In Situ X-ray Diffraction Study on the De/re-hydrogenation Processes of the $\text{K}_2[\text{Zn}(\text{NH}_2)_4]\cdot 8\text{LiH}$ System

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Abstract

In this work, the hydrogen absorption and desorption properties of the system $\text{K}_2[\text{Zn}(\text{NH}_2)_4]$ - 8LiH are investigated in detail via *in situ* synchrotron radiation powder X-ray diffraction (SR-PXD), Fourier Transform Infrared spectroscopy (FT-IR) and volumetric methods. Upon milling, $\text{K}_2[\text{Zn}(\text{NH}_2)_4]$ and 8LiH react to form 4LiNH_2 - 4LiH - K_2ZnH_4 , and then 4LiNH_2 - 4LiH - K_2ZnH_4 releases H_2 in multiple steps. The final products of the desorption reaction are KH , LiZn_{13} and Li_2NH . During re-hydrogenation, KH reacts with LiZn_{13} under 50 bar of hydrogen producing K_3ZnH_5 . This phase appears to enhance the hydrogenation process which after its formation at ca. 220 °C takes place in only 30 seconds. The system 4LiNH_2 - 4LiH - K_2ZnH_4 is shown to be reversible under the applied conditions of vacuum at 400 °C for desorption and 50 bar of H_2 at 300 °C for absorption.

Introduction

Amide-hydride systems are regarded as promising candidates for on-board hydrogen storage applications.¹ In the early 2000's Chen and co-workers reported the first example of a reversible amide-hydride system with an appealing hydrogen storage capacity (i.e. LiNH_2 - 2LiH).² The decomposition reaction of the LiNH_2 - 2LiH mixture takes place in two steps (equation 1). The overall weight loss for this reaction is 10.3 wt %:

However, only the first reaction step is suitable for hydrogen storage purposes due to its favorable thermodynamics and reasonable H_2 capacity ($\Delta H \approx 45$ kJ/mol, 7 wt % of H_2). As the first, Ichikawa et al.,³ described the beneficial effects of Ti-based additives to LiNH_2 - LiH , both on the reaction kinetics and the purity of the desorbed H_2 . Following this work, several other transition metal (TM)-based additives were tested on the LiNH_2 - LiH system.⁴ The enhancement

of the reaction kinetics observed for the material doped with TM-based additives might be explained by the capability of TMs to chemisorb and split hydrogen molecules into hydrogen atoms lowering the energy barriers.⁵

Recently, the hydrogenation and de-hydrogenation properties of several amide-hydride composites were investigated.⁶ For example, replacing LiH with MgH₂ in LiNH₂-LiH, it is possible to obtain a new hydrogen storage system with a hydrogen capacity of 8.2 wt % and an attractive reaction enthalpy ($\Delta H \approx 29.7$ kJ/mol-H₂).⁷ In this respect, Lu et al.,⁸ showed that LiNH₂-MgH₂ system mixed by roll milling technique can release ca. 8.1 wt % of H₂ at the temperature range between 160 and 220 °C. Reducing the ratio of LiNH₂ and MgH₂ to 2:1, represents a promising on-board hydrogen storage system which releases H₂ according to equation 2.^{6g, 9} The addition of KH/RbH to this composite allows to achieve a H₂ equilibrium pressure of roughly 2 bar at 107 °C.^{6b, 6d, 10}

Recently, we have investigated several ternary alkali metal transition metal amides as hydrogen storage materials owing to their excellent hydrogen absorption properties.¹¹ Among them, the product of the decomposition of K₂[Zn(NH₂)₄]-8LiH was observed to fully re-hydrogenate within 30 seconds at 230 °C and 50 bar of H₂. This result is the fastest absorption reaction rate measured in amide-hydride systems to the best of our knowledge.^{11a} Unfortunately, most of the phases involved in the de/re-hydrogenation paths remain unknowns, hindering the full understanding of reaction mechanism. In this work, *in situ* SR-PXD, FTIR and volumetric techniques were combined to investigate the reaction mechanisms of hydrogen desorption and absorption in the K₂[Zn(NH₂)₄]-8LiH system.

