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The ternary amide $KLi_3(NH_2)_4$: an important intermediate in the potassium compounds-added Li–N–H systems

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In this paper, the KH-added LiH–NH_3, KH-added LiH–$LiNH_2$, KH-added $LiNH_2$, and KNH_2-added $LiNH_2$ systems were systematically investigated. It was found that the ternary amide $KLi_3(NH_2)_4$ was an important intermediate that was inclined to be formed in the dehydrogenation and hydrogenation processes of the potassium compounds-added Li–N–H system. Further investigations revealed that both the solid state reaction of $LiNH_2$ with KNH_2 and the solid state reaction of $LiNH_2$ with KH under mechanical ball milling or heat treatment condition will lead to the formation of the $KLi_3(NH_2)_4$ ternary amide. Moreover, the ternary amide $KLi_3(NH_2)_4$ single phase was successfully synthesized by the mechanical ball milling and its ammonia desorption and hydrogenation properties were investigated. It was observed that the ammonia desorption rate of $KLi_3(NH_2)_4$ was faster than that of $LiNH_2$ and the hydrogen absorption kinetic of $KLi_3(NH_2)_4$ was between those of KNH_2 and $LiNH_2$.

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1. Introduction

The safe and efficient storage of hydrogen represents one of the most significant technological challenges to the widespread adoption of a hydrogen-based energy economy. Chemical hydrogen storage materials, due to their high hydrogen contents, are expected as potential hydrogen sources for fuel cells. Among them, nitrogen- and boron-based compounds, such as $LiNH_2$-LiH, N_2H_4, and NH_3BH_3 have attracted much attention.[1–3]

Metal–N–H hydrogen storage system has been investigated over the world since it is first reported by Chen *et al* in 2002, who indicates that Li_3N reversibly stores over 10 mass% hydrogen in the two consecutive reactions (reaction 1).[4]

$$Li_3N + 2H_2 \leftrightarrow Li_2NH + LiH + H_2 \leftrightarrow LiNH_2 + 2LiH \qquad (1).$$

Later, the lithium amide ($LiNH_2$)-lithium hydride (LiH) system is also proposed as a sound solid-state storage system, as it offers relatively high gravimetric storage capacity (approximately 6.5 weight percent hydrogen released from reaction 2).[5–7]

$$Li_2NH + H_2 \leftrightarrow LiNH_2 + 2LiH \qquad (2).$$

Whilst this system exhibits a relatively advantageous set of target thermodynamic parameters, the temperatures required for the dehydrogenation of lithium amide and the hydrogenation of lithium imide are still too high for the application of this system as a commercial hydrogen store. Various efforts have been devoted to improve its hydrogen absorption and desorption kinetics.[8–14] It has been demonstrated recently that potassium compounds, including potassium hydride and potassium amide, possess superior catalytic effects on the improvement of hydrogenation/dehydrogenation kinetics of metal–N–H system.[8,9] The hydrogen desorption/absorption kinetics for the LiH-NH_3 system can be improved drastically by addition of 5 mol% KH.[8] In addition, remarkable enhancement in the kinetics of dehydrogenation was achieved by introducing 3 mol% KH into the $Mg(NH_2)_2$/2LiH system, of which a ternary amide phase $KLi_x(NH_2)_y$ may play important roles in the dehydrogenation process.[9] Such an improvement was further confirmed recently by introducing KH into the $2LiNH_2$–MgH_2 system.[10] Unfortunately, the improving mechanisms of hydrogen storage performance for the potassium-added metal–N–H system have not been clarified completely so far. The investigation on potassium intermediate compounds would provide valuable information for understanding the reaction mechanisms of potassium-catalyzed metal–N–H hydrogen storage system.

In present work, the KH-added LiH–NH_3, KH-added LiH–$LiNH_2$, KH-added $LiNH_2$, and KNH_2-added $LiNH_2$ systems were systematically investigated. It was found that the ternary amide $KLi_3(NH_2)_4$ was an important intermediate that was inclined to be formed in the KH or KNH_2-added Li–N–H system. The possible formation mechanism was clarified on the basis of experimental results. Moreover, the ternary amide $KLi_3(NH_2)_4$ single phase was successfully synthesized by the mechanical ball milling and its ammonia desorption and hydrogenation properties were investigated.

2. Experimental Procedure

2.1 Sample preparation

Lithium hydride (LiH) (98%, J&K Chemical Ltd., China), lithium amide ($LiNH_2$) (95%, Aldrich), and NH_3 (99.999%) were used for the following experiments. As additives, potassium hydride (KH) (99.5%, Aldrich) and potassium amide (KNH_2) (synthesized from the KH and NH_3) were chosen. The additives were dispersed into the samples by the following mechanical ball-milling method. A weighed amount of LiH or $LiNH_2$, together with 30 steel balls (6 mm in diameter) and each additive, was put into a milling vessel made of steel of which the inner volume is about 50 cm^3, where the amount of additive was 5 mol% to 300 mg of LiH or $LiNH_2$. And then, the ball milling was performed under 0.1 MPa argon (>99.999%) atmosphere for 2 hours using a planetary ball mill apparatus (QM-3SP4). The ball-to-powder weight ratio was about 90:1. To minimize the temperature increment of the samples, the milling process was paused for 30 minutes every hour of milling. The hand-milled samples were obtained with a pestle in an agate mortar and the powdering time was about 30 minutes. All the samples were handled in a Ar-filled (>99.999%) glove box (Mikrouna, China) equipped with a circulative purification system, in which the typical H_2O/O_2 levels are below 0.1 ppm.

