Development of potential organic-molecule-based hydrogen storage materials: Converting C–N bond-breaking thermolysis of guanidine to N–H bond-breaking dehydrogenation

Xiuquan Zhou, Wei Zhou, Terrence J. Udovic, Taner Yildirim, John J. Rush, Efrain E. Rodriguez, Hui Wu

Abstract

The small organic molecule guanidine C3N3H5 can be anionized via a facile reaction with alkali-metal hydrides or amides with the formation of metal guanidinates (MCN3H4) and their guanidine adducts. The crystal structures and thermal decomposition properties of these organic-molecule-based complex hydrides were carefully investigated. Through metallation, MCN3H4 can completely preserve carbon atoms in the system and exhibit a largely improved thermal decomposition compared to C3N3H5 regarding the extent of C–N bond breaking. By pairing H+ in C3N3H5 or MCN3H4 with H− from metal hydrides, the resulting composite can further reduce ammonia libration and promote an endothermic dehydrogenation.

Introduction

Many hydride systems have been investigated for potential onboard vehicular hydrogen storage applications including metal hydrides, complex hydrides, and chemical hydrides. The two main DOE criteria on hydrogen capacities (both gravimetric 5.5 wt.% and volumetric 40 gH2 L−1) and cycling capabilities (1500 cycles at −40–85 °C and 4 atm) eliminated most of the studied systems [1]. To achieve high storage capacity with minimal weight requires strong chemical bonds between hydrogen and host materials as in metal hydrides (e.g. MgH2) [2–5], complex hydrides (e.g. LiBH4, Mg(BH4)2, LiNH2) [6–11], and chemical hydrides (e.g. ammonia borane) [12–14]. To achieve fast cycling at accessible conditions, however, requires weak chemical bonds, fast kinetics, and short diffusion lengths. Thus, the concomitant requirement of...
fast recycling is quite challenging for these high-hydrogen-capacity hydride materials.

Small organic hydrogenous molecules or polymers are groups of materials with high hydrogen contents. However, thermolysis of these compounds usually results in C–C bond (346 kJ mol⁻¹) instead of C–H bond (411 kJ mol⁻¹) rupture due to the high energy barrier for activating the C–H bond [15–17]. On the other hand, cyclic hydrocarbons and hetero-organic molecules with heteroatoms N, O, S, etc. can be dehydrogenated via the breaking of C–H and/or X–H bonds with the aid of catalysts [18]. A recent study on some primary amines showed promising results on the dehydrogenation properties of these materials at elevated temperatures [19,20]. The composites comprised of primary amines and metal hydrides resemble the extensively studied amide/hydride systems especially with respect to their endothermic dehydrogenation. Therefore, it would be of great interest to study such hybrid systems of inorganic and organic hydrogenous compounds, which show both high hydrogen capacities as well as possible reversibility.

Herein, we report on one of the oldest and the most important small organic molecules, guanidine (HNC(NH₂)₂), and its potential application as a hydrogen storage material. Guanidine has played a remarkable role within various chemistry and biochemistry fields. For example, it serves as a base with two amino groups attached to an imine central resultant guanidine-based building blocks are essential in hybrid systems of inorganic and organic hydrogenous composites comprised of primary amines and metal hydrides. Guanidine has been studied in both ionic liquid [23] and vapor phase [24], displaying an exothermic concomitant H₂ and NH₃ release. In this study, we investigated another ionic form of guanidine, negatively charged guanidinate ions, that can be used as a hydrogen storage material.

**Experimental**

High-purity guanidine (CN₃H₅) was prepared using a modified method reported in literature [28]. Stoichiometric amount of Na metal and guanidinium carbonate (2:1 M ratio) were separately dissolved in anhydrous ethanol in a nitrogen filled glove box. The two solutions were mixed and filtered to yield a colorless ethanol solution of guanidine. Solid guanidine was obtained by evaporating ethanol under vacuum, and the product was further purified by sublimation on a Schlenk line. The yield for the final purified product was about 60%. The LiH–CN₃H₅ (or LiNH₂–CN₃H₅) and NaH–NH₃BH₃ powder mixtures were milled using a Fritsch Pulverisette 7 planetary mill at 200 rpm for 1 h (20 min for the amide mixture) and 200 rpm for 10 min, respectively. After milling, the mixtures were stored in a He-filled glovebox for further structural and property characterizations. All sample handling was performed in the He-filled glovebox due to the air-sensitivity of these complex hydrides.

