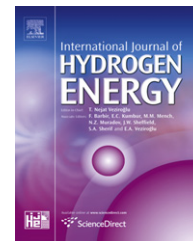


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# Hydrogen production from solid reactions between $\text{MAlH}_4$ and $\text{NH}_4\text{Cl}$

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## ABSTRACT

Solid reactions between alkali aluminum hydrides ( $\text{MAlH}_4$ ,  $\text{M} = \text{Li}$  or  $\text{Na}$ ) and  $\text{NH}_4\text{Cl}$  (at mole ratio 1:1) at 170 °C were investigated quantitatively using temperature programmed reaction (TPR), thermo-gravimetric analysis (TGA), differential scanning calorimetry (DSC) and x-ray diffraction (XRD). The release of 3 mol of  $\text{H}_2$  from per mole of  $\text{MAlH}_4$  was measured, corresponding to 5.6 wt.%  $\text{H}_2$  capacity for the  $\text{NaAlH}_4/\text{NH}_4\text{Cl}$  system and 6.6 wt.% for  $\text{LiAlH}_4/\text{NH}_4\text{Cl}$ , respectively. By ball milling of the precursor compounds prior to the mixing, the reaction proceeded fast and  $\text{NH}_3$  production as the by-product could be avoided. The quick solid reactions may be attributed to the low melting temperatures of  $\text{MAlH}_4$  and the exothermic nature of the reactions. The reaction mechanism was also discussed.

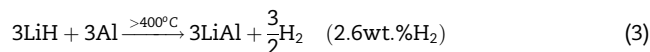
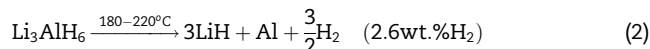
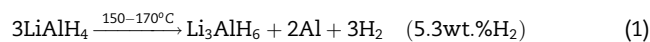
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## 1. Introduction

One approach to mitigate green house gas (GHG) emission and global warming is the application of hydrogen and fuel cell technologies to replace fossil fuels as energy source in future. Hydrogen has highest energy density by weight, and can generate power and heat with zero GHG. However for vehicle and portable applications, hydrogen gas is difficult to store and transport. Chemical hydrogen storages generate hydrogen through chemical reactions, and can reach very high wt.% of  $\text{H}_2$ , though they are not easily reversible and 'spent fuels' must be regenerated ex-situ.

$\text{LiAlH}_4$  and  $\text{NaAlH}_4$  are complex metal hydrides with high hydrogen contents [1–3]. For example,  $\text{LiAlH}_4$  liberates

hydrogen in three steps at various temperatures, following the equations shown below [4]:



At temperature 175 °C, ~5.3 wt.%  $\text{H}_2$  can be produced in the presence of some catalysts or additives [5–12]. It was recently found in our lab that by solid-state chemical reaction with ammonium halide (e.g.  $\text{NH}_4\text{Cl}$ ), 1 mol of  $\text{LiAlH}_4$  can generate

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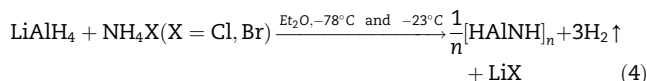
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3 mol of H<sub>2</sub> at similar temperature ~170 °C with very fast kinetics, corresponding to 8.1 wt.% H<sub>2</sub> with respect to the LiAlH<sub>4</sub>/NH<sub>4</sub>F system. Similar reaction between LiAlH<sub>4</sub> and NH<sub>4</sub>Br was previously reported, which was however carried out in Et<sub>2</sub>O solution at sub-ambient temperatures [13], following the equation below.



There are very few papers, studying the solid-state reactions between alkali aluminum hydrides and ammonium halide [14], and the reaction mechanism for the solid reactions is not clear.

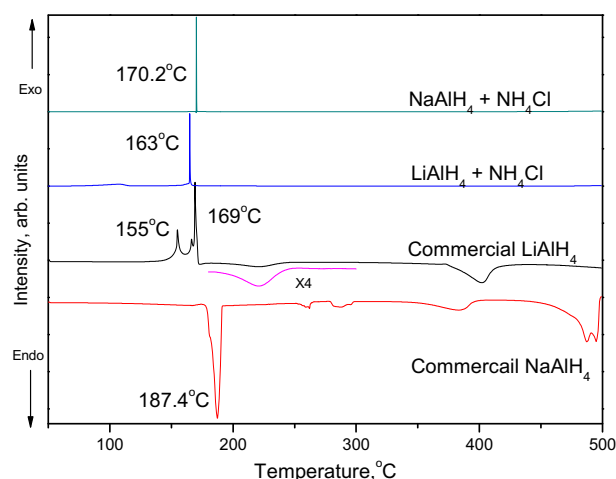
In this paper, solid reactions between alkali aluminum hydrides (MAH<sub>4</sub>, M = Li or Na) and NH<sub>4</sub>Cl were investigated quantitatively using temperature programmed reaction (TPR), thermo-gravimetric analysis (TGA), differential scanning calorimetry (DSC) and x-ray diffraction (XRD). The reaction mechanism was discussed.