2.2 Experimental techniques

The reactions of KH-added LiH with ammonia were performed as follows. A weighed amount of 5 mol% KH-added LiH was packed into a pressure vessel. NH_3 pressure of 0.5 MPa with a ratio of NH_3/MH (M=Li and K) = 1 mol/mol was introduced into the vessel at 100 °C. Ammonia (m/e =16) release of the just synthesized $KLi_3(NH_2)_4$ and raw $LiNH_2$ was monitored using mass spectroscopy (MS; Netzsch QMS 403 D Aëolos®, Germany) attached to a synchronous thermal analysis (DSC/DTA-TG; Netzsch STA 449 F3 Jupiter®). In the analysis, high purity argon (>99.999%) was flowed as a carrier gas, and the heating rate was fixed at 10 °C/min. The H_2 absorption conditions of MNH_2 (M=Li or K) were examined as follows. A weighed alkali amide (KNH_2, $LiNH_2$ or $KLi_3(NH_2)_4$) was treated at the designated temperature for 4 hours under 0.5 MPa of H_2 flow condition (open system) to examine the reactivity. The sample masses before and after the experiments were measured to calculate the reaction yield.

The structural characters of the produced composites were examined by X-ray diffraction (XRD) measurement (AXS D8 ADVANCE, Bruker, German) in Testing Center of Yangzhou University. The samples were covered by a polyimide sheet to protect the samples from an oxidation during measurements. The N–H stretching modes of the amides were characterized by Fourier Transform IR spectrometer (FTIR) (TENSOR 27, Bruker, Canada) in transmission mode. The test samples were prepared by cold pressing a mixture of power samples and potassium bromide (KBr) powder at a weight ratio of 1:20 to form a pellet. Each spectrum was created from 16 scans with a scan resolution of 4 cm^{-1}. The morphologies of the samples were characterized by a scanning electron microscope (S-4800II, Hitachi, Japan). X-ray photoelectron spectroscopy (XPS) analysis was performed on a PHI 5000 VersaProbe system using monochromatic Al Ka radiation (1486.6 eV) at an accelerating power of 15 kW.

3. Results and Discussion

3.1 The assignment of the $KLi_3(NH_2)_4$ ternary amide in the Li-N-H system

Ammonia (NH_3) is 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.[15,16] Reaction 3 was shown to be ultrafast and exothermic, leading to full consumption of NH_3 by LiH, and therefore this system has been recognized as a good Li–N–H hydrogen storage system.

$$LiH + NH_3 \rightarrow LiNH_2 + H_2 \qquad (3).$$

It was found that, when a little amount of KH (5 mol%) was added into the LiH-NH_3 hydrogen storage system, the hydrogen desorption kinetics of this system at 100 °C was drastically improved by the "pseudo-catalytic" effect of KH.[8] Studies on potassium intermediate compounds formed in the KH-added LiH–NH_3 system will contribute to understanding the improving mechanism of hydrogen desorption kinetics. Therefore, the following two experiments were designed and 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. 1, for the first experiment, the diffraction peaks of $LiNH_2$, LiH and KH were observed, but there were no diffraction peaks of KNH_2. A weak diffraction peak located at 33.4° was found, which was assigned to $KLi_3(NH_2)_4$. In contrast, new diffraction peaks at 12.8, 16.5, 33.4, 58.9 and 62.1° due to $KLi_3(NH_2)_4$ become obvious in the second experiment, which demonstrates that the ternary amide $KLi_3(NH_2)_4$ is formed in the KH-added LiH–NH_3 system during dehydrogenation. The interactions of LiH, $LiNH_2$, KH, and KNH_2, which is involved in the dehydrogenation process of KH-added LiH–NH_3 system may result in the formation of $KLi_3(NH_2)_4$ phase. This phenomenon implies that the $KLi_3(NH_2)_4$ ternary amide would be formed in the metal–N–H hydrogen storage system including KH, LiH and NH_3 and may play important roles in reaction process.

Since remarkable enhancement in the kinetics of dehydrogenation can be achieved by introducing 3 mol% KH into the $Mg(NH_2)_2$–2LiH system, hydrogen storage performances of the $LiNH_2$–LiH system may be improved by doping a little amount of KH. The interactions of KH with LiH–$LiNH_2$ system was also studied here. Structure examinations have been performed on the 3 mol% and 5 mol% KH-added LiH–$LiNH_2$ systems by means of XRD. It is noted that the diffraction peaks of KH almost can not be observed for the KH-added samples after ball milling (Fig. 2a and 2b). However, a new diffraction peak at 33.4° due to $KLi_3(NH_2)_4$ appeared. As shown in Fig. 2, for the 5 mol% KH-added LiH system after ball milling, the diffraction peaks of KH keep obvious and sharp in the XRD patterns of Fig. 2c, indicating that KH is difficult to become the amorphous form by ball milling for 2 hours. The diffraction peaks located at 33.5 and 56.1° in Fig. 2c are not due to $KLi_3(NH_2)_4$ phase, but due to Li_2O phase that is the contamination produced during ball milling. The results demonstrate that the $KLi_3(NH_2)_4$ ternary amide will be formed in the KH-added $LiNH_2$–LiH system after ball milling and the interaction of KH with $LiNH_2$ may result in the formation of this ternary amide.

