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Improvement of hydrogen desorption kinetics in the LiH–NH_3 system by addition of KH†

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It was found that, when a little amount of KH (5 mol%) was added in the LiH–NH_3 hydrogen storage system, the hydrogen desorption kinetics of this system at 100 °C was drastically improved by the KH "pseudo-catalytic" effect.

The development of high performance hydrogen storage materials is an important issue to establish suitable transportation technologies for a clean and sustainable society. As compared to approaches such as compression and liquefaction, solid-state hydrogen storage, especially for light elements containing systems, is able to realize high gravimetric and volumetric hydrogen densities.[1] Among them, ammonia (NH_3) would be recognized as one of the attractive hydrogen storage and transportation materials because it has a high hydrogen storage capacity of 17.8 mass% and is easily liquefied by compression under 1.0 MPa pressure at room temperature.[2–4] However, the practical application of NH_3 itself as a hydrogen storage material is limited, because a high temperature over 400 °C and a suitable catalyst are required to decompose NH_3 into hydrogen (H_2) and nitrogen (N_2).[5] Here, as promising hydrogen storage materials, metal–N–H systems are studied all over the world.[6–8] In these systems, ammonia (NH_3) is an important intermediate for the elemental reaction described as follows,[8]

$$\mathrm{LiH} + \mathrm{NH_3} \leftrightarrow \mathrm{LiNH_2} + \mathrm{H_2}. \qquad (1)$$

This reaction can be regarded as a hydrogen storage system.[2] The system has a high hydrogen capacity of 8.1 mass% and a suitable enthalpy change $\Delta H = 50 \pm 9$ kJ mol H_2^{-1} for practical use.[2] The hydrogen desorption reaction can proceed even at room temperature due to hydrolysis-type exothermic reaction. The reverse reaction from lithium amide ($LiNH_2$) into lithium hydride (LiH) and NH_3 occurred below 300 °C by removing NH_3 under 0.5 MPa of H_2 partial pressure flow conditions.[2] Thus, the lithium hydride (LiH) and NH_3 system should be recognized as a promising recyclable hydrogen storage system.

Recently, it was found that the reactivity of alkali metal hydrides with NH_3 is better in the order of Li < Na < K.[2] Although the KH–NH_3 system exhibits the best reactivity for both the hydrogen desorption and absorption reactions, the hydrogen capacity of the KH–NH_3 system is much less than that of the LiH–NH_3 system. An improvement of the hydrogen storage kinetics for the LiH–NH_3 system with higher H_2 capacity is necessary. In addition, remarkable enhancement in the kinetics of dehydrogenation was achieved by introducing 3 mol% KH into the $Mg(NH_2)_2/2LiH$ system, in which the KH plays important roles.[7]

In this study, the hydrogen desorption properties for the reactions of the alkali metal hydrides (LiH, KH, and the KH-added LiH) and NH_3 systems (NH_3: 0.5 MPa, NH_3/MH = 1 mol/mol) at room temperature and 100 °C were systematically investigated to design the system with better kinetic properties.

Fig. 1 shows the hydrogen generation profile of the reaction between MH (KH, the KH-added LiH, and LiH) and NH_3 at room temperature and 100 °C. The reaction yields for KH, the KH-added LiH, and LiH at room temperature for 60 minutes were 89.9, 32.5, and 31.3%, respectively, indicating that the reaction kinetics of KH was better than LiH. Actually, these results are consistent with the previous reports.[2] The KH-added

