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High temperature- pressure processing of mixed alanate compounds

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ABSTRACT

Mixtures of light-weight hydrides and elements were investigated to increase the understanding of the chemical reactions that take place between various materials. This report details investigations we have made into mixtures that include NaAlH₄, LiAlH₄, MgH₂, Mg₂NiH₄, alkali(ne) hydrides, and early third row transition metals (V, Cr, Mn). Experimental parameters such as stoichiometry, heat from ball milling versus hand milling, and varying the temperature of high pressure molten state processing were studied to examine the effects of these parameters on the reactions of the complex metal hydrides. © 2008 Elsevier Ltd. All rights reserved.

1. Introduction

Solid state materials which store hydrogen with high gravimetric and volumetric densities are needed to develop a hydrogen economy for transportation applications. To this end, hydrogen containing solids of the light-weight elements are under intensive investigation [1–6]. Desirable materials properties include a high weight percent hydrogen (ideally wt% ≥ 9), rapid release and uptake of H₂ at pressures of 100 atm or less, and operation at fuel cell compatible temperatures ($T \leq 120 \,^{\circ}$ C). This combination of properties is challenging to achieve in one material, and while there are a variety of materials that exhibit one or more of these properties, no material to date meets all of the criteria. For instance, magnesium is abundant, relatively inexpensive, and MgH₂ has a large weight percent hydrogen (7.9%) but the temperature required for hydrogen evolution is about 300 °C, and the kinetics of hydrogenation are slow [7]. Titanium catalyzed NaAlH₄ is reversible and releases hydrogen at acceptable temperatures, but the kinetics are slow and the weight percent of 5.6% is insufficient [8-10]. One method of tailoring hydrogen storage properties is to combine two or more materials to create a new material with intermediate properties. One interesting example of this is Mg₂NiH₄, where the mixed metal hydride has a lower dehydrogenation temperature (~250°C vs 300°C for MgH₂) and better kinetics of hydrogenation. Researchers have investigated the effect of combining Mg₂NiH₄ with a variety of materials, e.g. transition metal oxides, Pd, and excess MgH₂, in order to improve properties [11].

Even with the constraint of focusing on the light-weight elements, there is a wide variety of mixtures to be investigated with the goals of understanding the chemical reactions that take place between various materials, and possibly creating a new material with improved properties. This report details investigations we have made into mixtures that include NaAlH₄, LiAlH₄, MgH₂, Mg₂NiH₄, alkali(ne) hydrides, and early third row transition metals (V, Cr, Mn), where V is used in the hydrided form to explore the effect of transition metal hydride versus bare transition metal.

2. Experimental

Mixtures were made by dry mixing in a Spex 8000 ball mill. The vial volume is 65 mL and two 12.7 mm and four 6.4 mm balls were used for mixing. Mixture components and balls were loaded into ball mill vials under an inert atmosphere (argon gas). Samples were typically milled for 60 min. Cold ball milling was performed by chilling the vial on dry ice for 5–10 min, then ball milling in 10 min increments with chilling of the vial between each milling cycle. Hand milling was performed with an agate mortar and pestle under Argon atmosphere. X-ray diffraction (XRD) samples were pressed onto quartz plates, and sealed with a thin film of polyethylene under argon atmosphere, then transferred to the diffractometer for analysis using Cu K_{α} radiation. On select samples, whole pattern fitting of the entire XRD pattern with Rietveld least squares refinement was used to determine estimates of weight percent for the crystalline phases present in the product mixture. The standard deviations reported are only for the refinement, they do not include errors such as sampling, sample preparation, solid substitution, etc. The semi-quantitative XRD data provided weight percent estimates for all product species; however, it was only the transition metal species and the Na₂LiAlH₆ which were statistically differentiated due to the large standard deviations. Molten state processing (MSP), an SRNL patented technique, was used to heat ball milled mixtures under

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high hydrogen gas pressure (usually 4500 psi) in order to synthesize possible new phases [12,13]. The premise is that the high H₂ pressure will favor the formation of products with high hydrogen content, following Le Châtelier's principle. Vanadium forms hydrides rather easily, so vanadium powder (Sigma-Aldrich 99.5%) was heated under vacuum/hydrogen cycles to create V_2H_{11} for use in these experiments [14]. The fully hydrided vanadium was not achieved, likely due to our low vacuum system (H/M ratio is vacuum dependent, see [14]). Note that V and H form a solid solution and other phases such as $\ensuremath{\mathsf{VH}}_{0.81}$ are also a good match for the XRD pattern. $V_2H_{1.1}$ was chosen because the single crystal structural data can be used for Rietveld refinement of product mixtures containing the V phase. Most compounds were purchased from Sigma-Aldrich, compound and purities are listed here: Cr (99.5%), Mn (99.99%), LiAlH₄ (95%), TiCl₃ (99.999%), CaH₂ (99.9), NaH (95%), LiH (95%). KH was obtained dispersed in mineral oil and separated by filtration from excess diethyl ether. Other suppliers include Gelest, MgH₂ (95%), Albemarle, NaAlH₄ and Ergenics/Hera, Inc. Mg₂Ni.