3.2. The possible formation mechanism of the $KLi_3(NH_2)_4$ phase

With the aim of understanding the formation mechanism of $KLi_3(NH_2)_4$ phase in both KH-added LiH–NH_3 system and KH-added LiH–$LiNH_2$ system, the ball milled 5 mol% KH-added $LiNH_2$ and 5 mol% KNH_2-added $LiNH_2$ were characterized by XRD and FTIR. As shown in Fig. 3a and 3c, the diffraction peaks of KH and KNH_2 can not be observed after ball milling, but a new weak peak located at 33.4° due to $KLi_3(NH_2)_4$ phase appears for the both cases. To confirm the existence of $KLi_3(NH_2)_4$ phase in the KH-added or KNH_2-added $LiNH_2$ sample after ball milling, two additional XRD experiments were conducted, as shown in Fig. 3. The KH-added $LiNH_2$ and KNH_2-added $LiNH_2$ samples after ball milling were subjected to recrystallization at 200 °C under Ar atmosphere. After recrystallization, the diffraction peaks of $KLi_3(NH_2)_4$ phase, where are mainly located at 35.0, 33.4, 16.5 and 12.8°, become obvious and sharp (Fig. 3b and Fig. 3d), which confirmed the existence of the $KLi_3(NH_2)_4$ phase in both the samples of KH-added $LiNH_2$ and KNH_2-added $LiNH_2$ after ball milling. For the amide and imide compounds, the N–H stretching modes are active for the FTIR spectrum. As shown in Fig. S1, for the 5 mol% KH-added $LiNH_2$ after ball milling, only the N–H stretching vibration frequencies of $LiNH_2$ at 3312/3258 cm^{-1} are observed. Peaks due to the N–H stretching vibration frequency of $KLi_3(NH_2)_4$ may be overlapped by that of $LiNH_2$ (Fig. S1a). However, after treatment under Ar atmosphere at 200 °C for 4 hours, a new N–H stretching vibration frequency at 3298 cm^{-1} due to $KLi_3(NH_2)_4$ brings about (Fig. S1b), which indicates that KH reacts with $LiNH_2$ to produce $KLi_3(NH_2)_4$ ternary amide. In the case of the 5 mol% KNH_2-added $LiNH_2$ after ball milling, the new peak at 3298 cm^{-1} due to the N–H stretching vibration frequency of the $KLi_3(NH_2)_4$ ternary amide can be observed besides those of $LiNH_2$ at 3312/3258 cm^{-1} (Fig. S1c), indicating that KNH_2 reacts with $LiNH_2$ forming the $KLi_3(NH_2)_4$ under the ball milling condition. After treatment under Ar atmosphere at 200 °C for 4 hours, the N–H stretching vibration frequency at 3298 cm^{-1} becomes more obvious and sharper (Fig. S1d). The above discussion indicates that both KH and KNH_2 can interact with $LiNH_2$ to form $KLi_3(NH_2)_4$ under mechanical ball milling condition according to the reactions (4) and (5), respectively.

$$KH + 4LiNH_2 \rightarrow KLi_3(NH_2)_4 + LiH \quad (4).$$

$$KNH_2 + 3LiNH_2 \rightarrow KLi_3(NH_2)_4 \quad (5).$$

In addition, the interaction of KH or KNH_2 with $LiNH_2$ under heat-treatment condition was also investigated. Firstly, the sample of $KH/LiNH_2$ with molar ratio of 1/4 and the sample of $KNH_2/LiNH_2$ with molar ratio of 1/3 were hand-milled for 30 minutes in the glove box. Then, the two hand-milled samples were treated at 200 °C under 0.1 MPa Ar atmosphere for 48 hours. As shown in Fig. 4a and Fig. 4c, except the diffraction peaks of reactants, no new diffraction peaks appeared in the corresponding XRD patterns, indicating that both KH and KNH_2 do not react with $LiNH_2$ under hand-milled condition. However, obvious diffraction peaks of $KLi_3(NH_2)_4$ were observed for the two samples after heat-treatment (Fig. 4b and Fig. 4d), implying that both KH and KNH_2 can interact with $LiNH_2$ to form the $KLi_3(NH_2)_4$ under heat-treatment condition. To further prove the presence of proposed intermediate (the ternary amide $KLi_3(NH_2)_4$), the products after hand milled and heat-treatment were characterized by FTIR. As shown in fig S2, no new absorptions appeared for the two hand milled samples (Fig. S2a and Fig. S2c), but new absorption at 3298 cm^{-1} due to $KLi_3(NH_2)_4$ was clearly observed for the samples after heat-treatment (Fig. S2b and Fig. S2d), which consists with the characterization using XRD.

In this work, XPS was also applied to further prove the presence of the proposed intermediate (the ternary amide $KLi_3(NH_2)_4$). The Li 1s spectra for the $LiNH_2$, the just synthesized $KLi_3(NH_2)_4$ single phase and the potassium compound-added $LiNH_2$ systems were shown in Fig. S3. A XPS peak at 54.37 eV due to Li 1s of the $LiNH_2$ is observed, as shown in Fig. S3 (a). However, the position of the Li 1s peak for the just synthesized $KLi_3(NH_2)_4$ single phase is about 53.88 eV, which slightly shifts to lower binding energies (Fig. S3 (b)). It is known that the XPS shapes and positions associated with a particular metal ion depend on its valence state and electron densities between metal ions and donor atoms around. The difference of Li 1s spectra between $LiNH_2$ and $KLi_3(NH_2)_4$ may result from the different nature of the lithium-amino bond as well as different position of lithium ions that it occupies in the lattice[23,24]. For the products of $KH/LiNH_2$ with molar ratio of 1/4 after heat-treatment at 200 °C, the 1s binding energy of Li in the samples split into two peaks as 54.01 eV and 53.26 eV, which correspond to the Li 1s peaks of $LiNH_2$ and $KLi_3(NH_2)_4$, respectively (Fig. S3 (c)). For the products of $KNH_2/LiNH_2$ with molar ratio of 1/3 after heat-treatment at 200 °C, the 1s binding energy of Li in the samples split into two peaks as 54.25 eV and 53.26 eV, which corresponded to the Li 1s peaks of $LiNH_2$ and $KLi_3(NH_2)_4$, respectively (Fig. S3 (d)).

Therefore, we concluded that both KNH_2 and KH can interact with $LiNH_2$ to form $KLi_3(NH_2)_4$ under mechanical ball milling or heat-treatment condition. These phenomena suggest that $KLi_3(NH_2)_4$ is a relatively stable ternary amide compound that is inclined to be formed in the hydrogen storage system including KH (or KNH_2) and $LiNH_2$. Recently, Liu *et al* have also found the $KLi_3(NH_2)_4$ and proved that $KLi_3(NH_2)_4$ played important roles in the process of hydrogen storage for the potassium compounds-catalyzed metal–N–H systems.[22] They proposed that the interactions of $LiNH_2$, $Li_2Mg_2N_3H_3$, and KH will result in the formation of KLi_3 $(NH_2)_4$. In our opinion, the formation of $KLi_3(NH_2)_4$ under that condition may result from the interaction of $LiNH_2$ with KH or KNH_2.

