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Synthesis and characterization of amide–borohydrides: New complex light hydrides for potential hydrogen storage

Philip A. Chater[a], Paul A. Anderson[a,*], James W. Prendergast[a], Allan Walton[b], Vicky S.J. Mann[b], David Book[b], William I.F. David[c,d], Simon R. Johnson[d], Peter P. Edwards[d]

[a] *School of Chemistry, The University of Birmingham, Edgbaston, Birmingham B15 2TT, UK*
[b] *Department of Metallurgy and Materials, School of Engineering, The University of Birmingham, Edgbaston, Birmingham B15 2TT, UK*
[c] *ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX11 0QX, UK*
[d] *Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR, UK*

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Abstract

The reactions $x\mathrm{LiNH_2} + (1-x)\mathrm{LiBH_4}$ and $x\mathrm{NaNH_2} + (1-x)\mathrm{NaBH_4}$ have been investigated and new phases identified. The lithium amide–borohydride system is dominated by a body centred cubic compound of formula $\mathrm{Li_4BH_4(NH_2)_3}$. In the sodium system, a new hydride of approximate composition $\mathrm{Na_2BH_4NH_2}$ has been identified with a primitive cubic structure and lattice parameter $a \approx 4.7$ Å. The desorption of gases from the two amide–borohydrides on heating followed a similar pattern with the relative proportions of H_2 and NH_3 released depending critically on the experimental set-up: in the IGA, ammonia release occurred in two steps – beginning at 60 and 260 °C for $\mathrm{Li_4BH_4(NH_2)_3}$ – the second of which was accompanied by hydrogen release; in the TPD system the main desorption product was hydrogen—again at 260 °C for $\mathrm{Li_4BH_4(NH_2)_3}$ accompanied by around 5% ammonia. We hypothesize that the $\mathrm{BH_4}^-$ anion can play a similar role to LiH in the $\mathrm{LiNH_2} + \mathrm{LiH}$ system, where ammonia release is suppressed in favour of hydrogen. The reaction $x\mathrm{LiNH_2} + (1-x)\mathrm{LiAlH_4}$ did not result in the production of any new phases but TPD experiments show that hydrogen is released from the mixture $2\mathrm{LiNH_2} + \mathrm{LiAlH_4}$, over a wide temperature range. We conclude that mixed complex hydrides may provide a means of tuning the dehydrogenation and rehydrogenation reactions to make viable storage systems.

Keywords: Hydrogen storage materials; Chemical synthesis; Amide; Borohydride; Temperature programmed desorption

1. Introduction

With volumetric hydrogen densities greater than observed in liquid (or solid) hydrogen and gravimetric storage densities that exceed DOE targets, the prospect of storing hydrogen in the form of light metal hydrides or complex hydrides remains highly desirable, in spite of problems with high desorption temperatures, impurities in the desorbed gas, and in rehydriding the solid desorption products under accessible conditions. Clearly, the search for new materials that may overcome these limitations has an important place in current hydrogen storage research. Here we report the results of our attempts to synthesize mixed anion complex hydrides of general formula $\mathrm{M_{(1+x)}(AH_4)(NH_2)_x}$ [A = Al, B] and our preliminary investigations into their desorption products.

2. Experimental details

The hydride, borohydride, amide and aluminium hydride starting materials (Sigma–Aldrich) were ground together by hand in the desired mole ratio in an argon atmosphere glovebox (O_2 content < 20 ppm). $\mathrm{Li_4BH_4(NH_2)_3}$ was prepared by methods described previously [1]. $\mathrm{Na_2BH_4NH_2}$ was prepared by placing the ground $\mathrm{NaBH_4} + \mathrm{NaNH_2}$ (1:1) mixture in a quartz tube, which was sealed with a Young's tap *via* an Ultra-Torr fitting and removed from the glovebox. The sample was then heated for 12 h at 190 °C in a tube furnace under argon gas at 1 bar. All other starting materials and mixtures were used without prior heating.