Phase identification and equilibrium were monitored on samples sealed in 0.7 mm glass capillaries using a Rigaku X-ray diffractometer with a Cu Kα source. Data for structural studies were collected over 24 h at room temperature in the 2θ range of 5–70° with a step size of 0.02°. Rietveld structural refinements were done using the GSAS package [30]. Neutron vibrational spectra (NVS) were measured at 5 K using the BT-4 Filter-Analyzer Neutron Spectrometer (FANS) with the Cu(220) monochromator under conditions that provided energy resolutions of 2–4.5% over the vibrational energy range probed.

Thermogravimetric analysis (TGA) measurements with simultaneous differential scanning calorimetry (DSC) were made with a Netzsch (STA 449 F1 Jupiter) TGA-DSC under He flow with Al sample pans and temperature ramp rates of 2 °C/min. Temperature readings were estimated to be accurate to within ±1 °C. Dehydrogenation of CN₃H₅–5LiH was further characterized by temperature-programmed desorption (TPD) performed on a Sieverts-type apparatus described previously [31]. Mass spectrometry (MS) measurements were conducted using a Hiden RGA mass spectrometer. Samples for TPD and MS measurement were heated to 400 °C at 2 °C/min.

The XRD pattern of LiCN₃H₄·2CN₃H₅ can be indexed using a monoclinic P2₁ unit cell with a = 10.770 Å, b = 9.275 Å, c = 4.651 Å, and β = 78.45°. The crystal structure was then partially solved using direct space methods. Due to the uncertain H positions, First-principles molecular dynamics simulated annealing were performed to confirm the CN₃H₄ and CN₃H₅ configuration with the lowest energy. Rietveld structural refinement on the optimal structural candidate was done using the GSAS package. The CN₃H₄ and CN₃H₅ groups were kept as rigid bodies with the C–N and N–H bond lengths and bond angles constrained as the DFT calculated values due to the inadequate number of XRD observations. One CN₃H₄ and two CN₃H₅ groups together with lattice parameters were refined, yielding the agreement factors of Rwp = 0.0590, Rp = 0.0777, χ² = 1.712. The refined XRD pattern is shown in Fig. S2. The crystal structures of LiCN₃H₄ and NaCN₃H₅ were solved and refined similarly. The Rietveld fit to the XRD pattern of LiCN₃H₄ and NaCN₃H₅ are shown in Figs. S1 and S3, with Rwp = 0.0284, Rp = 0.0364, χ² = 1.450, and Rp = 0.0940, χ² = 1.252, respectively. More crystallographic...
Ionization of the neutral molecular guanidine \( \text{CN}_3\text{H}_5 \) can be achieved through reaction between \( \text{CN}_3\text{H}_5 \) and metal hydrides (MH). One proton \( \text{H}^+ \) from one amino group in \( \text{CN}_3\text{H}_5 \) can be readily attracted by the hydridic \( \text{H}^- \) from MH, leading to the formation of the \( \text{CN}_3\text{H}_4^- \) anion. The \( \text{CN}_3\text{H}_4^- \) anion can also be obtained by reacting \( \text{CN}_3\text{H}_5 \) with metal amide (\( \text{MNH}_2 \)) with the production of gaseous ammonia.

