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Large amount of hydrogen desorption and stepwise phase transition in the chemical reaction of $NaNH_2$ and $LiAlH_4$

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Abstract

More than 5 wt.% of hydrogen can be quickly desorbed from the mixture of $NaNH_2$ and $LiAlH_4$ near ambient temperature. A stepwise phase transition was observed in the solid residue during the hydrogen desorption. $Li_3Na(NH_2)_4$, $LiNa_2AlH_6$ and a new Li–Al–N–H compound are formed in the mid of the desorption process.

Keywords: Amide; Hydride; Hydrogen desorption; Ball milling

1. Introduction

The metal–N bond in alkali metal amide (MNH_2, M represents alkali metal) is fairly ionic as evidenced by the Mulliken charges at metal, H and N atoms calculated by ab initio molecular orbital theory [1,2]. N, negative charged, shows strong proton (cation) affinity. Therefore, alkali metal amides can be applied in a number of chemical synthesis as efficient deprotonating agents [3]. In ionic metal hydrides, elements possessing positive charges are metals, while H is negatively charged [4]. The lone pair of N in amide may execute Coulombic potential onto the metal (cation) in the hydride when these two chemicals are closely contacted. Such an attraction may weaken or even break down the N–H and M–H bonds of corresponding amide and hydride. On the other hand, H in amide will probably forms a dihydrogen bonding with H in hydride, which favors the formation of hydrogen molecule. In the mean time, compositional and structural changes will be due in the solid residue. A few recent experimental observations evidence the chemical process described above. For example, $LiNH_2$ reacts with LiH and results in the formation of H_2 and Li_2NH [5]. The chemical reaction between $Mg(NH_2)_2$ and LiH gives out $Li_2Mg(NH)_2$ and H_2 [6–8]. The significances of the amide–hydride reaction lie in, on the one hand, that a variety of metal–N-based solid materials may be formed, which are rarely investigated before and may exhibit distinct chemical and physical natures. On the other hand, due to substantial amount of hydrogen desorption, the amide–hydride reaction can be regarded as a sole hydrogen production process or a reversible hydrogen storage process depending on the reversibility of the reaction. In the present study, the chemical reaction between $NaNH_2$ and $LiAlH_4$ was investigated. A stepwise phase transition associated with more than 5 wt.% of hydrogen production was observed by XRD, FTIR, ball milling and volumetric release. $Li_3Na(NH_2)_4$ and $LiNa_2AlH_6$ were formed in the mid of the reaction. A new Li–Al–N–H structure was developed at the end of reaction and was studied by XPS.

2. Experimental

2.1. Chemicals and synthesis

$LiAlH_4$ and $NaNH_2$ are supplied by Fluka with purity of 97% and 95%, respectively. All the sample handlings were conducted in a MBRAUN glovebox. The calculation of number of hydrogen atoms detached from the mixture was modified by the purities of the starting chemicals.

A Fritsch planetary ball mill was applied. The ball to powder ratio is about 30:1. The ball mill jar is equipped with two gas outlets. After the sample was ball milled for a certain period of time, the jar was connected to a pressure gauge to measure the gas pressure within the jar. The gas generated during the ball

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milling was analyzed firstly by a mass spectrometer (MS) and H_2 was found to be the only product. As ammonia was likely to be formed and be under the detection limit of MS the gaseous products were then slowly introduced from the milling jar to 30 ml distilled water. The dissolved ammonia in water converts to ammonium ions (NH_4^+) with its concentration determined by a Metrohm 781 pH/Ion Meter (Switzerland) equipped with an NH_3-selective electrode. By this quantitative analysis the ammonia concentration in gaseous product by the end of milling process was found below 10 ppm.