A home built temperature programmed desorption (TPD) apparatus (see Fig. 1) coupled to a quadrupole mass spectrometer (Thermo Electron, VG ProLab) was used to study the gases desorbed from $\mathrm{LiAlH_4}$, $\mathrm{LiNH_2}$, $\mathrm{LiNH_2} + \mathrm{LiH}$, $2\mathrm{LiNH_2} + \mathrm{LiAlH_4}$, $\mathrm{Li_4BH_4(NH_2)_3}$, $\mathrm{NaNH_2}$ and $\mathrm{Na_2BH_4NH_2}$ samples. Approximately 0.2 g of each sample was loaded in an argon glovebox into a quartz

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* Corresponding author. Tel.: +44 121 414 4447; fax: +44 121 414 4403.
E-mail address: p.a.anderson@bham.ac.uk (P.A. Anderson).

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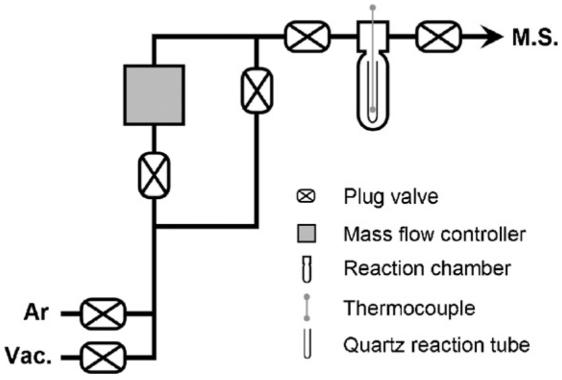

Fig. 1. Schematic of the TPD apparatus.

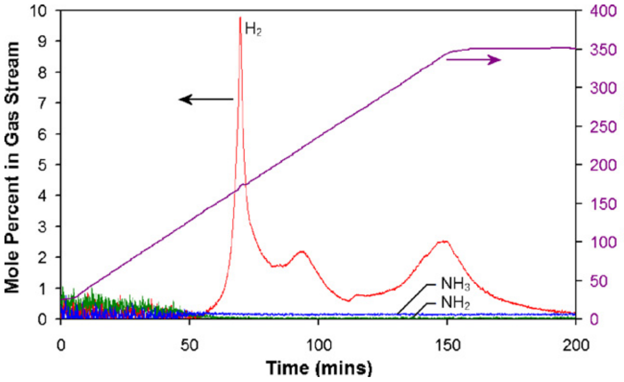

Fig. 2. Thermal desorption analysis of $2LiNH_2 + LiAlH_4$.

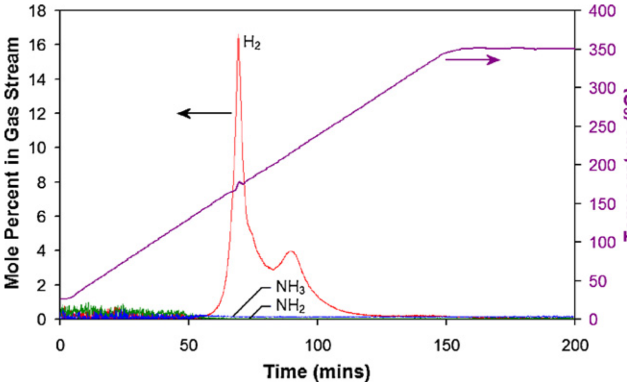

Fig. 3. Thermal desorption analysis of $LiAlH_4$.

reaction tube sealed at one end, which was positioned in a vertical position in the reaction chamber, removed from the glovebox and loaded onto the apparatus without exposing the sample to the atmosphere. Argon gas was then flowed past the sample at 100 ml min^{-1}. Once a steady flow had been reached the sample was heated at 2 °C min^{-1} up to 350 °C and held at this temperature until the sample stopped desorbing. A heated capillary was used to sample the desorbing gas species from the argon flow on the downstream side of the reaction vessel. The Faraday detector of the mass spectrometer was used to record mass channels of 2 ($H_2^{\bullet+}$), 16 ($NH_2^{\bullet+}$) fragment of NH_3 corresponding to 80% intensity of the 100% $NH_3^{\bullet+}$ peak), 17 ($NH_3^{\bullet+}$ or $OH^{\bullet+}$), 18 ($H_2O^{\bullet+}$), 28 ($N_2^{\bullet+}$), 32 ($O_2^{\bullet+}$) and 40 ($Ar^{\bullet+}$).