Experimental Details

$K_2[Zn(NH_2)_4]$ is synthesized under supercritical ammonia in a custom-built austenitic nickel-chromium-based super-alloy autoclave, from a mixture of Zn (Alfa-Aesar, 99.9%) and K (Aldrich, 99.5%) in the ratio of 1:2 under 300 °C and 150 bar of NH_3 .¹² K_2ZnH_4 is prepared according to the literature¹³ by heating a mixture of KH (Aldrich, 30 wt% dispersion in mineral oil, it is washed 6 times by cyclohexane and then dried under vacuum for 12h before using) and Zn powder in the ratio of 2:1 under 100 bar of H_2 and 380 °C for 6h. LiH is purchased from Alfa-Aesar with a purity higher than 97%. $LiNH_2$ (95% purity) is supplied by Strem. The mixtures of $K_2[Zn(NH_2)_4]$ -8LiH and $4LiNH_2$ -4LiH- K_2ZnH_4 are ball milled for 12 h under 50 bar of H_2 at 250 rpm with a Fritsch Pulverisette 6 classic line planetary mill, using a ball to powder ratio of ca. 40:1. Handling and milling are carried out in an MBraun Argon glovebox with water and oxygen levels below 10 ppm.

De/re-hydrogenation experiments are performed using a Sievert's type apparatus (Hera, Quebec, Canada). Desorption processes are investigated heating the samples from room temperature (RT) to 400 °C under vacuum (0.001bar) with a heating rate of 3 °C/min. The absorption processes are performed heating the samples from RT to 300 °C under 50 bar of H_2 using a heating rate of 3 °C/min.

In situ SR-PXD investigations were performed in the beamline P.02.1 at the PETRA III synchrotron facility of DESY, Germany. The used wavelength (λ) is 0.20775 Å and the pattern is acquired at a plate image detector with 2048*2048 pixel of 200*200 μm^2 each; the distance from sample to detector is about 1460 mm. The samples are charged in sapphire capillaries and mounted in a specially designed cell for *in situ* SR-PXD measurements.¹⁴ The *in-situ* de/re-hydrogenation has been conducted heating the sample from RT to 400 and 300 °C with a heating

rate of 2 °C/min, under vacuum and 80 bar of H₂, respectively. The software FIT2D is employed to integrate the 2-dimensional diffraction images.¹⁵ Quantitative analyses on the diffraction data are performed via Rietveld method using the software MAUD.¹⁶ The composition of the solid solution $K(NH_2)_xH_{(1-x)}$ ($x < 0.05$) at 357 °C is calculated using the linear thermal expansion coefficients according to the Vegard's law based on previously reported data for $T = 20$ °C and $T = 270$ °C.¹⁷ The cell parameter at $T = 357$ °C (used for the final calculation) is determined by Rietveld refinement of the corresponding diffraction pattern. The corresponding Rietveld fits of the $K_2[Zn(NH_2)_4] \cdot 8LiH$ sample at different dehydrogenation states are shown in Figures S1 to S4 (Supporting information).

Bruker FTIR equipment (Model Tensor 27) is used to record the FTIR spectra. Samples are grinded with anhydrous KBr. The weight ratio of sample to KBr is about 1:30. Spectra are recorded at RT in the range of 400-4000 cm⁻¹ with a resolution of 4 cm⁻¹.

Results and discussion

Figure 1. SR-PXD analysis of dehydrogenation of the $K_2[Zn(NH_2)_4] \cdot 8LiH$. The sample was heated under vacuum from RT to 400 °C (heating rate of 2 °C/min, $\lambda = 0.20775 \text{ \AA}$).

In-situ SR-PXD is a powerful tool for investigating the reaction mechanism and structural transformation during hydrogen absorption and desorption. The 3D plot of the SR-PXD patterns *vs* temperatures of the desorption reaction of $\text{K}_2[\text{Zn}(\text{NH}_2)_4]\cdot 8\text{LiH}$ is shown in Figure 1. The starting diffraction pattern collected at RT shows the reflection peaks of K_2ZnH_4 ,¹⁸ LiNH_2 and LiH , which could be due to the fact that $\text{K}_2[\text{Zn}(\text{NH}_2)_4]$ reacts with 8LiH forming K_2ZnH_4 , LiNH_2 along with LiH already during milling. Upon heating, at ca. 280 °C, the intensity of the peaks belonging to K_2ZnH_4 increases before disappearing at ca. 290 °C. This event is accompanied by the appearance of K_3ZnH_5 ,¹⁹ which is stable up to 340 °C. With the disappearance of K_3ZnH_5 , the signal of $\text{K}(\text{NH}_2)_x\text{H}_{(1-x)}$ ($x < 0.05$) is arising. The K-based solid solution is most likely a product of the reaction between K_3ZnH_5 and LiNH_2 . Increasing the temperature furtherly the formation of Li_2NH and LiZn_{13} are observed. The diffraction pattern of the sample at 400 °C does not show the presence of any known K-containing phases. In order to understand if such phases are in a molten and/or in an amorphous state, the sample is cooled down to RT with a rate of 20 °C/min (Figure 2). Upon cooling down, at around 300 °C the diffraction reflections of KH appear. These results well match with our previous findings.^{11a}