Similarly, a few kinds of ternary amide or imide phases such as $Li_2Mg(NH_2)_2$, $Li_2Ca(NH_2)_2$, $K_2Mg(NH_2)_4$ and $KMg(NH)(NH_2)$ were found as intermediates playing very important roles in the hydrogen desorption of metal–N–H hydrogen storage system.[17–21] $KLi_3(NH_2)_4$ represents the first ternary amide phase found in the potassium compound-added Li–N–H system, which may play important roles in the process of hydrogen storage.

3.3. The properties of the $KLi_3(NH_2)_4$ ternary amide

Since $KLi_3(NH_2)_4$ is inclined to be formed in the potassium compounds-added Li–N–H system, it is necessary to investigate its properties for elucidating its possible roles in the process of hydrogen storage. The $KLi_3(NH_2)_4$ ternary amide single crystal was prepared by the reaction of ammonia with the metals in high-pressure autoclaves as early as 1984.[23] The ternary amide phase ($KLi_3(NH_2)_4$) was observed after ball milling the KNH_2-added $LiNH_2$, which indicates that the $KLi_3(NH_2)_4$ single phase can be produced using the mixture of KNH_2 and $LiNH_2$ with 1/3 molar ratio under the mechanochemical conditions, as expressed by reaction 4. The powder XRD profile for the synthesized $KLi_3(NH_2)_4$ phase by this new method was given in Fig. 5. Apparently, the profile obtained shows the single phase. In addition, it was reported recently that a similar ternary amide phase of $NaLi_3(NH_2)_4$ can also be prepared in the same way.[24,25]

SEM was performed to examine the morphologies and particle size of the samples. For the raw $LiNH_2$ and KNH_2, the particles are not very regular in shape and size. Especially for the KNH_2, the surface of KNH_2 is very coarser compared with $LiNH_2$, as shown in Fig. 4s (a and b). The particle size of the samples is about 1-10 um in average. However, after the $LiNH_2$ and KNH_2 reacted with each other in molar ratio of 1/3 by ball milling for 8h, the particles of the product (the $KLi_3(NH_2)_4$ single phase) become nearly-oval flakes and the size of most particles is more uniform and less than 500 nm (Fig. 4s (c)).

The just synthesized $KLi_3(NH_2)_4$ single phase was also characterized by FTIR. As shown in Fig. 6, the N–H stretching vibration frequency of $KLi_3(NH_2)_4$ at 3298 and

3253 cm^{-1} is about 14 and 5 cm^{-1} red-shifted from that of $LiNH_2$, respectively, which indicates that, compared with those of $LiNH_2$, the N-H bonds in $KLi_3(NH_2)_4$ are weakened. The weakened N–H bonds may facilitate further interaction of $KLi_3(NH_2)_4$ with LiH, which may result in the enhancement of dehydrogenation kinetics of the metal–N–H system. However, the N–H stretching vibration frequency of $KLi_3(NH_2)_4$ is about 40 and 46 cm^{-1} blue-shifted from those of KNH_2, respectively (Fig. 6), suggesting that N–H bonds of $KLi_3(NH_2)_4$ are much more stable than those of KNH_2.

Temperature-programmed desorption (TPD) of the $KLi_3(NH_2)_4$ single phase was performed to investigate its thermal decomposition properties. As shown in Fig. 7, decomposition curve of $LiNH_2$ was also involved for comparison. Clearly, the ammonia desorption behavior of $KLi_3(NH_2)_4$ is different from that of $LiNH_2$. For $KLi_3(NH_2)_4$, ammonia desorption shows three distinct peaks. The initial ammonia desorption peak around 92 °C with an onset temperature of approximate 65 °C is a broad peak, followed by a small peak at approximate 167 °C and a large broader peak at approximate 260 °C. It is noteworthy that the onset ammonia desorption temperature and all the peaks of ammonia desorption for $KLi_3(NH_2)_4$ is much lower than that of $LiNH_2$, indicating that the ammonia desorption rate of $KLi_3(NH_2)_4$ is faster than that of $LiNH_2$. It can be inferred that, if $KLi_3(NH_2)_4$ and $LiNH_2$ coexist under heat-treatment condition, $KLi_3(NH_2)_4$ is much easier to release ammonia.

The hydrogen absorption property of $KLi_3(NH_2)_4$ was also investigated and compared with those of KNH_2 and $LiNH_2$. All the amide samples were treated under H_2 flow condition at the designated temperature for 4 hours. The reaction yield on the hydrogen absorption reaction of ball milled KNH_2, $KLi_3(NH_2)_4$, and $LiNH_2$ for 4 hours at 100, 200, and 300 °C was shown in Fig. 8. The post-milled KNH_2 and $LiNH_2$ show the fastest and slowest reactivity, respectively, which is largely faster than that of the corresponding raw sample reported in the previous articles.[26] The $KLi_3(NH_2)_4$ shows a little faster reactivity at 100 °C than that of $LiNH_2$ because of the doping of KNH_2 with superior reactivity. The reaction yield at 200 °C is 97.2%, 36.7%, and 24.3% for KNH_2, $KLi_3(NH_2)_4$, and $LiNH_2$, respectively. Due to the increase of the heat-treatment temperature, the increases of reaction yield, compared with that at

100 °C, are 11.4%, 31.5%, and 23.1% for KNH_2, $KLi_3(NH_2)_4$, and $LiNH_2$, respectively. It is noteworthy that the hydrogen absorption kinetics is better in order of KNH_2>$KLi_3(NH_2)_4$>$LiNH_2$ and $KLi_3(NH_2)_4$ shows much faster reactivity than that of post-milled $LiNH_2$ at 200 °C, which indicates that, if $KLi_3(NH_2)_4$ and $LiNH_2$ coexist in H_2 atmosphere, $KLi_3(NH_2)_4$ is preferential to react with H_2.