A pressure controlled thermogravimetric balance (Hiden IGA) was used to monitor weight changes from a 100 mg sample of $Li_4BH_4(NH_2)_3$ (accuracy of ±0.5 μg) over the same temperature range. The samples were loaded onto the IGA using a portable glovebox attached to the instrument (O_2 content <20 ppm). Once loaded, a flow of argon was passed over the sample at 100 ml min^{-1} flowing into a quadrupole mass spectrometer (Hiden HPR20) recording mass channels of 2 ($H_2^{\bullet+}$), 16 ($NH_2^{\bullet+}$), 17 ($NH_3^{\bullet+}$/$OH^{\bullet+}$), 18 ($H_2O^{\bullet+}$), 28 ($N_2^{\bullet+}$), 32 ($O_2^{\bullet+}$) and 40 ($Ar^{\bullet+}$) *via* a heated capillary. The mass channels chosen were selected after a preliminary mass spectrum confirmed that these were the only gases present in the gas stream and that no other gases, such as diborane, were desorbed from these samples. The sample was then heated with a ramp rate of 2 °C min^{-1} up to 350 °C and held at this temperature until mass loss ceased. Mass loss from the sample was recorded *versus* time and temperature.

FTIR spectra were acquired from samples contained in pressed KBr disks on a Nicolet Magna FTIR spectrometer equipped with a liquid nitrogen cooled MCTB detector, at a resolution of 2 cm^{-1}. Powder X-ray diffraction data were obtained on a Siemens D5000 X-ray diffractometer, using a Cu K_α 1 source.

3. Results and discussion

3.1. $2LiNH_2 + LiAlH_4$

Thermal treatment of mixtures of $LiNH_2$ and $LiAlH_4$ did not result in the production of any new crystalline phases. Fig. 2 shows the thermal desorption from a 2:1 mole ratio mixture of $LiNH_2$ and $LiAlH_4$. There were three main desorption peaks starting at approximately 150, 200 and 300 °C. The desorption from $LiAlH_4$ is shown in Fig. 3; the first and second peaks correspond to the formation of Li_3AlH_6 and Al, and the formation of LiH and Al, respectively [2]. The first two desorption peaks of the lithium amide–aluminium hydride mixture can be attributed to these decompositions. There was no significant change in the temperature at which hydrogen desorption occurred, and the profile is in good agreement with previous work [2,3]. The third peak in the desorption profile of the lithium amide–aluminium hydride mixture is consistent with the decomposition of a $LiNH_2 + LiH$ mixture, as shown in Fig. 4. It appears that LiH, formed through the decomposition of $LiAlH_4$, reacted with $LiNH_2$ in the same way as pure LiH [4,5].

This mixture has potential for releasing hydrogen over a large temperature range up to 500 °C, resulting in the final product Li_3AlN_2 [5]. The decomposition in the range up to 350 °C was exactly as expected for $LiAlH_4$ decomposing to LiH and Al, with release of hydrogen, followed by reaction of LiH with $LiNH_2$. No mutual destabilization or lowering of decomposition temperatures was observed, in contrast to previously reported results for $LiNH_2 + 2LiAlH_4$ [6] and $LiNH_2 + LiAlH_4$ [7] mixtures.