Figure 2. SR-PXD patterns of dehydrogenation of the $K_2[Zn(NH_2)_4] \cdot 8LiH$, it was cooled down from 400 °C to RT (cooling rate of 20 °C/min, $\lambda=0.20775 \text{ \AA}$).

In order to better visualize the events taking place in the temperature range between 249 and 382 °C a contour plot of the *in situ* SR-PXD analysis is reported in Figure 3. This figure clearly shows that the dehydrogenation of $K_2[Zn(NH_2)_4] \cdot 8LiH$ is a multi-step process. In the first step LiH, $LiNH_2$ and K_2ZnH_4 react with each other by forming K_3ZnH_5 and Li_2NH . In the second step K_3ZnH_5 and Li_2NH react together to form an $K(NH_2)_xH_{(1-x)}$ ($x < 0.05$) solid solution and $LiZn_{13}$. Finally, at around 370 °C the diffraction peaks of the $K(NH_2)_xH_{(1-x)}$ solid solution disappear. As discussed above, after milling $K_2[Zn(NH_2)_4] \cdot 8LiH$, the $K_2[Zn(NH_2)_4]$ seems to disappear and it is replaced by $LiNH_2$ and K_2ZnH_4 . A possible explanation is that $K_2[Zn(NH_2)_4]$ reacts with LiH during milling to produce $LiNH_2$, K_2ZnH_4 and LiH according to reaction 3:

Figure 3. Dehydrogenation contour plot of the $K_2[Zn(NH_2)_4]$ -8LiH at the temperature range between 249 and 382 °C (heating rate of 2 °C/min, $\lambda=0.20775$ Å).

To verify this possibility, de/re-hydrogenation volumetric analyses of the reference material $4LiNH_2$ - $4LiH$ - K_2ZnH_4 and of $K_2[Zn(NH_2)_4]$ -8LiH are shown in Figure 4. The dehydrogenation reactions of both materials occur in three steps which look alike. The first desorption step starts at around 120 °C and finishes at ca. 290 °C after releasing 2.6 wt% of H_2 (equiv. to 3.54 mol H_2 per mol material); during the second step, between 290 and 350 °C, the sample releases a further 0.6 wt% of H_2 and through the final step an overall gravimetric loss of 4.1 wt% of H_2 is achieved at 400 °C. During the re-hydrogenation, about 0.6 wt% of H_2 is absorbed at temperatures below 210 °C. At ca 220 °C, most of the hydrogen (>60% of the total hydrogen) is re-hydrogenated within 30 seconds, as described in our previous publication, which is the fastest re-hydrogenation rate so far observed in an amide-hydride system.^{11a} The volumetric curves reported in Figure 4 for the system $4LiNH_2$ - $4LiH$ - K_2ZnH_4 trace out those of the $K_2[Zn(NH_2)_4]$ -8LiH, thus confirming the conversion of $K_2[Zn(NH_2)_4]$ -8LiH into $4LiNH_2$ - $4LiH$ - K_2ZnH_4 during milling. The observed

dehydrogenation reaction steps also do well agree with the multistep desorption process observed in the *in situ* SR-PXD analysis reported in Figures 1 and 3

Figure 4. Volumetric de/re-hydrogenation curves of the $K_2[Zn(NH_2)_4]-8LiH$ and the $4LiNH_2-4LiH-K_2ZnH_4$, heated from RT to 400 and 300 °C with a heating rate of 3 °C/min for dehydrogenation and re-hydrogenation, respectively. Dehydrogenation was investigated under vacuum, and re-hydrogenation was carried out at 50 bar of H_2 . “K+Number” meaning samples of $K_2[Zn(NH_2)_4]-8LiH$ at different de/re-hydrogenation status.