4. Conclusions

In summary, the KH-added LiH–NH_3, KH-added LiH–$LiNH_2$, KH-added $LiNH_2$, and KNH_2-added $LiNH_2$ systems were systematically investigated. It was found that the ternary amide $KLi_3(NH_2)_4$ was an important intermediate that was inclined to be formed in dehydrogenation and hydrogenation processes of the potassium compounds-added Li–N–H system. Further investigations revealed that both the solid state reaction of $LiNH_2$ with KNH_2 and the solid state reaction of $LiNH_2$ with KH under mechanical ball milling or heat treatment condition will lead to the formation of the $KLi_3(NH_2)_4$ ternary amide. Moreover, the ternary amide $KLi_3(NH_2)_4$ single phase was successfully synthesized by the mechanical ball milling and its ammonia desorption and hydrogenation properties were investigated. TPD experiments shows that the ammonia desorption rate of $KLi_3(NH_2)_4$ is faster than that of $LiNH_2$. Furthermore, it was observed that the hydrogen absorption kinetics is better in order of KNH_2>$KLi_3(NH_2)_4$>$LiNH_2$.

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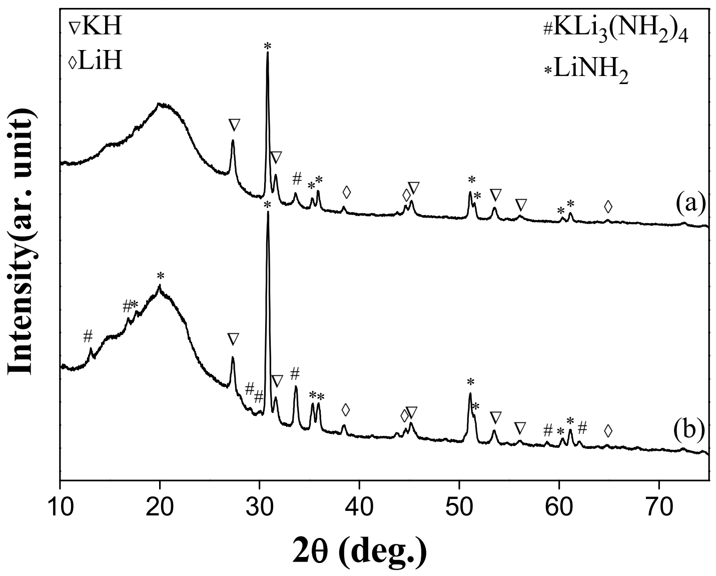


Fig. 1 XRD patterns of products by reactions of the 5 mol% KH-added LiH with NH_3 (0.5 MPa, NH_3/MH = 1 mol/mol) under different operations: (a) reacting at 100 °C for 60 minutes, (b) reacting at 100 °C for 60 minutes and then at room temperature for 15 minutes.

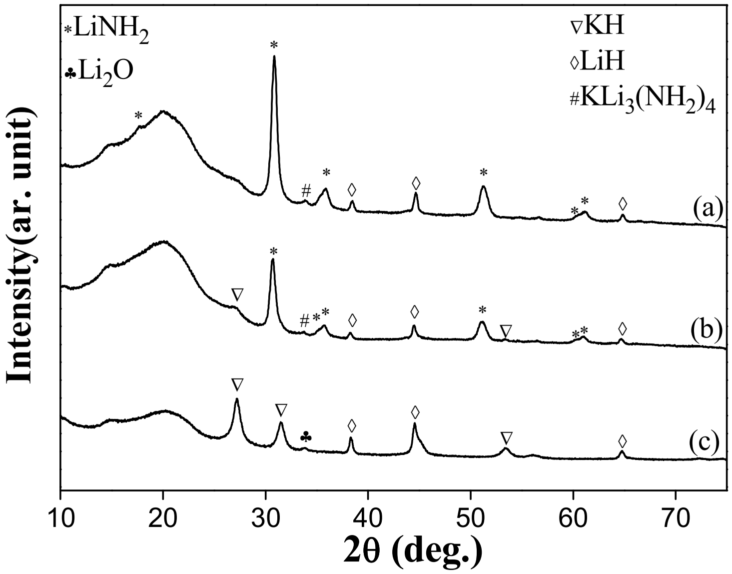


Fig. 2 XRD patterns of $LiNH_2$ and LiH systems with 3 mol% KH added (a) or 5 mol% KH added (b) and the 5 mol% KH-added LiH system (c) after ball milling.

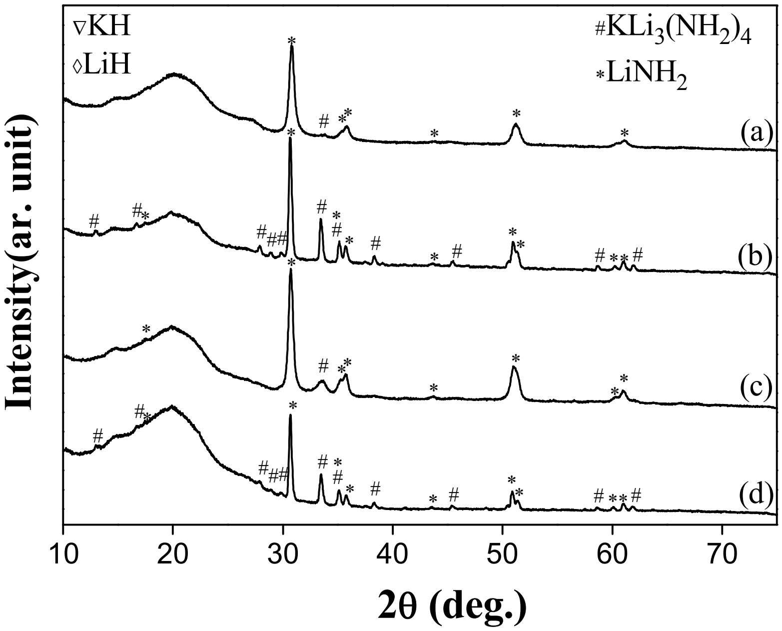


Fig. 3 XRD patterns of the 5 mol% KH-added $LiNH_2$ after ball milling (a) and treatment under Ar atmosphere at 200 °C for 4 hours (b); XRD patterns of the 5 mol% KNH_2-added $LiNH_2$ after ball milling (c) and treatment under Ar atmosphere at 200 °C for 4 hours (d).