2.2. Characterizations

Temperature-programmed-desorption (TPD) system has been described elsewhere [6]. ~100 mg of sample was tested. Purified Ar was applied as carrier gas. Temperature was raised at 2 °C/min from 25 to 200 °C. Volumetric release measurement on the amount of hydrogen released from the sample was conducted in a Gas Reaction Controller provided by Advanced Materials Co. ~500 mg of sample was tested. The system was evacuated at room temperature, and then, gradually heated to 200 °C at 2 °C/min. As the release chamber is much bigger than the sample chamber, temperature effect was negligible. Differential scanning calorimeter (DSC) was applied to measure the heat of reaction. ~10 mg of samples (the mixture of $NaNH_2$–$LiAlH_4$, pure $LiAlH_4$ and $NaNH_2$) were tested in a Netzsch DSC 204 HP unit. Ar was applied as carrier gas. Heating rate is 5 °C/min. Bruker D8-advance X-ray diffractometer (XRD) with Cu Kα radiation and equipped with an in situ cell was used to identify phase changes. A Perkin-Elmer FTIR-3000 unit was applied to identify the N–H vibration in the samples. DRIFT mode was adopted. X-ray photoelectron spectra were collected in an EACALAB Mk II spectrometer, using Mg Ka radiation (1253.6 eV) operating at 20 kV and 20 mA as an excitation source. The binding energies of the XPS peaks were referenced to the C 1s in the graphitic state at 284.6 eV. Peak decomposition was obtained using mixed Gaussian/Lorentzian curves, after applying Shirley background subtraction.

3. Results and discussion

Powdered $NaNH_2$ and $LiAlH_4$ samples with a molar ratio of 1:1 were ground by a pestle and mortar as fine as possible. The mixture was then tested by means of DSC, TPD and volumetric release. As shown in Fig. 1a, a burst of hydrogen liberation occurs at temperatures around 120 °C. Through a volumetric release measurement, the amount of hydrogen released is ~5.1 wt.% of the starting material (Fig. 1b), which is equivalent to 3.9 H atoms per $NaNH_2 + LiAlH_4$. Also evidenced from DSC measurement is that the hydrogen desorption is an exothermic process. The heat of reaction calculated is ~−15.7 kJ/mol-H_2. The overall thermodynamics of the process is absolutely different from those of the starting chemicals. As shown in Fig. 1c, $NaNH_2$ first exhibits an endothermic decomposition around 210 °C and then after, gives an exothermic peak at 270 °C. $LiAlH_4$, on the other hand, presents a mild exothermic decomposition at ~130 °C and two consequent endothermic decompositions at 200 and 380 °C, respectively. Clearly, a kind of interaction between amide and hydride occurred during the thermal treatment, which induces a different reaction path compared with the thermal decomposition of pure starting chemicals. The exothermic nature of the abovementioned reaction reveals that it should be thermodynamically favored at lower temperatures if the reaction kinetic barrier can be overcome. The kinetics of solid state reaction can be effectively improved by reducing the particle size of reactants. Ball milling of the starting chemicals is, therefore, expected to bring the occurrence of the reaction at lower temperatures. In this context $NaNH_2$ and $LiAlH_4$ with molar ratio of 1:1 were milled in a planetary ball mill at ambient temperature and 200 rpm. The ball milling treatment was stopped at certain time intervals, when the gas pressure within the ball mill jar was measured and samples were collected for XRD and FTIR characterizations. Results show that hydrogen gas was generated upon ball milling, evidencing the occurrence of the chemical interaction between the reactants. As shown in Fig. 2 hydrogen gas was rapidly accumulated in the ball mill vessel. Within 30 min of ball milling 178 psi of hydrogen (or 3.9 H atoms per $NaNH_2 + LiAlH_4$) was released, which is of the same quantity as that determined by the volumetric release (Fig. 1b). It is worth mentioning that $LiAlH_4$ hardly releases detectable hydrogen under the same condition even after 24 h of ball milling (Fig. 2).

