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

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Abstract

The small organic molecule guanidine CN_3H_5 can be anionized via a facile reaction with alkali-metal hydrides or amides with the formation of metal guanidates (MCN_3H_4) and their guanidine adducts. The crystal structures and thermal decomposition properties of these organic-molecule-based complex hydrides were carefully investigated. Through metallation, MCN_3H_4 can completely preserve carbon atoms in the system and exhibit a largely improved thermal decomposition compared to CN_3H_5 regarding the extent of C-N bond breaking. By pairing H^+ in CN_3H_5 or MCN_3H_4 with H^- from metal hydrides, the resulting composite can further reduce ammonia libration and promote an endothermic dehydrogenation.

Keywords

Hydrogen storage, endothermic dehydrogenation, crystal structure determination, guanidine, metal guanidates

Introduction

Many hydride systems have been investigated for potential on board 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),^{2,3,4,5} complex hydrides (e.g. LiBH₄, Mg(BH₄)₂, LiNH₂),^{6,7,8,9,10,11} and chemical hydrides (e.g. ammonia borane).^{12,13,14} 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.^{15,16,17} 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 the central subunit for constructing numerous biomolecules²¹; by coordinating with different organic ligands, the resultant

guanidine-based building blocks are essential in supermolecular chemistry,²² etc. Guanidine is a strong base with two amino groups attached to an imine central bond. It contains ~8.5 wt. % hydrogen, which are all protic on amino (-NH₂) or imino (-NH) groups. Due to its strongly basic character, the neutral guanidine molecule easily attracts a proton, forming the mesomerism-stabilized guanidinium cation CN₃H₆⁺. The dehydrogenation of guanidium borohydride has been studied in both ionic liquid²³ and solid state form,²⁴ displaying an exothermic concomitant H₂ and NH₃ release. In this study, we investigated another ionic form of guanidine, negatively charged guanidinate anion CN₃H₄⁻. Metalating guanidine by alkali metals leads to the formation of alkali guanidates.^{25,26,27} The previously reported synthesis of light weight alkali metal guanidates involved a complicated and expensive reaction of pure alkali metals and guanidine in liquid ammonia in an autoclave under moderate pressure for extended time (e.g. 3 to 5 days).²⁵ Although guanidine was first synthesized more than 150 years ago, its crystal structure was only revealed recently,^{28,29} and the decomposition properties of guanidine and its related metal guanidate salts have never been investigated. Furthermore, different from the reported primary amines and metal-hydride composites,¹⁹ there is neither C-C bond breaking nor H(C) migration necessary in thermolysis of CN₃H₅. Therefore the thermal decomposition of guanidine and its derivatives would involve a different reaction mechanism. In this paper, we first report on a facile method for synthesizing crystalline lithium and sodium guanidates and a related guanidine adduct of lithium guanidate, then discuss their crystal structures, and finally investigate their thermal decomposition properties and mechanism.

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 molar 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 K_{α} 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 $\text{CN}_3\text{H}_5\cdot 5\text{LiH}$ 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 $\text{LiCN}_3\text{H}_4\cdot 2\text{CN}_3\text{H}_5$ can be indexed using a monoclinic $P2_1$ unit cell with $a=10.770$ Å, $b=9.275$ Å, $c=4.651$ Å, and $\beta=78.45^\circ$. 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 CN_3H_4^- and CN_3H_5 configuration with the lowest energy. Rietveld structural refinement on the optimal structural candidate was done using the GSAS package. The CN_3H_4^- and CN_3H_5 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 CN_3H_4^- and two CN_3H_5 groups together with lattice parameters were refined, yielding the agreement factors of $R_{\text{wp}}=0.0590$, $R_p=0.0777$, $\chi^2=1.712$. The refined

XRD pattern is shown in Figure S2. The crystal structures of LiCN_3H_4 and NaCN_3H_4 were solved and refined similarly. The Rietveld fit to the XRD pattern of LiCN_3H_4 and NaCN_3H_4 are shown in Figure S1 and S3, with $R_{\text{wp}}=0.0284$, $R_p=0.0364$, $\chi^2=1.450$, and $R_{\text{wp}}=0.0940$, $R_p=0.1253$, $\chi^2=1.252$, respectively. More crystallographic details such as atomic coordinates of these compounds can be found in the corresponding CIFs.