The re-hydrogenation of $K_2[Zn(NH_2)_4]-8LiH$ is also investigated via SR-PXD technique (Figure 5). At RT the diffraction peaks of KH, Li_2NH and $LiZn_{13}$ are visible. Increasing the temperature to ca. 220 °C, K_3ZnH_5 quickly appears and, at around 250 °C disappears. Finally, above 260 °C, $LiNH_2$, K_2ZnH_4 , LiH are formed, whereas $LiZn_{13}$ seems stable under these reaction conditions.

Figure 5. Re-hydrogenation SR-PXD patterns of the $K_2[Zn(NH_2)_4]-8LiH$. It was heated under 50 bar of H_2 from RT to 300 °C (heating rate of 2 °C/min, $\lambda=0.20775 \text{ \AA}$).

To better visualize the events involved in the re-hydrogenation of the $K_2[Zn(NH_2)_4]-8LiH$, a specific range of temperatures between 209 and 276 °C belonging to the analysis reported in Figure 5, is shown in Figure 6. K_3ZnH_5 forms at ca. 220 °C along with the disappearance of KH. In Figure 4, a sudden increase of the hydrogenation rates is observed at ca. 220 °C for both $K_2[Zn(NH_2)_4]-8LiH$ and the reference material. This temperature matches well with that of the formation of K_3ZnH_5 . Consequently, the formation of K_3ZnH_5 is responsible for the extremely fast hydrogenation step observed in Figure 4. The absorption jump from K6 to K7 (“K+Number” marked in Figure 4, meaning samples of $K_2[Zn(NH_2)_4]-8LiH$ at different de/re-hydrogenation states), could be due to the hydrogenation of K_3ZnH_5 to K_2ZnH_4 . Meanwhile, K_3ZnH_5 works on the hydrogenation of Li_2NH , which meaning reaction (4) occurs together with reaction 1.

The continuous hydrogenation from K7 to K8 comes from the absorption of the excess Li_2NH ; this phenomenon is observed also in the reference material. The absorption jump from K8 to K9

could be due to the molten and the asymmetry of Li_2NH in the dehydrogenated sample as discussed in our previous work.^{11a} This finding is confirmed by the FTIR results which are presented in the following text. Finally, K_2ZnH_4 , LiNH_2 , LiZn_{13} and LiH are observed in the completely absorbed sample.

Figure 6. Re-hydrogenation contour plot of the $\text{K}_2[\text{Zn}(\text{NH}_2)_4]\cdot 8\text{LiH}$ at the temperature range between 209 and 276 °C (heating rate of 2 °C/min, $\lambda=0.20775 \text{ \AA}$).

Different samples of $\text{K}_2[\text{Zn}(\text{NH}_2)_4]\cdot 8\text{LiH}$ at different steps of dehydrogenation/re-hydrogenation are compared to understand its reversibility (Figure 7). As previously mentioned, part of the LiZn_{13} is present as a side product in the material hydrogenated at 300 °C, similarly to what observed in the SR-PXD pattern of the sample dehydrogenated at 110 °C (Figure x). In addition, due to its lower decomposition/melting temperature KH cannot be observed at 400 °C. This further confirms that $\text{K}_2[\text{Zn}(\text{NH}_2)_4]\cdot 8\text{LiH}$ changes to $4\text{LiNH}_2\cdot 4\text{LiH}\cdot \text{K}_2\text{ZnH}_4$ during ball milling, and $4\text{LiNH}_2\cdot 4\text{LiH}\cdot \text{K}_2\text{ZnH}_4$ is almost fully reversible.

FTIR is a technique widely employed to characterize materials which are in amorphous or nanostructured state.²⁰ As shown in Figure 4, the first five numbers (from K1 to K5) refer to the

dehydrogenation process, and the last four numbers (from K6 to K9) relate to the hydrogenation process. In addition, the IR spectrum of as prepared $K_2[Zn(NH_2)_4]$, named K0 is reported as a reference too.

Figure 7. SR-PXD patterns of the $K_2[Zn(NH_2)_4]$ -8LiH at different status: before dehydrogenation at 110 °C, full dehydrogenation at 400 °C and full absorption at 300 °C ($\lambda=0.20775$ Å).