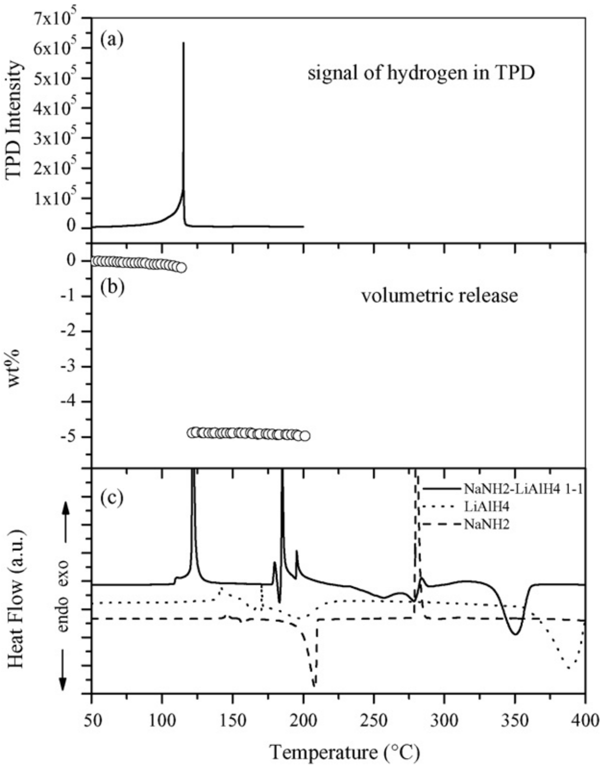

Fig. 1. TPD–MS, volumetric release and DSC measurements on the mixed $NaNH_2$–$LiAlH_4$ sample. For comparison, the decomposition of $LiAlH_4$ and $NaNH_2$ are illustrated in DSC.

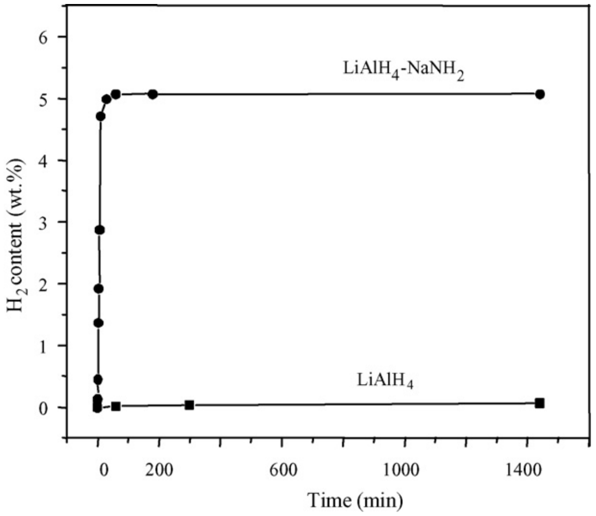

Fig. 2. Time dependence of hydrogen desorption from $LiAlH_4$ alone and the mixture of $LiAlH_4$–$NaNH_2$ (1/1) during ball milling treatment.

Consequential phase changes were observed in samples collected at different stages of ball milling, which were shown in Figs. 3 and 4 and summarized in Table 1. Sample collected after 1 min of ball milling consists of the starting chemicals and the newly developed $NaAlH_4$ and $Li_3Na(NH_2)_4$ indicating the occurrence of cation-exchange reaction (1) between amide and hydride at the very beginning of the ball milling,