## 2. Experimental

LiAlH<sub>4</sub> (Strem Chemicals, 95%), NaAlH<sub>4</sub> (Acros Organics, 93%) and NH<sub>4</sub>Cl (Kanto Chemical, 99%) were handled solely in an argon glove box. The reaction of LiAlH<sub>4</sub>/NH<sub>4</sub>Cl (or NaAlH<sub>4</sub>/NH<sub>4</sub>Cl) with 1:1 molar ratio was performed in a home-made TPR set-up. Each time, approximately 200 mg of the mixture was heated from room temperature to 50 °C in 30 min, and then to 500 °C with a ramp of 5 °C/min. Purified argon at 50 ml/min was used as the carrier gas. The outlet gas was monitored by on-line mass spectroscopy, while the quantities of hydrogen in the outlet gas were determined by water replacement method. Solid products were analyzed by XRD on Bruker AXS D8, using Cu-Kα<sub>1</sub> (λ = 1.8406 Å) radiation. DSC measurement was performed on Netzsch DSC-204, within an argon protected glove box. Purified helium was employed as carrier gas with a flow rate of 50 ml/min, and heating rate of 5 °C/min. Ball milling was carried out on a Retsch PM400/2 planetary ball mill machine, with stainless steel jars and balls. The ball/sample mass ratio was 30 and the jar volume was 250 ml. A tube furnace (Carbolite) was used to heat samples up to 1000 °C from room temperature with a ramp of 5 °C/min, argon was used as carrier gas with a flow rate of 30 ml/min.

## 3. Results and discussion

DSC profiles of the LiAlH<sub>4</sub>/NH<sub>4</sub>Cl and NaAlH<sub>4</sub>/NH<sub>4</sub>Cl mixtures (molar ratios were 1:1) in Fig. 1 show very sharp exothermic peaks (peaks width ~24 s, or 2 °C) at temperature 163 °C (for LiAlH<sub>4</sub>/NH<sub>4</sub>Cl) and 170 °C (NaAlH<sub>4</sub>/NH<sub>4</sub>Cl) respectively. There are no distinguished peaks from 200 °C to 500 °C. For comparison, DSC profiles of as-received pure LiAlH<sub>4</sub> and NaAlH<sub>4</sub> samples are also included in Fig. 1. The melting point of pure LiAlH<sub>4</sub> is 155 °C, while that of NH<sub>4</sub>Cl is 338 °C. The melting of LiAlH<sub>4</sub> should be endothermic. But due to the interaction of LiAlH<sub>4</sub> with surface hydroxyl impurities [15], exothermic peak is observed at 155 °C in Fig. 1, in agreement



**Fig. 1 – DSC profiles of as-received LiAlH<sub>4</sub> and NaAlH<sub>4</sub>; LiAlH<sub>4</sub>/NH<sub>4</sub>Cl and NaAlH<sub>4</sub>/NH<sub>4</sub>Cl mixtures (without ball milling).**

to some papers in literature [16,17]. It is widely accepted that the thermal decomposition of LiAlH<sub>4</sub> into Li<sub>3</sub>AlH<sub>6</sub>, H<sub>2</sub> and Al (which occurs at 150–170 °C as illustrated in Eq. (1)) is exothermic, while the decomposition of Li<sub>3</sub>AlH<sub>6</sub> into LiH, Al and H<sub>2</sub> (Eq. (2)) is endothermic [18]. Therefore the peak at 169 °C in Fig. 1 for the as-received LiAlH<sub>4</sub> is caused by the exothermic decomposition of LiAlH<sub>4</sub> into solid Li<sub>3</sub>AlH<sub>6</sub>, while the peak between 180 and 240 °C in Fig. 1 is the endothermic decomposition of Li<sub>3</sub>AlH<sub>6</sub>. The peak between 180 and 240 °C is not very strong compared to the exothermic peak. However by enlargement the peak position and the endothermic nature become evident. In comparison with pure LiAlH<sub>4</sub>, the exothermic peak at 163 °C in the DSC profile of LiAlH<sub>4</sub>/NH<sub>4</sub>Cl is most probably due to the reaction between LiAlH<sub>4</sub> and NH<sub>4</sub>Cl, since there is no thermal effect at higher temperature region (170–500 °C) and the LiAlH<sub>4</sub> decomposition can be excluded. Similarly, the melting and decomposition of as-received NaAlH<sub>4</sub> are observed at 182–187, 250–300, and 350–400 °C respectively (see the as-received NaAlH<sub>4</sub> profile in Fig. 1), and hence the DSC peak at 170 °C in the NaAlH<sub>4</sub>/NH<sub>4</sub>Cl DSC profile must be due to the reaction between NaAlH<sub>4</sub> and NH<sub>4</sub>Cl. These can be further confirmed by TPR equipped with mass spectroscopic (MS) analysis of the effluent gas.

The TPR-MS results of the mixtures of LiAlH<sub>4</sub>/NH<sub>4</sub>Cl and NaAlH<sub>4</sub>/NH<sub>4</sub>Cl (without ball milling) are shown in Fig. 2. There are sharp hydrogen peaks (blue color) at around 160 °C (for LiAlH<sub>4</sub>/NH<sub>4</sub>Cl) and 170 °C (for NaAlH<sub>4</sub>/NH<sub>4</sub>Cl) respectively. The NH<sub>3</sub> signal (black color) with low intensity is also observable in both LiAlH<sub>4</sub>/NH<sub>4</sub>Cl and NaAlH<sub>4</sub>/NH<sub>4</sub>Cl (without ball milling), starting at slightly lower temperature (than that of H<sub>2</sub>), reaching its maximum at the same peak temperatures as H<sub>2</sub>, with the second peak in a wide temperature range between 200 and 300 °C. There was no nitrogen found in the effluent gas. The H<sub>2</sub> release temperatures in the TPR-MS profiles coincide well with those in DSC profiles in Fig. 1, confirming that the sharp exothermic DSC peaks of the mixtures in Fig. 1

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