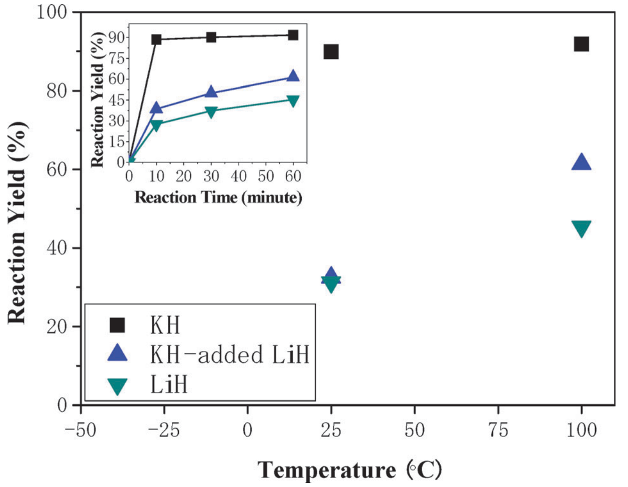

Fig. 1 Hydrogen generation profile for reactions between MH (KH, the KH-added LiH, and LiH) and NH_3 at room temperature and 100 °C for 60 minutes. Inset of the figure is the hydrogen generation profile for reactions at 100 °C for 10, 30, and 60 minutes.

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LiH showed a little faster reactivity than that of LiH at room temperature due to superior reactivity of the addition of 5 mol% KH. The reaction yields at 100 °C were 91.8%, 61.3%, and 45.4% for KH, the KH-added LiH, and LiH, respectively. In the case of the KH-added LiH, if KH has no catalytic effect, the expected yield should be calculated as 47.7% (= 91.8% × 0.05 + 45.4% × 0.95). However, the reactivity was enhanced due to the increase in temperature and it was about 30% and 13.6% higher than that at room temperature and the calculated value, respectively. The increase of yields of the KH-added LiH was significant, compared with the variation of other samples.

The inset of Fig. 1 also shows the reaction yield of the three kinds of hydride samples with NH_3 at 100 °C as a function of the reaction time. Although all the samples showed the increases of the reaction yield with the time, the KH-added LiH showed the larger increase than others. After the reaction for 10 minutes, the reaction yield for the KH-added LiH was a little more than that of LiH. However, the reaction yield of the KH-added LiH reached more than 60%, which was closer to that of KH even though the 95% sample corresponds to LiH. From the results, it was confirmed that the reaction yield at 100 °C was clearly improved when a little amount of KH was added in the LiH–NH_3 hydrogen storage system.

To understand the improving mechanism of hydrogen desorption kinetics for the KH-added LiH–NH_3 system, structural changes due to the reaction were investigated. The XRD patterns of the products formed in the reactions of MH (KH, the KH-added LiH, and LiH) with NH_3 at 100 °C for 60 minutes are shown in Fig. 2. The XRD patterns of each hydride and amide available in the database are shown as reference. After the reaction with NH_3, the diffraction peaks of the corresponding amide phase were observed for both hydrides. For the product obtained by the reactions of the KH-added LiH with NH_3, the diffraction peaks of $LiNH_2$ and KH were observed, however there were no diffraction peaks of KNH_2, indicating that the added KH was not consumed during the reaction. On the other hand, compared with the just ball-milled KH-added LiH (Fig. 2d), the ratio of diffraction intensity of LiH to KH decreases largely after reaction with NH_3 at 100 °C for 60 minutes. This indicates that some of LiH was consumed during the reaction to form amide.