Crystalline Li\( \text{CN}_3\text{H}_4 \) was prepared via ball milling a 1:1 (molar ratio) \( \text{CN}_3\text{H}_5 \)–LiH mixture for 1 h as well as a 1:1 \( \text{CN}_3\text{H}_5 \)–Li\( \text{NH}_2 \) mixture for 20 min. The X-ray diffraction (XRD) pattern on the final ball milling product can be fitted using a monoclinic structure with \( P_2_1/c \) symmetry and lattice parameters of \( a = 7.2964(8) \text{Å}, b = 4.5596(6) \text{Å}, c = 9.085(1) \text{Å}, \) and \( \beta = 103.560(6)^\circ \) (Fig. S1). The crystal structure of Li\( \text{CN}_3\text{H}_4 \) (Fig. 1) determined and refined from our room-temperature XRD pattern is consistent with a previous low-temperature single-crystal study [25]. Furthermore, the XRD pattern of \( \text{CN}_3\text{H}_5 \)–LiH collected after a shorter time of ball milling (e.g. 30 min) revealed the formation of an intermediate product (Fig. S2), indicating a progressive deprotonating process between \( \text{CN}_3\text{H}_5 \) and LiH. Its XRD pattern could be indexed using a \( P_2_1/c \) unit cell with \( a = 10.770 \text{Å}, b = 9.275 \text{Å}, \) and \( c = 4.651 \text{Å}, \) and \( \beta = 78.45^\circ \). The volume of the indexed unit cell and the crystal structure solved using combined direct space methods and first-principles molecular dynamics simulations annealing indicated a guanidine adduct of lithium guanidinate with a \( \text{Li(CN}_3\text{H}_4) \) \( 2\text{CN}_3\text{H}_5 \) stoichiometry (Fig. 1). The crystal structure of Li\( \text{CN}_3\text{H}_4 \) \( 2\text{CN}_3\text{H}_5 \) was then refined based on the XRD pattern, with good agreement (Fig. S2). Likewise, Na\( \text{CN}_3\text{H}_5 \) was synthesized via this facile method, i.e., ball milling a 1:1 (molar ratio) \( \text{CN}_3\text{H}_5 \)–NaH mixture, but only for 10 min due to a higher reactivity of NaH. Na\( \text{CN}_3\text{H}_5 \) adopts a monoclinic structure (\( P_2_1/c \)) with a different cation-anion arrangement compared to Li\( \text{CN}_3\text{H}_4 \) (Fig. 1). The refined lattice parameters of Na\( \text{CN}_3\text{H}_5 \) at room temperature are \( a = 7.9711(8) \text{Å}, b = 5.0771(6) \text{Å}, c = 9.418(1) \text{Å}, \) and \( \beta = 110.740(6)^\circ \) and the refined XRD profile is shown in Fig. S3. It should be noted that the refinement based on laboratory X-ray data cannot provide highly accurate atomic coordinates, especially for H. The atomic coordinates of H were obtained from first-principles calculations and the fully relaxed structures are shown in Fig. 1.

In the structure of Li\( \text{CN}_3\text{H}_5 \), each Li tetrahedrally coordinates to four \( \text{CN}_3\text{H}_4^- \) anions, with Li–N distances in a range of 2.079–2.113 Å. The two adjacent Li\( \text{CN}_3\text{H}_5 \) tetrahedra coordinating with the same N’s form edge-sharing tetrahedra pairs (Fig. 1). Such pairs of Li-tetrahedra were linked through \( \text{CN}_3\text{H}_4^- \) anions and spread over the bc-plane, forming infinite layers. The Li\( \text{CN}_3\text{H}_4^- \) structure is then comprised of these parallel layers running along the a axis. Na\( \text{CN}_3\text{H}_5 \) possesses a similar monoclinic layered structure with each Na tetrahedrally coordinated to \( \text{CN}_3\text{H}_4^- \) anions (Na–N bond distances ~2.310–2.443 Å). Whereas, within each layer, the neighboring Na\( \text{CN}_3\text{H}_4^- \) tetrahedra were corner-sharing at the same N moieties (Fig. 1). Different from Li\( \text{CN}_3\text{H}_5 \) and Na\( \text{CN}_3\text{H}_5 \), the Li\( \text{CN}_3\text{H}_4^- \) 2\( \text{CN}_3\text{H}_5 \) structure, each Li tetrahedrally coordinates to two \( \text{CN}_3\text{H}_4^- \) anions and two \( \text{CN}_3\text{H}_5 \) molecules. The \( \text{CN}_3\text{H}_4^- \) anions serve as the bridging ligands, connecting all these Li-tetrahedra to a chain-like cluster along the c direction. The whole structure is then built up from these isolated Li\( \text{CN}_3\text{H}_4^- \) 2\( \text{CN}_3\text{H}_5 \) chain clusters (Fig. 1).