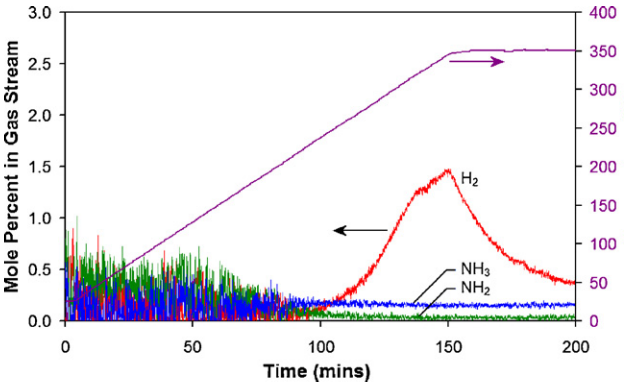

Fig. 4. Thermal desorption analysis of $LiNH_2 + LiH$.

Table 1
Observed vibrational frequencies (cm^{-1}) of selected vibrational modes of $LiNH_2$, $LiBH_4$, $Li_4BH_4(NH_2)_3$, $NaBH_4$, $NaNH_2$ and $Na_2BH_4NH_2$

Vibrational mode	$LiBH_4$	$LiNH_2$	$Li_4BH_4(NH_2)_3$	$NaBH_4$	$NaNH_2$	$Na_2BH_4NH_2$
ν_s(BH)	2284		2293	2284		2274
δ(HBH)	1121		1126	1110		1095
$\nu_{as}(NH_2)$		3313	3303		3313	3271
$\nu_s(NH_2)$		3258	3245		3258	3209
δ(HNH)		1563, 1539	1576, 1554			

3.2. $Li_4BH_4(NH_2)_3$

Heating a $3LiNH_2 + LiBH_4$ mixture at temperatures up to 180 °C under oxygen- and moisture-free conditions resulted in the formation of a new phase of stoichiometry $Li_4BN_3H_{10}$ [1]. This compound was also observed on mechanical milling of mixtures of $LiNH_2$ and $LiBH_4$ [8,9], and its structure was recently determined [1,10]. FTIR spectra (Table 1) indicate that both NH_2^- and BH_4^- ions remained intact, consistent with the formulation $Li_4BH_4(NH_2)_3$.

Thermal desorption data from pure $Li_4BH_4(NH_2)_3$ are shown in Fig. 5. The endothermic event at 220 °C can be attributed to the melting of $Li_4BH_4(NH_2)_3$. Hydrogen release occurring from the melt started at 260 °C and peaked at around 330 °C. There was a slight shoulder at around 300 °C in the hydrogen desorption peak which could indicate a two step desorption, however, a more detailed study is needed to verify this.

Although there was a small amount of ammonia released, it was impossible to quantify accurately as it was scarcely visible against the background signal from the mass spectrometer. The experiment was repeated with a larger sample in order to ascertain relative amounts of hydrogen and ammonia. From the larger sample it was possible to determine that ammonia accounts for only approximately 5% of the total desorbed gas. This is less than half that reported previously from a ball-milled $3LiNH_2 + LiBH_4$ mixture where ammonia was desorbed in amounts consistent with the loss of nitrogen necessary to yield the observed decomposition products, which include Li_3BN_2 and Li_2NH [11].

In order to investigate this discrepancy further, a sample of $Li_4BH_4(NH_2)_3$ was loaded into an IGA connected to a mass spectrometer. Figs. 6 and 7 show the thermogravimetric and mass spectrometric data, respectively. The sample heated in the IGA showed a two stage desorption trace: the first desorption started around 60 °C and the second at around 260 °C, ending at a final weight loss of 17.3 wt%. Interestingly, the first low temperature desorption was completely absent in the mass spectrum of the TPD experiment. A total mass loss of 17.3 wt% is not consistent with hydrogen, which makes up only 11.1 wt% of $Li_4BH_4(NH_2)_3$, being the majority desorption product. The mass spectrometric data confirmed that the first desorption was due only to ammonia and the second, higher temperature desorption, was due to ammonia and hydrogen, which is consistent with published results [11]. The weight loss associated with the first desorption was ∼5.8 wt %, equivalent to the loss of around 2.5 NH_3 molecules from the unit cell (eight formula units) of $Li_4BH_4(NH_2)_3$ [1,10].