First-principles calculations based on density-functional theory (DFT) were performed with the PWSCF package.³² We used a Vanderbilt-type ultrasoft potential with Perdew-Burke-Ernzerhof exchange correlation. A cutoff energy of 544 eV was found to be enough for the total energy to converge within 0.5 meV/atom. Car-Parrinello molecular dynamics simulations³³ were used to help in searching for the most likely crystal structures. Structure optimizations on the candidate structures were further performed with respect to atomic positions, with the lattice parameters fixed at the experimental values. Lattice dynamics calculations were then performed on the relaxed structures using the supercell method with finite displacements.³⁴

Results and discussion

Synthesis and Crystal structures of Guanidates

Ionization of the neutral molecular guanidine CN_3H_5 can be achieved through reaction between CN_3H_5 and metal hydrides (MH). One protic H^+ from one amino group in CN_3H_5 can be readily attracted by the hydridic H^- from MH, leading to the formation of the CN_3H_4^- anion. The CN_3H_4^- anion can also be obtained by reacting CN_3H_5 with metal amide (MNH_2) with the production of gaseous ammonia.

Crystalline LiCN_3H_4 was prepared via ball milling a 1:1 (molar ratio) CN_3H_5 -LiH mixture for 1 h as well as a 1:1 CN_3H_5 - LiNH_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 $P2_1/c$ symmetry and lattice parameters of $a=7.2964(8)$ Å, $b=4.5596(6)$ Å, $c=9.085(1)$ Å, and $\beta=103.560(6)^\circ$ (Fig. S1). The crystal structure of LiCN_3H_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 CN_3H_4 -LiH collected after a shorter time of ball milling (e.g. 30min) revealed the formation of an intermediate product (Fig. S2), indicating a progressive deprotonating process between CN_3H_5 and

LiH. Its XRD pattern could be indexed using a $P2_1$ unit cell with $a=10.770\text{ \AA}$, $b=9.275\text{ \AA}$, $c=4.651\text{ \AA}$, 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 simulated annealing indicated a guanidine adduct of lithium guanidinate with a $\text{Li}(\text{CN}_3\text{H}_4)\cdot 2\text{CN}_3\text{H}_5$ stoichiometry (Fig. 1). The crystal structure of $\text{Li}(\text{CN}_3\text{H}_4)\cdot 2\text{CN}_3\text{H}_5$ was then refined based on the XRD pattern, with good agreement (Fig. S2). Likewise, NaCN_3H_4 was synthesized via this facile method, i.e., ball milling a 1:1 (molar ratio) CN_3H_5 -NaH mixture, but only for 10 min due to a higher reactivity of NaH. NaCN_3H_5 adopts a monoclinic structure ($P2_1/c$) with a different cation-anion arrangement compared to LiCN_3H_5 (Fig.1). The refined lattice parameters of NaCN_3H_5 at room temperature are $a=7.9711(8)\text{ \AA}$, $b=5.0771(6)\text{ \AA}$, $c=9.418(1)\text{ \AA}$, 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 LiCN_3H_4 , each Li tetrahedrally coordinates to four CN_3H_4^- anions, with Li-N distances in a range of 2.079-2.113 $\text{\AA}$. The two adjacent $\text{Li}[\text{CN}_3\text{H}_4]_4$ tetrahedra coordinating with the same N's form edge-sharing tetrahedra pairs (Fig.1). Such pairs of Li-tetrahedra were linked through CN_3H_4^- anions and spread over the bc -plane, forming infinite layers. The LiCN_3H_4 structure is then comprised of these parallel layers running along the a axis. NaCN_3H_4 possesses a similar monoclinic layered structure with each Na tetrahedrally coordinated to CN_3H_4^- anions (Na-N bond distances ~ 2.310 -2.443 $\text{\AA}$). Whereas, within each layer, the neighboring $\text{Na}[\text{CN}_3\text{H}_4]_4$ tetrahedra were corner-sharing at the same N moieties (Fig. 1). Different from LiCN_3H_4 and NaCN_3H_4 , in the $\text{LiCN}_3\text{H}_4\cdot 2\text{CN}_3\text{H}_5$ structure, each Li tetrahedrally coordinates to two CN_3H_4^- anions and two CN_3H_5 molecules. The CN_3H_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 $\text{LiCN}_3\text{H}_4\cdot 2\text{CN}_3\text{H}_5$ chain clusters (Fig. 1).

Fig. 1. Crystal structures of LiCN_3H_4 , NaCN_3H_4 , and $\text{LiCN}_3\text{H}_4 \cdot 2\text{CN}_3\text{H}_5$. (Left column) MCN_3H_4 layers or chains along the a or c axis; (middle column) views along a or c axis, showing the in-layer tetrahedra connections for MCN_3H_4 and the isolated chain clusters for $\text{LiCN}_3\text{H}_4 \cdot 2\text{CN}_3\text{H}_5$; and (right column) different local cation coordination environments and M-tetrahedra arrangements. Li, Na, C, N and H are represented by yellow, pink, grey, blue and white spheres, respectively.

Fig. 2. Neutron vibrational Spectra and the calculated phonon modes of LiCN_3H_4 .