The charge distribution among all atoms is also changed upon deprotonating \( \text{CN}_3\text{H}_5 \) to \( \text{CN}_3\text{H}_4^- \). From the Mulliken population analysis based on first-principles calculations (Table S1), the H’s in \( \text{CN}_3\text{H}_5 \) are more positively charged before ionization, indicating their proclivity to react with the \( \text{H}^- \) from MH. After forming \( \text{CN}_3\text{H}_4^- \), both C and H become less positively charged with almost no electron density change in N, which results in less polarized C–N bonds and N–H bonds in the imino group but more polarized N–H bonds in the amino group in MCN\( \text{H}_4^- \). The structure and bonding environment of MCN\( \text{H}_4^- \) are further investigated by neutron vibrational spectroscopy (Fig. 2 and Fig. S4). The first-principles calculated NVs are also shown in Fig. 2 and Fig. S4. For MCN\( \text{H}_5 \), the observed phonon bands can be assigned to the rocking and librational modes of C–N (~70 meV) and scissoring modes of C–NH bonds (~76 meV); librational modes of N–H (~76–87 meV); bending modes of C–N bonds (~90–92 meV); bending modes of N–H (~99–109 meV); stretching mode of C–NH bonds (111–112 meV); bending modes of N–H in NH\(_2\) (120–124 meV); stretching mode of C–NH bonds (144–145 meV); rocking modes of N–H (149–152 meV); stretching and deformation modes of C–N (175–180 meV) and NH\(_2\) scissoring modes (199 meV). In general, the calculated spectra agree reasonably well with the observed NV spectra for both compounds, and thus further support the validity of our determined structures. Of the two calculated asymmetric N–H stretching modes from the –NH\(_2\) amino groups (380 meV and 410 meV), the lower energy is for the H showing the nearest distance with N in the neighboring CN\(_3\text{H}_4^- \) and the higher energy is for the other H in the same amino group, which does not have such a close H bond interaction. The calculated stretching modes in the –NH imino group where N is jointly shared by two cations (417 meV), and in the –NH where NH is coordinated by only one cation (420 meV) seem to be in similar energy ranges as those reported for \( \text{CN}_3\text{H}_5 \) [28] and primary amine/hydride composites [19], suggesting a similar N–H bonding strength in these compounds. However the lower energy (380 meV) of the
asymmetric N–H stretching from the amino group in CN₃H₄ is much less than those in metal amides (MNH₂) (characteristic lower end of N–H asymmetric stretching mode energies in MNH₂ are ~404 meV), indicating a weaker N–H bonding of the NH₂ group in MCN₃H₄.

Thermal decomposition of guanidinates

Thermal decomposition of guanidine and these guanidinates were investigated using thermogravimetry analysis (Fig. 3 and Fig. S5) and the qualitative gas desorption from these compounds were characterized using a mass spectrometer. Guanidine (CN₃H₅) completely decomposes (>95 wt.% loss) in the temperature range of 170–350 °C, releasing a mixture of NH₃, CH₄, H₂ (trace) and N₂ (trace) gases (Fig. 4). No hydrogen cyanide (CNH) or hydrazine (N₂H₄) gases were observed in the measured temperature range. These observations indicate a majority of bond-breaking of C–N bonds rather than of N–H bonds during thermolysis of CN₃H₅ due to the weaker C–N bonds (305 kJ mol⁻¹) than N–H bonds (386 kJ mol⁻¹).