$$4NaNH_2 + 3LiAlH_4 \rightarrow 3NaAlH_4 + Li_3Na(NH_2)_4 \qquad (1)$$

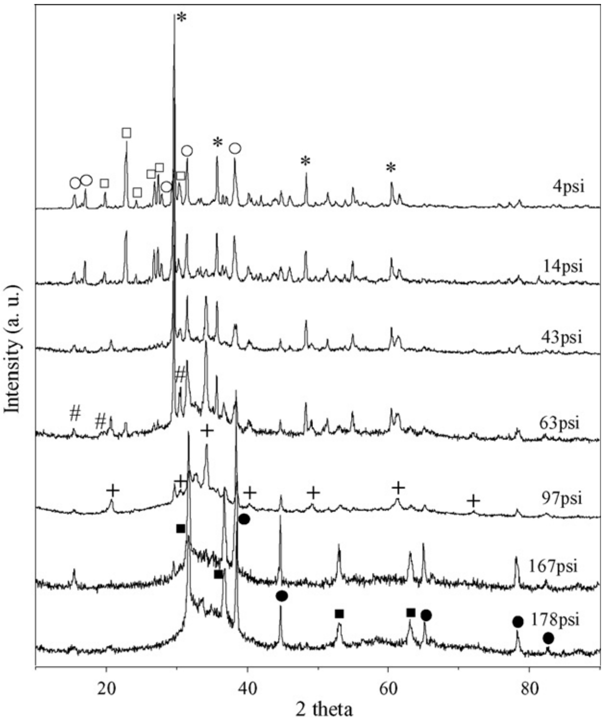

Fig. 3. XRD characterizations on samples collected at different stages of ball milling. (○) $NaNH_2$, (□) $LiAlH_4$, (*) $NaAlH_4$, (#) $LiNH_2$, (+) $LiNa_2AlH_6$, (■) NaH, and (●) Al. The main diffraction peaks of $Li_3Na(NH_2)_4$ overlap with that of $NaAlH_4$.

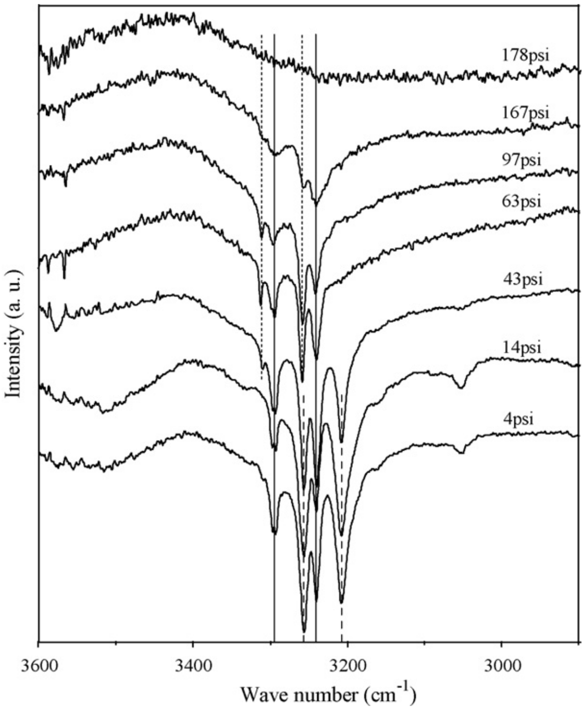

Fig. 4. IR spectra of samples collected at different ball milling stages. Peaks marked with solid lines are ascribed to $Li_3Na(NH_2)_4$, dashed line—$NaNH_2$, dotted line—$LiNH_2$.

As ball milling proceeded with continuous hydrogen desorption, $LiAlH_4$ and $NaAlH_4$ were gradually converted to AlH_6^{3-} based complex hydride. The only detectable AlH_6^{3-} containing substance is $LiNa_2AlH_6$ rather than Li_3AlH_6 and Na_3AlH_6, which may be due to the relatively stable nature of $LiNa_2AlH_6$ [9]. However, it should be noted that neither pure $LiAlH_4$ nor $NaAlH_4$, nor the mixture of them could decompose to AlH_6^{3-} containing compounds under even more severe ball milling conditions due to the high kinetic barrier in the solid state transition from $[AlH_4]^-$ to $[AlH_6]^{3-}$ [10,11]. The presence of amide may remove or reduce the barrier through a Coulombic attraction between N in amides and cations in hydrides, thus, the stabilizing effect of Na^+ or Li^+ to AlH_4^- is partially weakened, the decomposition of tetrahydrides is promoted accordingly.