The charge distribution among all atoms is also changed upon deprotonating CN_3H_5 to CN_3H_4^- . From the Mulliken population analysis based on first-principles calculations (Table S1), the H's in CN_3H_5 are much more positively charged before ionization, indicating their proclivity to react with the H^- from MH. After forming CN_3H_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_3H_4 . The structure and bonding environment of MCN_3H_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_3H_4 , 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 (~ 80 – 87 meV); bending modes of C-N bonds (~ 90 – 92 meV); bending modes of N-H (~ 99 – 109 meV); stretching mode of C-NH₂ bonds (111 – 112 meV); bending modes of N-H in NH₂ (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 NH₂ 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 -NH₂ amino groups (380 meV and 410 meV), the lower energy is for the H showing the nearest distance with N in the neighboring CN₃H₄⁻ 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 CN₃H₅²⁸ 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 Guanidines

Thermal decomposition of guanidine and these guanidines were investigated using thermogravimetry analysis (Fig. 3 and Fig. S5) and the qualitative gas desorption from these compounds were characterized using a mass spectrometer (MS). 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).

Fig. 3. TGA weight loss of CN_3H_5 , LiCN_3H_4 and $\text{LiCN}_3\text{H}_4\text{-4LiH}$ with 2 °C/min heating rate to 450 °C.

LiCN_3H_4 shows much less weight loss than that of CN_3H_5 , 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 H_2 observed during decomposition of LiCN_3H_4 (Fig. 4). In contrast to CN_3H_5 , little CH_4 was observed in the MS spectra, suggesting metalation stabilizes the CN_3H_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_3H_4 shows the formation of lithium cyanamide (Li_2CN_2 , Fig. S6), which further confirms the preservation of C/N species by the formation of more stable decomposition products. Li_2CN_2 was also observed in the decomposition product of $\text{LiBH}_4\text{-CN}_3\text{H}_5$ system in our recent study.³⁵

Since LiCN_3H_4 by itself could not dehydrogenate and liberate H_2 , a $\text{LiCN}_3\text{H}_4\text{-4LiH}$ 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 $\text{LiCN}_3\text{H}_4\text{-4LiH}$ mixture consistent with the mass spectra result where H_2 is the major component among the released gases (Fig. 3 and 4). Note: pure LiH decomposes and releases H_2 only at >600°C.

Fig. 4. MS from decomposition of CN_3H_5 , LiCN_3H_4 , and $\text{LiCN}_3\text{H}_4\text{-4LiH}$ with 2°C/min heating rate to 400°C .

The $\text{LiCN}_3\text{H}_4\text{-4LiH}$ composite was further studied in detail to understand the mechanism of its dehydrogenation. Since LiCN_3H_4 is made from a 1:1 ratio of $\text{CN}_3\text{H}_5/\text{LiH}$, the dehydrogenation from the composite of $\text{CN}_3\text{H}_5/5\text{LiH}$ was then directly measured. During volumetric temperature-programmed desorption (TPD), $\text{CN}_3\text{H}_5/5\text{LiH}$ composite decomposes initially at 90°C and releases ~ 1 H_2 equiv. per mol CN_3H_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_3H_4 according to eq. 1.

The production of LiCN_3H_4 from CN_3H_4 and LiH is irreversible, somewhat revealing its stability. With increasing temperature, both TPD and MS show irregular desorption profiles, starting from $\sim 150^\circ\text{C}$ with a subsequent sharp gas release peaked at $\sim 260^\circ\text{C}$. In this later desorption event, H_2 is still the major component but accompanied by a noticeable amount of NH_3 . Such desorption behaviour is nearly the same as that of the $\text{LiCN}_3\text{H}_4/4\text{LiH}$ composite (Fig. 4) and further confirms that LiCN_3H_4 is produced during the first H_2 gas release event. Furthermore, from DCS measurement, different from the 1st

H₂ release event, the desorption in the higher-temperature range is mildly endothermic (Fig. S7).

Since the second H₂ release event of the composite starts at much lower temperature (150 °C) than that of the pristine LiCN₃H₄, LiCN₃H₄ formed *in-situ* should first directly react with LiH and emit one H₂ through an H⁺ and H⁻ combination process.^{36,37}

This echoes the fact of the more polarized N-H bond in -NH₂ calculated from the Mulliken charge distribution and the weaker N-H bond in the amino group of LiCN₃H₄ observed in NVS compared to MNH₂, suggesting H in the amino group should dehydrogenate first. With increasing temperature and the observed concurrence of H₂ and NH₃, the intermediate Li₂CN₃H₃ should either react with the remaining LiH to liberate H₂ (eq. 3), or decompose to Li₂CN₂ and NH₃ (eq. 4). Such dehydrogenation and deammoniation processes compete in this temperature range.