LiCN₃H₄ shows much less weight loss than that of CN₃H₄, albeit still significant at elevated temperatures (~30 wt.%) from ~220 to 270 °C (Fig. 3). Mass spectra indicate the weight loss is mostly due to ammonia release. There is also a small amount of H₂ observed during decomposition of LiCN₃H₄ (Fig. 4). In contrast to CN₃H₅, little CH₄ was observed in the MS spectra,
suggesting metalation stabilizes the CN$_3$H$_5$ molecule (as also reflected in the less polarized C–N bonds from the charge population analysis) and mitigates the extent of C–N bond dissociation. The XRD pattern collected on the decomposition residue of LICN$_3$H$_4$ shows the formation of lithium cyanamide (Li$_2$CN$_2$, Fig. S6), which was further confirms the preservation of C/N species by the formation of more stable decomposition products. Li$_2$CN$_2$ was also observed in the decomposition product of LiBH$_4$–CN$_3$H$_5$ system in our recent study [35].

Since LiCN$_3$H$_4$ by itself could not dehydrogenate and liberate H$_2$, a LiCN$_3$H$_4$–4LiH composite was then prepared, which contains equal amounts of the oppositely charged H, aiming to suppress ammonia and ameliorate H$_2$ release. TGA results indeed show a significantly reduced weight loss from the LiCN$_3$H$_4$–4LiH mixture consistent with the mass spectra result where H$_2$ is the major component among the released gases (Figs. 3 and 4). Note: pure LiH decomposes and releases H$_2$ only at >600 °C.

The LiCN$_3$H$_4$–4LiH composite was further studied in detail to understand the mechanism of its dehydrogenation. Since LiCN$_3$H$_4$ is made from a 1:1 ratio of CN$_3$H$_5$/LiH, the dehydrogenation from the composite of CN$_3$H$_5$/5LiH was then directly measured. During volumetric temperature-programmed desorption (TPD), CN$_3$H$_5$/5LiH composite decomposes initially at 90 °C and releases ~1 H$_2$ equiv. per mol CN$_3$H$_5$ (Fig. 5). The MS indicates an exothermic pure H$_2$ release in this temperature range (Fig. 5 and Fig. S7), which is consistent with the formation of LiCN$_3$H$_4$ according to Eq. (1).

\[
\text{CN}_3\text{H}_5 + \text{LiH} \rightarrow \text{LiCN}_3\text{H}_4 + \text{H}_2
\]  

The production of LiCN$_3$H$_4$ from CN$_3$H$_5$ and LiH is irreversible, somewhat revealing its stability. With increasing temperature, both TPD and MS show irregular desorption profiles, starting from ~150 °C with a subsequent sharp gas release peaked at ~260 °C. In this later desorption event, H$_2$ is still the major component but accompanied by a noticeable amount of NH$_3$. Such desorption behavior is nearly the same as that of the LiCN$_3$H$_4$/4LiH composite (Fig. 4) and further confirms that LiCN$_3$H$_4$ is produced during the first H$_2$ gas release event. Furthermore, from DCS measurement, different from the 1st H$_2$ release event, the desorption in the higher-temperature range is mildly endothermic (Fig. S7).

Since the second H$_2$ release event of the composite starts at much lower temperature (150 °C) than that of the pristine
Deammoniation: \( \text{Li}_2\text{CN}_3\text{H}_3 \rightarrow \text{Li}_2\text{CN}_2 + \text{NH}_3 \) (4)

If these two reactions occur, we should observe the formation of \( \text{Li}_4\text{CN}_3\text{H}/\text{Li}_2\text{CN}_3 \) and \( \text{Li}_2\text{CN}_2 \) after decomposition completes. However, the XRD pattern collected on the decomposition residue of \( \text{CN}_3\text{H}_5/5\text{LiH} \) clearly shows a mixture of \( \text{Li}_3\text{CN}_2 \), \( \text{Li}_2\text{NH} \) and \( \text{LiH} \) (Fig. S8), which implies that more complicated reactions emerge in this temperature range.