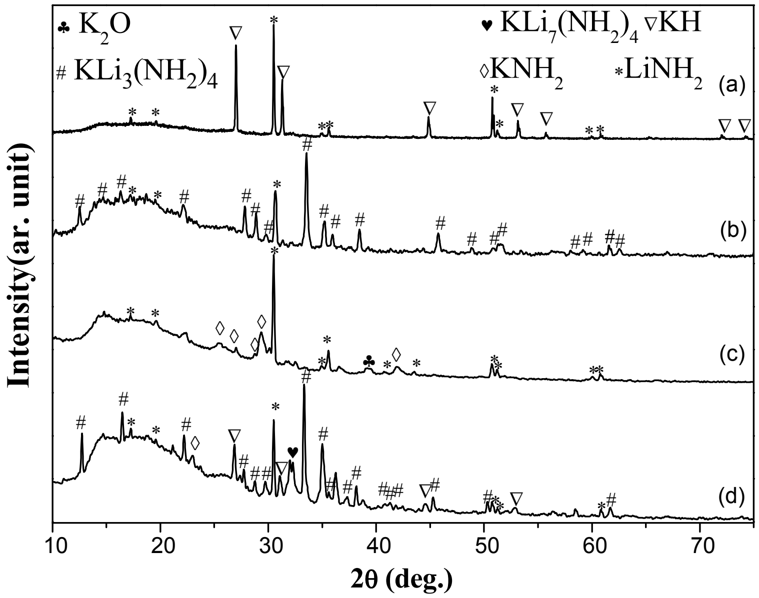


Fig. 4 XRD patterns of $KH/LiNH_2$ with molar ratio of 1/4 after hand milling (a) and treatment under Ar atmosphere at 200 °C for 48 hours (b); XRD patterns of $KNH_2/LiNH_2$ with molar ratio of 1/3 after hand milling (c) and treatment under Ar atmosphere at 200 °C for 48 hours (d).

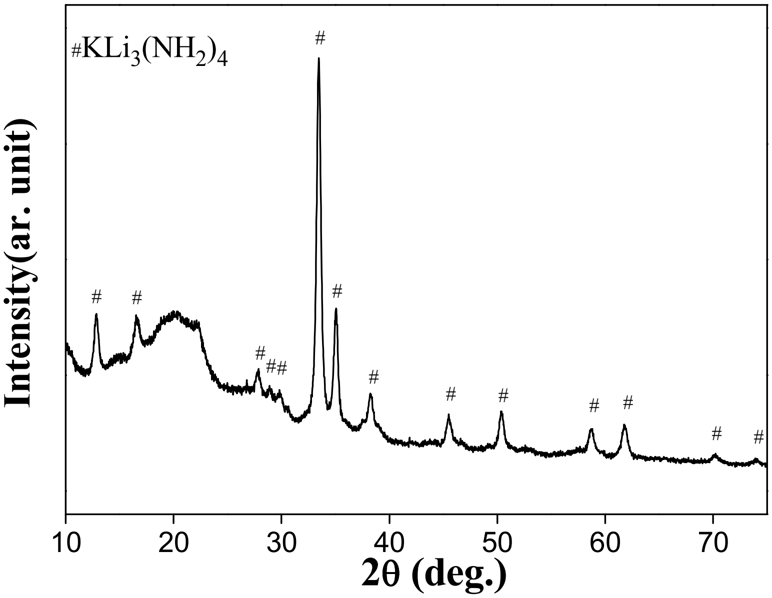


Fig. 5 XRD pattern of the synthesized KLi$_3$(NH$_2$)$_4$ single phase.

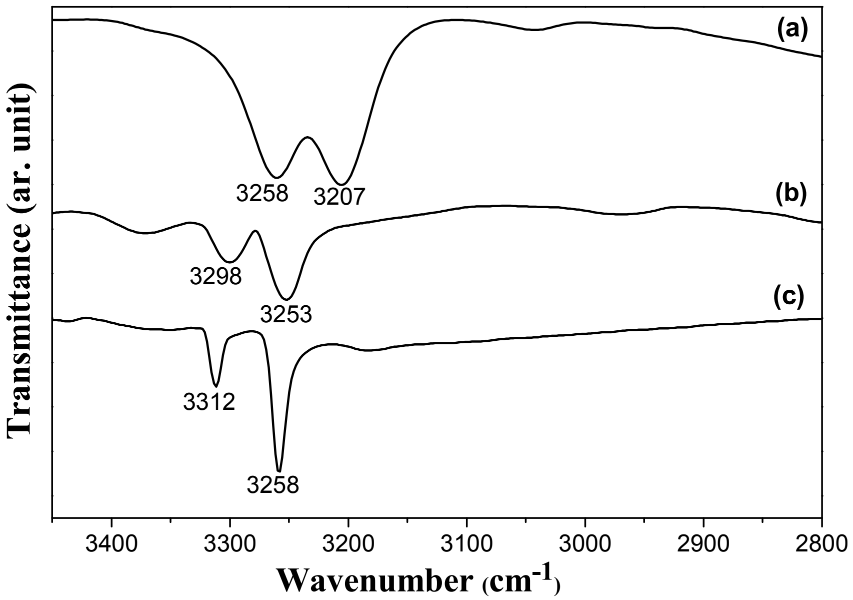


Fig. 6 FTIR of KNH_2 (a), the just synthesized $KLi_3(NH_2)_4$ (b), and $LiNH_2$ (c).

