form solid solution with its imide, i.e., $2\text{CaNH} + 1\text{Ca}(\text{NH}_2)_2$. In the process of hydrogen absorption/desorption over Ca-Na-N-H system solid solutions with diverse compositions will be yielded at different reaction stages, which makes them difficult to be investigated. In this study, by summarizing the number of hydrogen detached from the reactants and the phase transitions, the following reaction is suggested to describe reversible hydrogen absorption and desorption over $\text{Ca}(\text{NH}_2)_2\text{-NaH}$ system:



As 1H atom released from $\text{Ca}(\text{NH}_2)_2 + \text{NaH}$ (1 + 1) mixture Ca-N-H solid solution joined with more $-\text{NH}$ units appeared to be the dominant. On the other hand, $-\text{NH}_2$ unit tended to increase in solid composition with hydrogen absorbed, but conversion of $-\text{NH}$ to $-\text{NH}_2$ unit seems at significantly low rates. More investigations are necessary to look into nature of this kind of solid solution. To obtain the equilibrium absorption and desorption pressure of Ca-Na-N-H system, isotherms were measured on a post-dehydrogenated $\text{Ca}(\text{NH}_2)_2\text{-NaH}$ (1/1) sample. Fig. 8 showed P-C-T isotherm (only desorption) obtained at 220°C . As expected the capacity for hydrogen storage over this system is ~ 1.0 wt%. Though there is hysteresis in desorption its curve still return to the origin but with relatively low plateau pressure,

about 0.772 psi at this temperature. At other temperature points of 230 and 240°C isotherms were also measured with similar shape (not shown) but different plateau pressure. Van't Hoff plots generated from those isotherms are shown in Fig. 9, from which the heat-of-formation of one mole H_2 in the Ca-Na-N-H system is calculated at 92.1 kJ. Difference between this value and the one derived from DSC measurement seems reasonable since a fraction of imide species survived due to the slow kinetics of hydrogenation and hence changed the reaction enthalpy.

In conclusion, post-milled $\text{Ca}(\text{NH}_2)_2\text{-NaH}$ (1/1) sample can release 1.1 wt% of hydrogen upon heating it to 270°C , which equals to 1H atom detached from one $\text{Ca}(\text{NH}_2)_2\text{-NaH}$ (1 + 1) mixture. NaNH_2 , together with a Ca-N-H solid solution were identified to be the dehydrogenation product. 0.96 wt% of hydrogen was found to be recharged on above product.

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