Continuous Na–Li exchange between amides ($NaNH_2$ and $Li_3Na(NH_2)_4$) and hydrides ($LiAlH_4$ and $LiNa_2AlH_6$) was observed through out the ball milling treatment. $LiNH_2$ gradually developed (Fig. 4), which evidences that Li has stronger affinity towards N than Na. In the meantime NaH was gradually formed.

With extending the ball milling treatment, more hydrogen was evolved from the solid reactants; $LiNa_2AlH_6$ and amides were gradually consumed (Figs. 3 and 4). The relatively stable nature of $LiNa_2AlH_6$ excludes the possibility of the self thermal decomposition under the ball milling treatment condition [9]. Therefore, a kind of reaction between amides (both $LiNH_2$ and $Li_3Na(NH_2)_4$) and hydrides (mainly $LiNa_2AlH_6$) should occur. As evidenced by the XRD and FTIR measurements the chemical reaction finally leads to the formation of metallic Al,

Table 1
The content of solid residue at different ball milling intervals

Time (min.)	Pressure (psi)	Phase							
0	0	**$NaNH_2$**	**$LiAlH_4$**						
1	4	$NaNH_2$	$LiAlH_4$	**$Li_3Na(NH_2)_4$**	**$NaAlH_4$**				
2	14	$NaNH_2$	$LiAlH_4$	$Li_3Na(NH_2)_4$	**$NaAlH_4$**	$LiNa_2AlH_6$	Al		
3	43	$NaNH_2$		$Li_3Na(NH_2)_4$	$NaAlH_4$	$LiNa_2AlH_6$	Al	$LiNH_2$		
5	63			$Li_3Na(NH_2)_4$	$NaAlH_4$	$LiNa_2AlH_6$	Al	**$LiNH_2$**		Unknown
7	97			$Li_3Na(NH_2)_4$		**$LiNa_2AlH_6$**	Al	$LiNH_2$	NaH	Unknown
10	167			$Li_3Na(NH_2)_4$		$LiNa_2AlH_6$	**Al**	$LiNH_2$	**NaH**	**Unknown**
30	178						**Al**		**NaH**	**Unknown**

The darker the font color, the higher content the respective structure.

NaH, an unknown compound or complex with broad diffraction peaks in the range of 25–40° (Fig. 3) and the disappearance of $LiNH_2$ and $Li_3Na(NH_2)_4$. Since no NH_3 or N_2 was detected in the gaseous product, the element N should remain in the unknown compound or complex. By summarizing the experimental observations, Na, Li and Al have gone through the following phases in the process of hydrogen desorption:

$$\text{Na}: \quad NaNH_2 \rightarrow NaAlH_4 \text{ and } Li_3Na(NH_2)_4 \rightarrow LiNa_2AlH_6 \rightarrow NaH$$

$$\text{Li}: \quad LiAlH_4 \rightarrow Li_3Na(NH_2)_4 \rightarrow LiNa_2AlH_6 \rightarrow LiNH_2 \rightarrow \text{unknown compound or complex}$$

$$\text{Al}: \quad LiAlH_4 \rightarrow NaAlH_4 \rightarrow LiNa_2AlH_6 + Al \rightarrow Al + \text{unknown compound or complex}$$

It is unlikely that Na is involved in the unknown compound or complex. We have conducted the thermal decomposition of the solid residue (after 30 min ball milling) to temperatures above 320 °C, where the decomposition of NaH occurs. The amount of hydrogen released corresponds well with one unit of NaH in the residue. Therefore, the elements made of the unknown compound or complex are Li, Al, N and H. However, the rather poor crystallinity of this unknown compound or complex brings difficulties to the structural analysis. We applied stoichiometric calculation to identify the chemical composition of Li–Al–N–H by counting the number of H atoms detached from the mixture during the ball milling, the content of metallic Al in the solid residue, and the valences of Li, Al, N and H. It was determined that ~3.9 H atoms have been detached from the $NaNH_2$–$LiAlH_4$ after ball milling, thus, the number of H left in the unknown compound or complex is ~1 (NaH has one H). The content of metallic Al in the solid residue was also calculated through XRD measurement using NaH as internal reference [12]. It revealed that the amount of metallic Al is equivalent to ~70% of NaH. In other words ~0.3 Al is left in the Li–Al–N–H structure. Therefore, the chemical composition of Li–Al–N–H can be interpreted as $LiAl_{0.33}NH$. The overall reaction can be written as:

$$LiAlH_4 + NaNH_2 \rightarrow NaH + 0.67Al + LiAl_{0.33}NH + 2H_2 \tag{2}$$

The heat of formation of $LiAl_{0.33}NH$ is −218 kJ/mol as calculated by DSC (Fig. 1c).

XPS was applied to look at the electron binding energies of Al, N and Li in $LiAl_{0.33}NH$, respectively. The 1s binding energy of Li is 54.6 eV, almost the same as those of $LiNH_2$ and Li_2NH (figure not shown). Al exhibits one symmetric peak positioned at 72.9 eV with FWHM of 2.0 eV (Fig. 5). As the typical XPS peak width of contaminated C and O is ~2.0 eV, it may not be reasonable to deconvolve Al into separated peaks. Therefore,

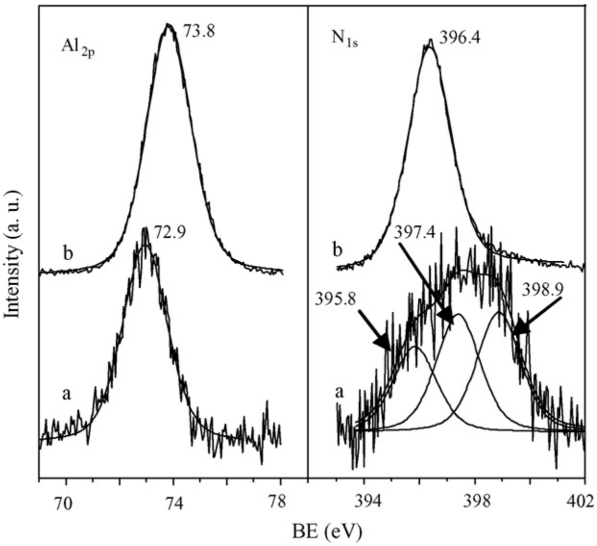

Fig. 5. XPS spectra of Al 2p and N 1s of Li–Na–N–H (a) and AlN (b).

Al possesses a reduced chemical state in the compound excluding the existence of AlN (Fig. 5) [13]. The chemical state of N, on the other hand, is relatively complicated. The broad and asymmetric peak can be deconvolved into at least three separated peaks positioned at ∼395.8, 397.4 and 399.0 eV, respectively (Fig. 5). It is suggested that N with the lowest 1s binding energy at 395.8 eV may be surrounded largely by electron donating elements, such as Li. N bonding with H normally positions at higher energy (i.e., 397.4 eV) [14]. It is uncertain the chemical environment of N with highest binding energy. One of the possibilities is Al-rich environment. Al in reduced state may not donate much electron to N, therefore, the 1s binding energy of N is expectedly higher. Further investigations are necessary to gather detailed structural and electronic properties of this newly developed Li–Al–N–H compound.

4. Conclusions

After 30 min ball milling approximately 5 wt.% of hydrogen was released from the mixture of $NaNH_2$ and $LiAlH_4$ at a molar ratio of 1:1. The interaction between $NaNH_2$ and $LiAlH_4$, which took place near ambient temperature, was found to be of exothermic nature. During the hydrogen desorption process, the exchange reactions of cations Li^+ and Na^+ associated with the transformations of $[AlH_4]^-$ to $[AlH_6]^{3-}$ anion were observed. By the end of milling process Al, NaH and a new compound of Li–Al–N–H were found as solid products.

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