If these two reactions occur, we should observe the formation of Li₄CN₃H/Li₅CN₃ and Li₂CN₂ after decomposition completes. However, the XRD pattern collected on the decomposition residue of CN₃H₅/5LiH clearly shows a mixture of Li₂CN₂, Li₂NH and LiH (Fig. S8), which implies that more complicated reactions emerge in this temperature range.

Fig. 5. a) TPD results of the $\text{CN}_3\text{H}_5\text{-5LiH}$ composite with $2^\circ\text{C}/\text{min}$ heating rate to 400°C . The amount of H_2 gas released (top panel) has been normalized as $n(\text{H}_2 \text{ gas})/\text{mol CN}_3\text{H}_5$; b) MS results of $\text{CN}_3\text{H}_5\text{-5LiH}$ composite with $2^\circ\text{C}/\text{min}$ heating rate to 400°C .

As evidenced by the presence of 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. LiNH_2/LiH . The ammonia generated from eq. 4 can react with the excess LiH present in the system following the chain reactions reported in the literature,³⁸ and can be simplified as:

The temperature range for the second gas desorption event in the current system ($\sim 200\text{-}400^\circ\text{C}$) is consistent with the dehydrogenation temperature of the LiNH_2/LiH composite. Therefore, after the initial direct combination of LiCN_3H_4 and 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, 5 and 6 also explains the upper shift of the desorption peak (i.e. 260 °C) of CN₃H₅/5LiH compared to that of LiCN₃H₄.

In Fig. 5, after the concomitant peak of NH₃ and H₂, it is interesting that only H₂ liberates from the system at higher temperatures (>270 °C). This resembles the MS signal of LiCN₃H₄, where no more NH₃ releases after the sharp NH₃ peak at ~238 °C. Therefore, in CN₃H₅/5LiH after the complete deammoniation from LiCN₃H₄ formed *in-situ* (eq 4), the remaining dehydrogenation should follow eq. 6 between the remaining LiH and the LiNH₂ produced in eq. (5). For the complete decomposition process of CN₃H₅/5LiH up to 450 °C, a final reaction equation can be obtained by summing eqs. 1, 2, 4, 5, and 6:

The total amount of H₂ release agrees well with the TPD measurement (Fig. 5). From eqs. (1), (2), and (5), only three equiv. LiH were used, the remaining LiH should be in large excess to react with LiNH₂ in eq. 6, which may explain why little ammonia was observed after 270 °C. Finally, although later desorption from the LiCN₃H₄/4LiH mixture is endothermic, the loss of NH₃ prevents a complete H₂ restoration.

Previous studies have shown that increasing Li⁺ ion mobility would help reduce the dehydrogenation temperature and NH₃ liberation,^{40,41,42} which will promote a direct amide/hydride reaction rather than the ammonia-mediated process. In the LiCN₃H₄ structure, Li is tightly linked by N from four surrounding CN₃H₄⁻ anions, and there are no structural channels or cation vacancies for Li⁺ ions 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 electronegativity⁴³ 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 behaviour 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, CN_3H_4^- , through a facile reaction of guanidine with alkali-metal hydrides (LiH, NaH) or amide (LiNH_2). The crystal structures of the resulting alkali-metal guanidates, i.e. LiCN_3H_4 and NaCN_3H_4 , and their guanidine adducts, i.e. $\text{LiCN}_3\text{H}_4 \cdot 2\text{CN}_3\text{H}_5$ were investigated using combined XRD and molecular dynamics simulated-annealing methods. Metal guanidates MCN_3H_4 exhibit largely improved thermal decomposition properties compared to CN_3H_5 in terms of the alleviated extent of C-N bond-breaking. By further pairing the H^+ from CN_3H_5 or LiCN_3H_4 with the H^- from metal hydrides, i.e. LiH, the resulting composite system is able to convert the dominant deammoniation of MCN_3H_4 during thermolysis to major endothermic dehydrogenation. Detailed investigation into the dehydrogenation mechanism suggests that both $\text{CN}_3\text{H}_5/5\text{LiH}$ and $\text{LiCN}_3\text{H}_4/4\text{LiH}$ 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 MCN_3H_4 , and/or the introduction of more reactive H^- into the system.

Appendix: Supplementary material

Extra structure and property characterizations associated with this article can be found in the supplementary data. Crystallographic data (CIFs) of LiCN_3H_4 , $\text{LiCN}_3\text{H}_4 \cdot 2\text{CN}_3\text{H}_5$ and NaCN_3H_4 can be found in ICSD database with number CSD-431825, CSD-431826 and CSD-431827.

Funding Sources

This work was partially supported by the DOE-EERE Grant No. DE-EE0002978 (T.J.U.).

Notes

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

Acknowledgments

We would like to thank Dr. Qiang Ye (NCNR, NIST) for his assistance with the mass spectrometer setup.

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