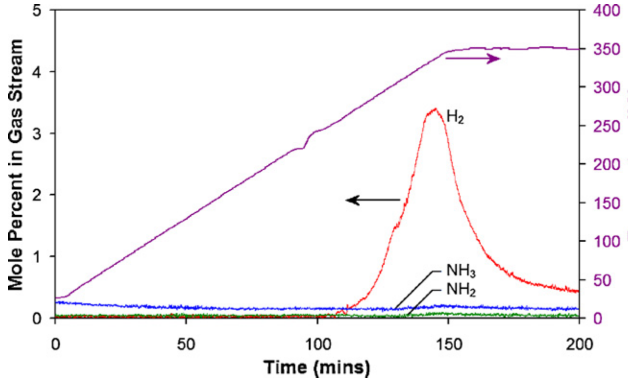

Fig. 5. Thermal desorption analysis of $Li_4BH_4(NH_2)_3$.

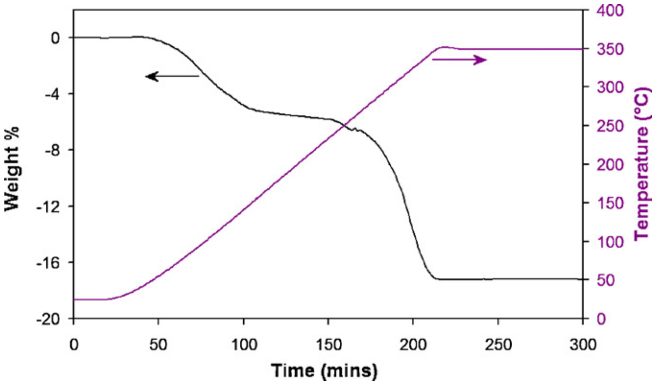

Fig. 6. Thermo-gravimetric data from $Li_4BH_4(NH_2)_3$.

Clearly, the nature of the desorption was different in the IGA and the TPD experiments. An important difference between the experiments was how the argon flowed around the sample. In the

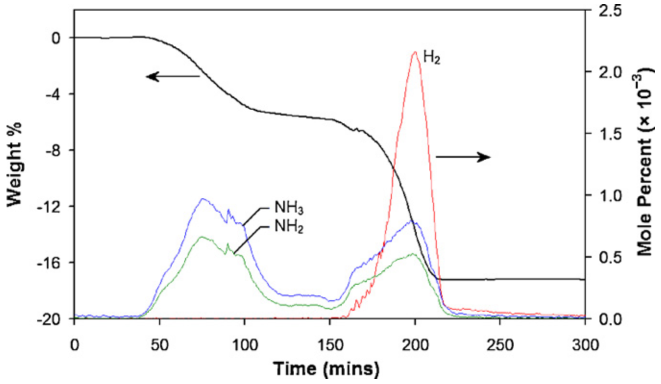

Fig. 7. Gravimetric trace from $Li_4BH_4(NH_2)_3$ including thermal desorption analysis.

IGA, the argon flow passed directly over the sample, and was sampled to the mass spectrometer from adjacent to the material. Any ammonia released could be quickly swept away from the sample into the mass spectrometer. In the TPD system, the argon flowed over the end of the reaction tube, which was at right angles to the flow (Fig. 1), before passing into the mass spectrometer. Any gases released would therefore have a longer contact time with the desorbing melt, and we hypothesize that, in this case, ammonia released was able to react again with the sample before it entered the exhaust to the mass spectrometer.

Evidently, the interaction of ammonia with the sample at low temperature did not result in the evolution of hydrogen. The temperature at which hydrogen was first observed, 260 °C, was the same in both the TPD and IGA experiments, and similar to the temperature of first release of hydrogen from the $LiH + LiNH_2$ system. The fact that the desorption of ammonia was suppressed in our TPD experiments suggests that it may be the primary desorption product and that hydrogen was produced only upon reaction of desorbed gas with the sample. Our results are therefore consistent with the suggestion that NH_3 is an intermediate in the evolution of hydrogen from $Li_4BH_4(NH_2)_3$, and we note that it has been proposed to play a similar role in the desorption of hydrogen in the $LiH + LiNH_2$ system [12,13].