As evidenced by the presence of \( \text{NH}_3 \) in the mass spectra and \( \text{Li}_2\text{NH}/\text{LiH} \) residues in the decomposition products, an ammonia-mediated mechanism may also play a role in the current system, as proposed in the amide/hydride systems [38,39], e.g. \( \text{LiNH}_2/\text{LiH} \). The ammonia generated from Eq. (4) can react with the excess \( \text{LiH} \) present in the system following the chain reactions reported in the literature [38], and can be simplified as:

\[
\text{NH}_3 + \text{LiH} \rightarrow \text{LiNH}_2 + \text{H}_2
\] (5)

\[
\text{LiNH}_2 + \text{LiH} \rightarrow \frac{1}{2}\text{NH}_3 + \frac{1}{2}\text{Li}_2\text{NH} \rightarrow \ldots \rightarrow \text{Li}_2\text{NH} + \text{H}_2
\] (6)

The temperature range for the second gas desorption event in the current system (~200–400 °C) is consistent with the dehydrogenation temperature of the \( \text{LiNH}_2/\text{LiH} \) composite. Therefore, after the initial direct combination of \( \text{LiCN}_3\text{H}_4 \) and \( \text{LiH} \) at 150 °C, a subsequent ammonia-mediated mechanism is highly likely in the \( \text{CN}_3\text{H}_5/5\text{LiH} \) composite. The concurrence of Eqs. (4)–(6) also explains the upper shift of the desorption peak (i.e. 260 °C) of \( \text{CN}_3\text{H}_5/5\text{LiH} \) compared to that of \( \text{LiCN}_3\text{H}_4 \).

In Fig. 5, after the concomitant peak of \( \text{NH}_3 \) and \( \text{H}_2 \) is observed, the total amount of \( \text{H}_2 \) release agrees well with the TPD measurement (Fig. 5). From Eqs. (1), (2), and (5), only three equiv. \( \text{LiH} \) were used, the remaining \( \text{LiH} \) should be in large excess to react with \( \text{LiNH}_2 \) in Eq. (6), which may explain why little ammonia was observed after 270 °C. Finally, although later desorption from the \( \text{LiCN}_3\text{H}_4/4\text{LiH} \) mixture is endothermic, the loss of \( \text{NH}_3 \) prevents a complete \( \text{H}_2 \) restoration.

Previous studies have shown that increasing \( \text{Li}^+ \) ion mobility would help reduce the dehydrogenation temperature and \( \text{NH}_3 \) liberation [40–42], which will promote a direct amide/hydride reaction rather than the ammonia-mediated process. In the \( \text{LiCN}_3\text{H}_4 \) structure, \( \text{Li} \) is tightly linked by \( \text{N} \) from four surrounding \( \text{CN}_3\text{H}_4 \) anions, and there are no structural channels or cation vacancies for \( \text{Li}^+ \) ions

\[
\text{Li}_2\text{CN}_3\text{H}_4 \rightarrow \text{Li}_2\text{CN}_3\text{H}_4 + \text{LiH}
\]
to migrate. Therefore, the CN₃H₅/5LiH composite shows noticeable NH₃ emission and an ammonia-mediated dehydrogenation mechanism at high temperatures. Different approaches have been used to facilitate dehydrogenation (e.g. Eq. (3)) and suppress NH₃ generation: i) weakening the N–H bonds by introducing cations with higher electronegativity [43] such as Mg²⁺ so as to promote the H⁺ and H⁻ combination, e.g. Eq. (3); ii) introducing more reactive H⁻-containing hydrides such as borohydrides. The results of these related projects will be reported in subsequent papers.

Through ionization we have successfully demonstrated the modification on the thermal decomposition behavior of guanidine. Due to the endothermic nature of N–H bond-breaking or even C–H bond-breaking in organic molecules during dehydrogenation, organic-molecule-based complex hydrides would open up a new direction for developing reversible hydrogen storage systems with high-H capacities.