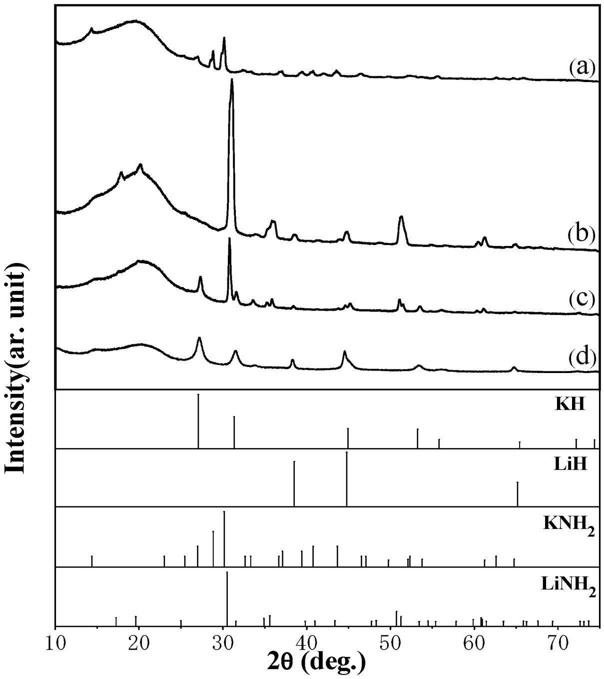

Fig. 2 XRD patterns of products by reactions of ball-milled KH (a), LiH (b), and the KH-added LiH (c) with NH_3 (0.5 MPa, NH_3/MH = 1 mol/mol) at 100 °C for 60 minutes and the XRD patterns of the just ball-milled 5 mol% KH-added LiH (d).

In the previous reports, it has been proved that the reactivity of KH with NH_3 is much better than that of LiH.[2] Thus, when KH and LiH coexist in an NH_3 atmosphere, KH would preferentially react with NH_3 by reaction (2).

$$KH + LiH + NH_3 \rightarrow KNH_2 + LiH + H_2 \qquad (2)$$

Here, the enthalpy change ΔH for the reaction of KNH_2 and LiH to form $LiNH_2$ and KH expressed by eqn (3) is -17.8 kJ mol H_2^{-1}, considering that the standard enthalpies of formation ΔH^0 of the compounds are -128.9 (KNH_2), -90.5 (LiH), -57.7 (KH), and -179.5 ($LiNH_2$).[9]

$$KNH_2 + LiH \rightarrow KH + LiNH_2 \qquad (3)$$

This ΔH is negative, suggesting that this reaction can easily proceed in an exothermic manner. Actually, by ball-milling a mixture of KNH_2 and LiH with a 1/1 molar ratio for 2 hours under a 1.0 MPa H_2 atmosphere, the diffraction peaks corresponding to KH and $LiNH_2$ were observed from the XRD measurement (Fig. S1a, ESI†). The N–H stretching modes due to $LiNH_2$ were observed from the IR measurement (Fig. S2, ESI†). This result indicates that reaction (3) proceeds under the mechanochemical conditions. To confirm whether reaction (3) can proceed by heating to 100 °C or not, the hand-milled KNH_2 and LiH with a 1/1 molar ratio was prepared and heated at 100 °C for 60 minutes. Fig. S1b and c (ESI†) show the XRD patterns after hand milling and heat treatment. In the XRD pattern of the hand-milled mixture, there are only the diffraction peaks of KNH_2 and LiH, suggesting that the reaction cannot proceed by the hand-milling at the room temperature. After heating to 100 °C, KNH_2 and LiH phases were almost changed to KH and $LiNH_2$ (see Fig. S1c, ESI†), indicating that the heating to at least 100 °C is necessary to induce reaction (3).

On the basis of the above experiments, the mechanism of the improvement of hydrogen desorption kinetics for the KH-added LiH–NH_3 system was proposed as the following reaction (eqn (4)).

$$KH + NH_3 \rightarrow KNH_2 + H_2$$

$$KNH_2 + LiH \rightarrow KH + LiNH_2$$

$$1KH + 20LiH + 21NH_3 \rightarrow 1KNH_2 + 20LiNH_2 + 21H_2 \qquad (4)$$

In the KH-added LiH–NH_3 system, KH can immediately react with NH_3 to form KNH_2 and release H_2. Then, at 100 °C, the generated KNH_2 reacts with LiH to form $LiNH_2$ by the solid–solid reaction, resulting in recovery of KH. Therefore, these two reactions can be regarded as cyclic reaction, which would continue until LiH is exhausted. The reason for the kinetic improvement of the hydrogen desorption reaction on the LiH–NH_3 system is that KH with