Our experiments and previous work [9,11] show that the presence of the BH_4^- anion – like LiH – is capable of altering the decomposition pathway of $LiNH_2$ in favour of hydrogen production. The amide–borohydride system differs in that the BH_4^- anions are incorporated with NH_2^- in a single compound. The crystal structure of $Li_4BH_4(NH_2)_3$, however, exerts no influence over hydrogen desorption properties as desorption of hydrogen was observed only at temperatures above the melting point.

3.3. $Na_2BH_4NH_2$

Reactions between $NaBH_4$ and $NaNH_2$, in a variety of different ratios, under oxygen- and moisture-free conditions at 190 °C resulted in a new compound of approximate stoichiometry Na_2BNH_6, with a primitive cubic structure and a unit cell parameter of *ca* 4.7 Å (Fig. 8a). FTIR spectra (Table 1) indicate that both NH_2^- and BH_4^- ions remained intact, consistent with the formulation $Na_2BH_4NH_2$.

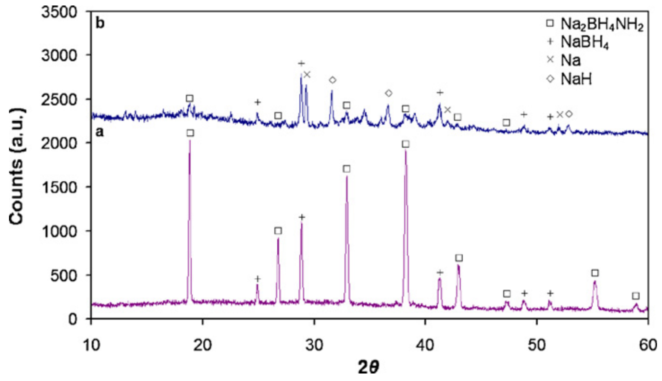

Fig. 8. Powder X-ray diffraction patterns of (a) $Na_2BH_4NH_2$ and (b) $Na_2BH_4NH_2$ after thermal desorption in TPD apparatus. Reflections due to $Na_2BH_4NH_2$ (□), $NaBH_4$ (+), Na (×) and NaH (◇) are shown.

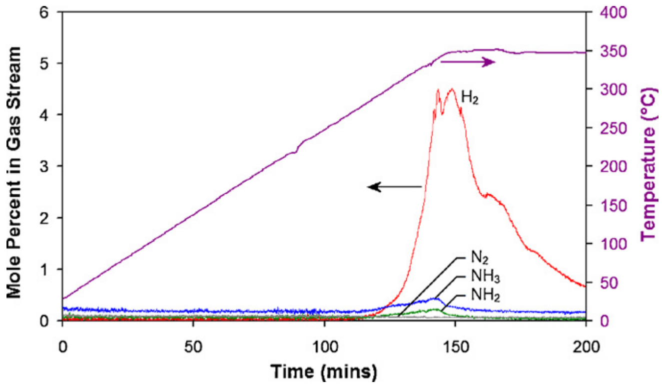

Fig. 9. Thermal desorption analysis of $Na_2BH_4NH_2$.

Fig. 9 shows thermal desorption data from this sample. The endothermic event at 215 °C is attributed to the melting of the sample. Hydrogen release started at around 290 °C and did not peak until the maximum temperatures reached in this experiment of ∼350 °C. Ammonia was the only other gas observed and was a minor component making up approximately 7% of the total desorbed gas. At the peak of ammonia production at 340 °C around 9.5% of the desorbing gas was NH_3.

Fig. 10 shows desorption of ammonia from $NaNH_2$ starting at around 280 °C, just below the onset temperature of hydrogen evolution from the amide–borohydride. No nitrogen or hydrogen – the main decomposition products reported [14] – were observed in the mass spectrometer traces from $NaNH_2$. $NaBH_4$ is reported not to decompose until above 400 °C [15].