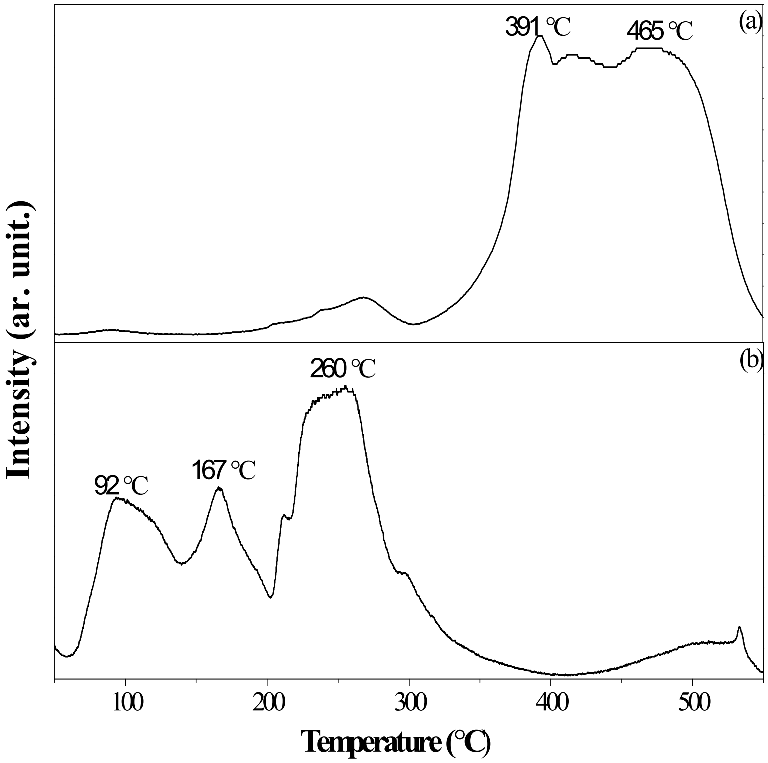


Fig. 7 Temperature dependence of NH_3 (m/z 16) desorption from $LiNH_2$ (a) and the $KLi_3(NH_2)_4$ single phase (b), the temperature was increased at a rate of 5 °C/min.

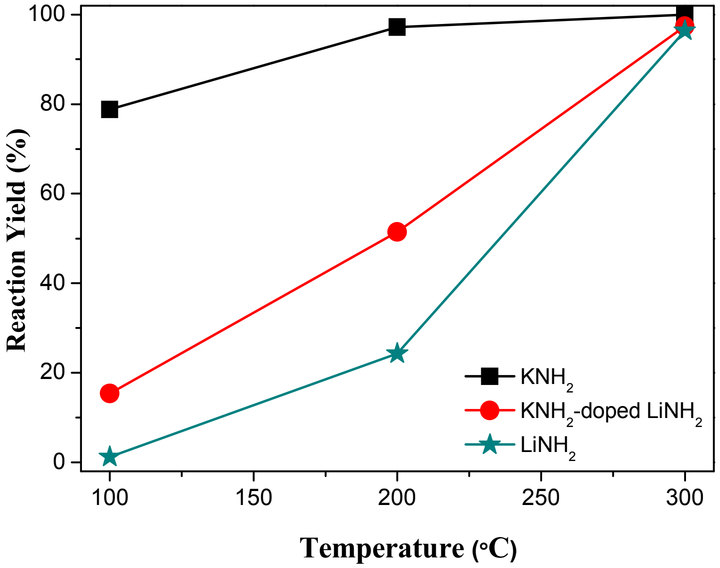
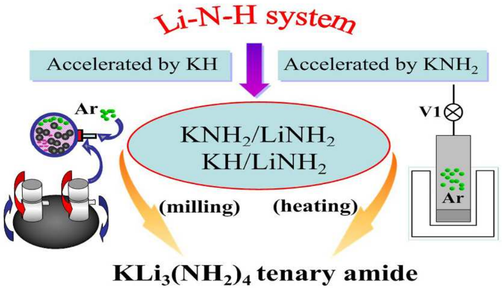


Fig. 8 Hydrogenation profile for MNH_2 (the KNH_2, $KLi_3(NH_2)_4$ and $LiNH_2$) under H_2 flow at 100, 200, and 300 °C for 4 hours.



Formation mechanism of KLi$_3$(NH$_2$)$_4$ as an important intermediate in the potassium compounds-added Li-N-H system were clarified.

(Supplementary information)

The ternary amide $KLi_3(NH_2)_4$: an important intermediate in the potassium compounds-added Li–N–H systems

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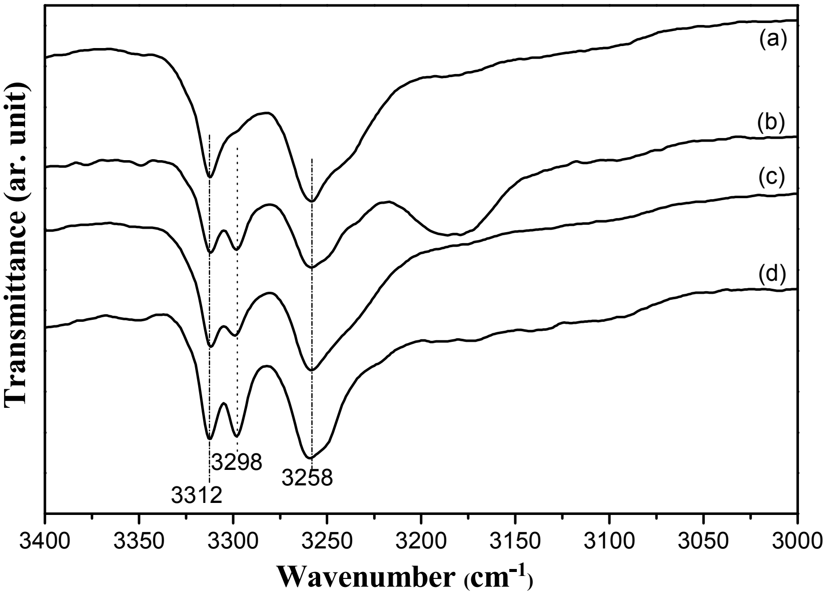

Fig. S1 FTIR of $KH/LiNH_2$ with molar ratio of 1/4 after ball milling (a) and treatment under Ar atmosphere at 200 °C for 48 hours (b); $KNH_2/LiNH_2$ with molar ratio of 1/3 after ball milling (c) and treatment under Ar atmosphere at 200 °C for 48 hours (d).