Conclusions

We successfully prepared the anion form of guanidine, CN₃H₄, through a facile reaction of guanidine with alkali-metal hydrides (LiH, NaH) or amide (LiNH₂). The crystal structures of the resulting alkali-metal guanidinates, i.e. LiCN₃H₄ and NaCN₃H₄, and their guanidine adducts, i.e. LiCN₃H₄·2CN₃H₄, were investigated using combined XRD and molecular dynamics simulated-annealing methods. Metal guanidinates MCN₃H₄ exhibit largely improved thermal decomposition properties compared to CN₃H₄ in terms of the alleviated extent of C=N bond-breaking. By further pairing the H⁺ from CN₃H₄ or LiCN₃H₄ with the H⁻ from metal hydrides, i.e. LiH, the resulting composite system is able to convert the dominant deammoniation of MCN₃H₄ during thermolysis to major endothermic dehydrogenation. Detailed investigation into the dehydrogenation mechanism suggests that both CN₃H₄/5LiH and LiCN₃H₄/4LiH composites dehydrogenate initially via the direct combination reaction of H⁺ and H⁻ at low temperature and then through an ammonia-mediated pathway at high temperatures. To enhance the potential of these materials for hydrogen storage, future studies need to focus on more effectively promoting hydrogenation by the further activation of H⁺, the weakening of the N–H bond in MCN₃H₄, and/or the introduction of more reactive H⁻ into the system.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.ijhydene.2016.08.129.

References


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Notes

Certain commercial suppliers are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the NIST.
Supporting Information

Development of potential organic-molecule-based hydrogen storage materials: Converting the C-N bond-breaking thermolysis of guanidine to N-H bond-breaking dehydrogenation

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Table S1. Mulliken Population Analysis of Charge Densities

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<td>C</td>
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Figure S1. Experimental (circles), calculated (line), and difference (line below observed and calculated patterns) XRD profiles for LiCN$_3$H$_4$ at room temperature (CuKa radiation). Vertical bars indicate the calculated positions of Bragg peaks. $R_{wp} = 0.0284$, $R_p = 0.0364$, $\chi^2 = 1.450$. 

![XRD profiles](image-url)
Figure S2. Experimental (circles), calculated (line), and difference (line below observed and calculated patterns) XRD profiles for LiCN₃H₄·2CN₃H₅ at room temperature. Vertical bars indicate the calculated positions of Bragg peaks from LiCN₃H₄·2CN₃H₅ (72.60(9) wt. %), unreacted precursors CN₃H₅ (12.0(2) wt. %) and LiH (5.6(3) wt. %), and already formed LiCN₃H₄ (9.8(2) wt. %) (from the top). R_wp=0.0590, R_p=0.0777, χ²=1.712.
Figure S3. Experimental (circles), calculated (line), and difference (line below observed and calculated patterns) XRD profiles for NaCN$_3$H$_4$ at room temperature. Vertical bars indicate the calculated positions of Bragg peaks. $R_{wp}=0.0940$, $R_p=0.1253$, $\chi^2=1.252$. 
Figure S4 Neutron vibrational spectra and the calculated phonon modes of NaCN$_3$H$_4$. 

![Graph showing neutron vibrational spectra and calculated phonon modes of NaCN$_3$H$_4$](image-url)
Figure S5. TGA and MS weight loss of NaCN$_3$H$_4$ with 2 °C/min heating rate to 400 °C.
Figure S6. XRD pattern of the residue of LiCN$_3$H$_4$ after thermal decomposition up to 400°C. Besides Li$_2$CN$_2$ there are peaks that cannot match any known phase in the Li-C-N-H quaternary phase diagram or be indexed using a single phase.
Figure S7. DSC result of thermal decomposition of LiCN₃H₄ and CN₃H₅-5LiH with 2 °C/min heating rate to 450 °C.
Figure S8. XRD pattern on the residue of CN₃H₅·5LiH after thermal decomposition up to 400 °C.