After heating the sodium amide–borohydride to 350 °C in the TPD apparatus, the quartz reaction tube contained a reactive metallic solid (sodium metal) and a smaller amount of fine crystals. Powder X-ray diffraction data from the solid products (Fig. 8b), showed reflections that could be indexed to $NaBH_4$, NaH, Na and $Na_2BH_4NH_2$, and some weaker reflections that have not yet been indexed. There was also a higher than normal background in the diffraction pattern, which could indicate the presence of an amorphous product such as boron or boron nitride.

Unlike the lithium amide based systems, where there are stable imide and nitride structures as possible reaction products, and the ternary compound Li_3BN_2, the sodium analogues of these do

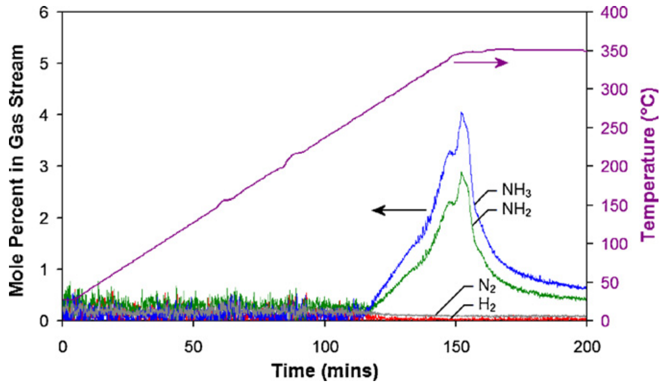

Fig. 10. Thermal desorption analysis of $NaNH_2$.

not readily form. Sodium imide is unknown, and sodium nitride and sodium boron nitride have only been produced by non-conventional methods [16] and high pressure techniques [17], respectively. In spite of the lack of alternative possible dehydrogenation products, the observation of sodium metal is slightly surprising as sodium hydride is reportedly stable to 425 °C [18].

Preliminary desorption data indicate that, in a similar fashion to $Li_4BH_4(NH_2)_3$, ammonia was the primary decomposition product in a two step desorption in the IGA, and that ammonia release was suppressed in the TPD experimental set-up, in favour of hydrogen.

4. Conclusions

Hydrogen desorption has been observed from $Li_4BH_4(NH_2)_3$ and the new material, $Na_2BH_4NH_2$, starting at 260 and 290 °C, respectively. It has been found that the relative amount of hydrogen to ammonia released from these systems depends significantly on the experimental set-up. We hypothesize that relatively long contact times between desorbed ammonia and the residual material can suppress the release of ammonia, in favour of hydrogen releasing reaction pathways. These results are consistent with observations of an ultra-fast reaction between LiH and ammonia in LiH–$LiNH_2$ hydrogen releasing systems [12]. It appears that not only LiH is capable of reacting with ammonia in this way to give hydrogen, but also BH_4^-.

We conclude that mixed complex hydrides may provide a route to viable new storage materials provided that rehydriding pathways can be established. Although endothermic events corresponding to the melting points of $Li_4BH_4(NH_2)_3$ and $Na_2BH_4NH_2$ were visible in our TPD traces, the sensitivity of these measurements was not sufficient to determine whether hydrogen desorption was exothermic or endothermic. Previous studies on rehydriding $Li_4BH_4(NH_2)_3$ have not been promising [8,19], but the exact composition of dehydrided materials, after dehydriding under different conditions, is not yet fully characterized for either of the amide–borohydride systems. Reversibility of these systems may depend critically on controlling the decomposition pathways and products. More detailed calorimetric studies and experiments aimed at reducing the hydrogen release temperature are under way.

On the basis of desorption results reported here, we believe that the problem of ammonia release from amide-based hydrogen storage materials could be minimized through careful design of the geometry of the fuel tank.

Acknowledgments

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