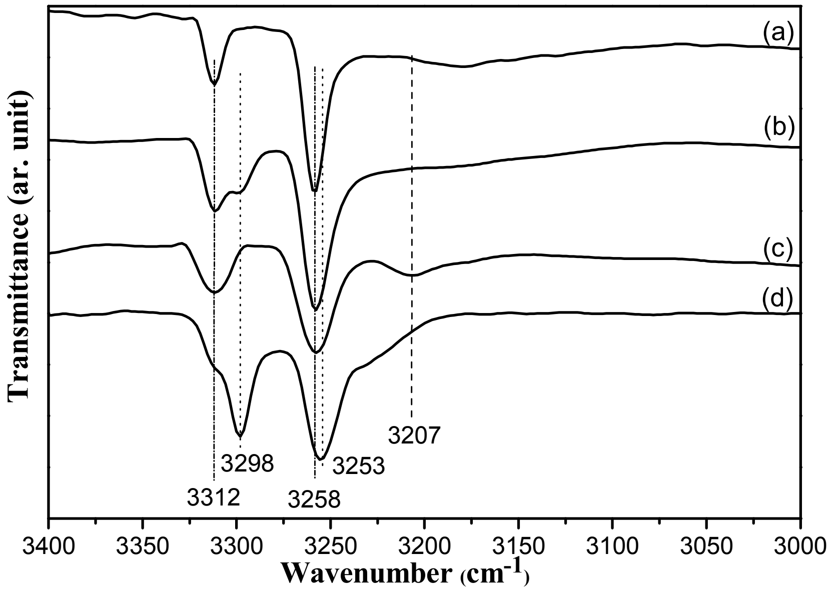

Fig. S2 FTIR of KH/LiNH$_2$ with molar ratio of 1/4 after hand milling (a) and treatment under Ar atmosphere at 200 °C for 48 hours (b); KNH$_2$/LiNH$_2$ with molar ratio of 1/3 after hand milling (c) and treatment under Ar atmosphere at 200 °C for 48 hours (d).

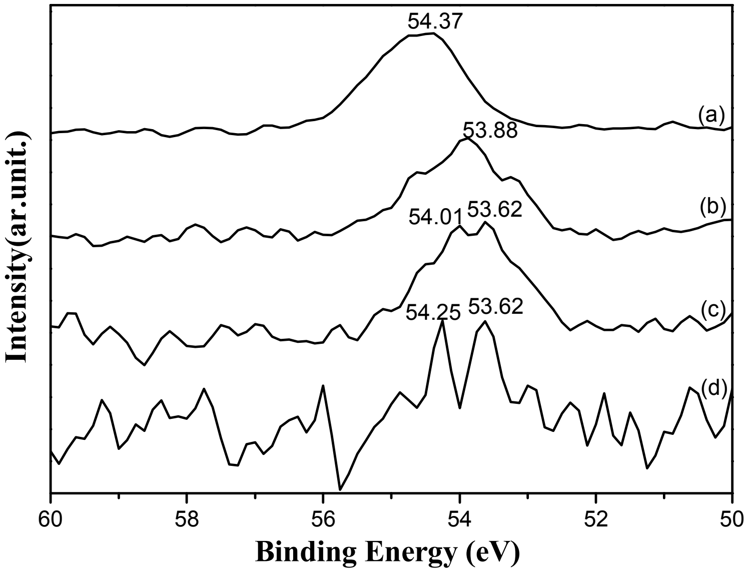

Fig. S3 XPS Li(1s) spectra of the raw $LiNH_2$ (a), the just synthesized $KLi_3(NH_2)_4$ single phase by ball milling (b), $KH/LiNH_2$ with molar ratio of 1/4 after hand milling and treatment under Ar atmosphere at 200 °C for 48 hours (c), $KNH_2/LiNH_2$ with molar ratio of 1/3 after hand milling and treatment under Ar atmosphere at 200 °C for 48 hours (d).

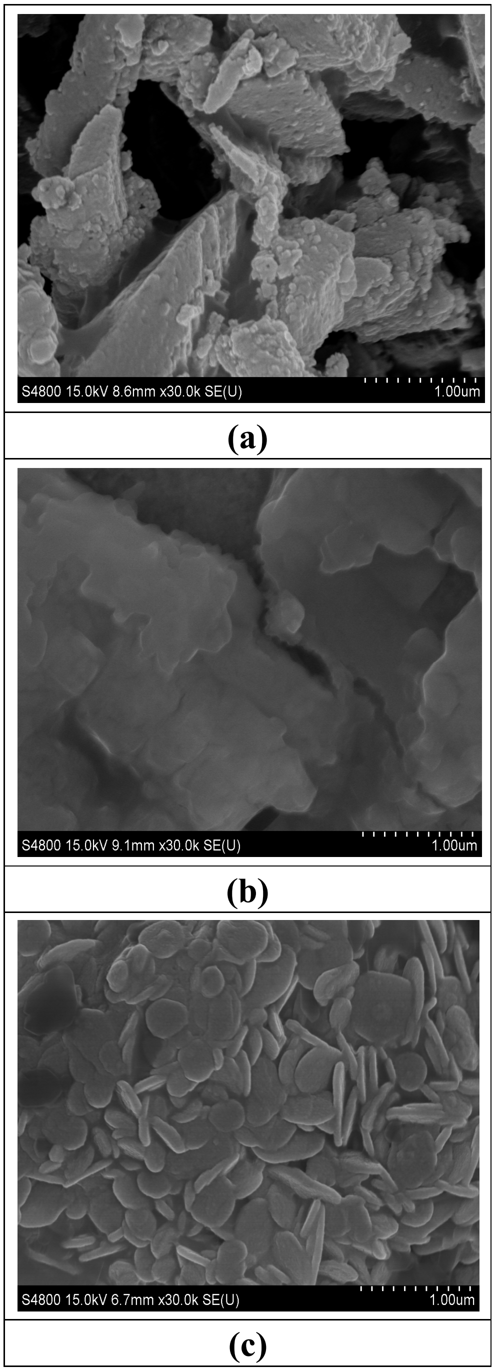

Fig. S4 SEM micrographs of the raw $LiNH_2$ (a)、raw KNH_2 (b) and the just synthesized $KLi_3(NH_2)_4$ by ball milling (c).