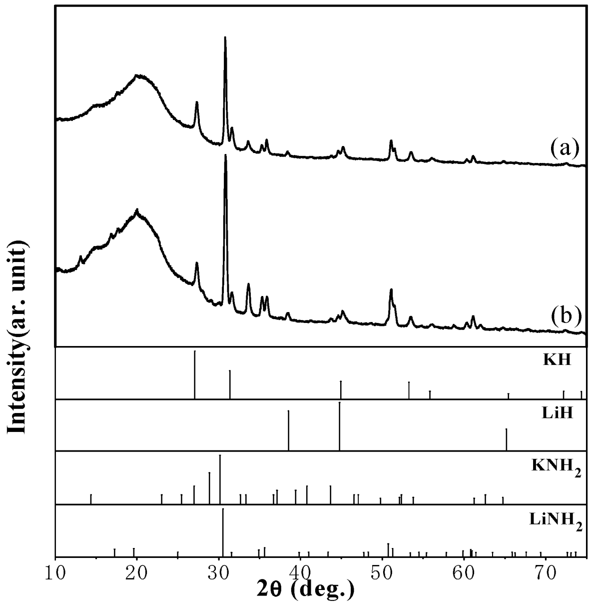

Fig. 3 XRD patterns of products by reactions of the 5 mol% KH-added LiH with NH_3 (0.5 MPa, NH_3/MH = 1 mol/mol) under different operations: (a) reacting at 100 °C for 60 minutes, (b) reacting at 100 °C for 60 minutes and then at room temperature for 15 minutes.

superior reactivity to NH_3 can accelerate the formation of $LiNH_2$ by the "*pseudo-catalytic*" effect. To confirm this mechanism, the following two experiments were performed. After the reaction between the KH-added LiH and NH_3 at 100 °C for 60 minutes, (1) the gas inside the vessel was evacuated immediately, (2) gas evacuation was carried out after decreasing the temperature to room temperature and keeping for 15 minutes. The products obtained by two different operations were identified by XRD. As shown in Fig. 3, for the products in the first experiment, there were no diffraction peaks corresponding to KNH_2 (Fig. 3(a)). On the other hand, obvious diffraction peaks of KNH_2 were observed for the products in the second experiment (Fig. 3(b)), where the characteristic peaks were located at 30.2 and 28.8°. These results indicate that reaction (3) can proceed at 100 °C even though it is stopped at room temperature. As a result, it is expected that KNH_2 generated by the reaction between KH and NH_3 remains at room temperature. Thus, the above experimental facts are consistent with the proposed mechanism. As shown in Fig. 3(b), new diffraction peaks at 12.8°, 16.5°, and 33.4° are identified as the $Li_3K(NH_2)_4$ ternary amide, indicating that partially formed KNH_2 reacted with $LiNH_2$. It is worthy to note that the ternary amide may also play important roles as the intermediate state in the reaction process, which should need further investigation.

By considering the present and previous studies, the following remarks can be made on the mechanism about the improvement of the dehydrogenation kinetics in the KH-added Li–Mg–N–H system.[7] It is well known that NH_3 is an important intermediate for the dehydrogenation of the Li–Mg–N–H system.[8] In the KH-added $Mg(NH_2)_2$/2LiH system, KH can immediately react with NH_3 from the decomposition of $Mg(NH_2)_2$ to form KNH_2 and release H_2 under the heat-treatment conditions. Then, under these conditions, the generated KNH_2 reacts with LiH to regenerate KH. These two reactions can be regarded as cyclic reaction, which would continue until LiH is exhausted. Therefore, a possible reason for the improvement of dehydrogenation kinetics in the KH-added Li–Mg–N–H system is that KH with superior reactivity to NH_3 can accelerate the interaction between LiH and NH_3 by the "*pseudo-catalytic*" effect as mentioned above.

In conclusion, the hydrogen desorption kinetics of the LiH–NH_3 system was clearly improved by addition of a little amount of KH and heating up to 100 °C. The reason for the improvement is that KH with superior reactivity to NH_3 can play the role of a catalyst to immediately form $LiNH_2$ as the reaction product by solid–solid reaction indicated in eqn (3).

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