Figure 8 summarizes the FTIR spectra of these samples collected at different dehydrogenation states. The stretching bands (3674 , 3313 , and 3258 cm^{-1}) and bending bands (1564 and 1538 cm^{-1}) of $LiNH_2$ ²¹ are visible in K1, K2 and K3. The peak at 1402 cm^{-1} belonging to K_2ZnH_4 ^{18, 22} is also detected in K1, K2 and K3. From K2, the characteristic peak of Li_2NH at 3180 cm^{-1} can be observed and it is visible in all the samples desorbed furtherly. Finally, the absorption bands of Li_2NH , K_3ZnH_5 (1445 and 1361 cm^{-1})¹⁹ along with those of $LiZn_{13}$ (1484 cm^{-1})²³ are observed in K5. Based on these FTIR results, it can be concluded likely that: $K_2[Zn(NH_2)_4]$ reacts with LiH changing to $LiNH_2$ and K_2ZnH_4 during ball milling; after heating $LiNH_2$ interacts with K_2ZnH_4 and LiH forming Li_2NH and K_3ZnH_5 ; Finally, Li_2NH , $LiZn_{13}$ and some of K_3ZnH_5 are present in the fully desorbed sample. These results well support the SR-PXD results of Figures 1 and 3.

Figure 8. FTIR spectra of the $K_2[Zn(NH_2)_4]-8LiH$ at different dehydrogenation stages (labels denote the sampling points in the Figure 4), as well as the prepared $K_2[Zn(NH_2)_4]$ (K0).

The FTIR spectra of the re-hydrogenated samples are plotted in Figure 9. The presence of $LiNH_2$ (3674 , 1564 and 1538 cm^{-1}) along with Li_2NH (3180 cm^{-1}), K_3ZnH_5 (1445 and 1361 cm^{-1}) and little of K_2ZnH_4 (1404 cm^{-1}) are visible in the spectrum of K6. This is slightly different from the spectrum of K5. The peak belonging to $LiZn_{13}$ (1484 cm^{-1}) is weaker in K6. Similarly to what observed in the SR-PXD analysis of Figures 5 and 6, $LiZn_{13}$, Li_2NH and KH interact with H_2 forming K_3ZnH_5 and $LiNH_2$. In this spectrum, the intensities of the absorption bands belonging to $LiNH_2$ and K_2ZnH_4 in K7 are much higher than that in K6, and the signals of K_3ZnH_5 disappears. Increasing the hydrogenation degree to K8 and K9, bands at 3674 , 1404 , 3608 , 3562 and 3498 cm^{-1} are visible. This suggests that $K_2[Zn(NH_2)_4]$ (3608 , 3562 and 3498 cm^{-1}) is present in K8 and K9. This could be due to the interaction of $LiNH_2$ with K_2ZnH_4 producing amorphous $K_2[Zn(NH_2)_4]$.

Figure 9. FTIR spectra of the $K_2[Zn(NH_2)_4]-8LiH$ at different re-hydrogenation stages (labels denote the sampling points in the Figure 4).

Conclusion

The reaction mechanism of $K_2[Zn(NH_2)_4]-8LiH$ was investigated by combination of *in situ* SR-PXD, FTIR and volumetric release techniques. $K_2[Zn(NH_2)_4]$ reacts with LiH producing K_2ZnH_4 and $LiNH_2$ already during ball milling, and $K_2[Zn(NH_2)_4]-8LiH$ converts to $4LiNH_2-4LiH-K_2ZnH_4$. During heating, $4LiNH_2-4LiH-K_2ZnH_4$ releases hydrogen in a three-steps reaction: firstly, $LiNH_2$, LiH and K_2ZnH_4 react with each other forming K_3ZnH_5 and Li_2NH at ca. 265 °C; and then, at around 330 °C, K_3ZnH_5 interacts with Li_2NH forming a $K(NH_2)_xH_{(1-x)}$ solid solution along with $LiZn_{13}$; finally, above 380 °C the dehydrogenation sample is composed by $LiZn_{13}$, Li_2NH and K-based species in a molten state. After cooling down, KH, Li_2NH and $LiZn_{13}$ are visible. During absorption, KH partially reacts with $LiZn_{13}$ and H_2 forming K_3ZnH_5 . The reaction continues through the hydrogenation of K_3ZnH_5 to K_2ZnH_4 which enormously increases the hydrogenation rate of Li_2NH . After re-hydrogenation, the sample converts back to $4LiNH_2-4LiH-K_2ZnH_4$ plus a small amount of side product.

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