3. Results and discussion

Table 1 provides a comprehensive list of the mixtures that were investigated in this study. The mixtures we have explored include NaAlH₄, LiAlH₄, MgH₂ and Mg₂NiH₄ as the primary materials, with addition of alkali(ne) hydrides, and/or early third row transition metals (V, Cr, Mn) and occasionally TiCl₃. The metals Cr and Mn were chosen because they do not easily form hydrides under the conditions of our experiment, so the effect of a transition metal in "metal" form could be examined. Vanadium,

Table 1

Mixtures investigated in this study

immediately to the left of Cr on the periodic table, does form a hydride so $V_2H_{1.1}$ was used to explore the difference in chemical reactions of a transition metal versus a transition metal hydride additive. Note that the vanadium was not fully hydrided. Experimental parameters such as stoichiometry, temperature of ball milling, use of hand milling, and temperature of MSP were varied to study the effects of these parameters on the products. Starting materials are abbreviated SM for brevity in the table, and this indicates that all of the starting materials are seen in the XRD pattern of the indicated reaction step.

3.1. Mixtures of alanates and transition metals

3.1.1. Mixtures with Cr metal

The quaternary mixture, which has NaAlH₄, LiAlH₄, and MgH₂ mixed with Cr was first investigated with a simple 1:1:1:1 mixture. This treatment produced starting materials and aluminum metal. Previous observations have shown that the binary mixture of LiAlH₄ and various transition metals yields aluminum and starting materials, which have also been observed here [15]. This decomposition reaction is shown below:

$$3\text{LiAlH}_4 \rightarrow \text{Li}_3\text{AlH}_6 + 2\text{Al} + 3\text{H}_2 \tag{1}$$

Note that only the Al product is seen in the XRD pattern. Any Li_3AlH_6 produced does not show up in the XRD pattern, which is not uncommon as many of the expected Li containing species are not seen in XRD patterns of the products in this study. There are several possible reasons for the lack of XRD signal, including formation of an amorphous phase, X-ray absorption, or formation of nanoparticles.

Starting materials	Mol ratios	Milling conditions	MSP condi-tions (°C-psi H ₂ -time)	Ball milling products	Molten state processing products
NaAlH4:LiAlH4:Cr	1:1:1	Spex BM 60 min	170–4500–2h	SM+Al	NaAlH4, Cr, Na2LiAlH6, Al, NaH
NaAlH4:LiAlH4:Mn	1:1:1	Spex BM 60 min	190–4500–2h	SM+Al	Mn, Na ₂ LiAlH ₆ , Al, NaH
NaAlH4:LiAlH4:Mn	1:1:1	Spex BM 60 min	170–4500–2h	SM+Al	Mn, Na ₂ LiAlH ₆ , Al, NaH
NaAlH4:LiAlH4:MgH2:V2H1.1	1:1:1:1	Spex BM 60 min	170–4500–2h	SM+Al	LiAlH4:MgH2:V2H1.1, Al, Na2LiAlH6, NaMgH3, NaH
NaAlH ₄ :LiAlH ₄ :MgH ₂ :Cr	1:1:1:1	Spex BM 60 min	170–4500–2h	SM+Al	MgH ₂ , Cr, Al, Na ₂ LiAlH ₆ , NaMgH ₃ , NaH
NaAlH ₄ :LiAlH ₄ :MgH ₂ :Cr	1:1:1:1	Spex BM 60 min	60-4500-3 h	SM+Al	SM+Al, Li ₃ AlH ₆
NaAlH ₄ :LiAlH ₄ :MgH ₂ :Cr	1:1:1:1	cold ball mill	60-4500-3 h	SM	SM+Al, Li ₃ AlH ₆
NaAlH ₄ :LiAlH ₄ :MgH ₂ :Cr	1:1:1:2	Spex BM 60 min		SM+Al	
NaAlH4:LiAlH4:MgH2:Cr	1:1:1:4	Spex BM 60 min		NaAlH4, MgH2, Cr, Al, Li3AlH6	
NaAlH4:LiAlH4:MgH2:Cr	1:1:2:2	Spex BM 60 min		SM+Al	
NaAlH ₄ :LiAlH ₄ :MgH ₂ :Cr	1:1:2:1	Spex BM 60 min		SM+Al	
NaAlH ₄ :LiAlH ₄ :MgH ₂ :Mn	1:1:1:1	Spex BM 60 min	170–4500–2h	NaAlH ₄ :LiAlH ₄ :MgH ₂ MnH _{0.07} , Al	MgH ₂ , Mn, Na ₂ LiAlH ₆ , NaMgH ₃ , Al, NaH
NaAlH ₄ :V ₂ H _{1.1}	1:1	Spex BM 60 min		n/a-outgases	
NaAlH ₄ :Cr	1:1	Spex BM 60 min	190–4500–2h	SM	SM, Na ₃ AlH ₆
NaAlH ₄ :Mn	1:1	Spex BM 60 min	190–4500–2h	SM	SM, Na ₃ AlH ₆
LiAlH4:Cr	1:1	Spex BM 60 min	170–4500–2h	SM+Al	SM+Al, L _{i3} AlH ₆
LiAlH ₄ :Mn	1:1	Spex BM 60 min	170–4500–2h	SM+Al	Mn, Al
LiAlH ₄ :KH:TiCl ₃	1:2:.04	BM 40 min		LiAlH4, KAlH4, K3AlH6	LiAlH ₄ , KAlH ₄ , K ₃ AlH ₆ , KCl
LiAlH ₄ :MgH ₂ :TiCl ₃	1:1:.04	BM 40 min		MgH ₂ , Li ₃ AlH ₆ , Al, LiCl, Mg	MgH ₂ , Al, LiCl
LiAlH ₄ :CaH ₂ :TiCl ₃	1:1:.04	BM 40 min		SM, Li_3AlH_6 , Al	CaH _{2.} Al, LiCl, LiH
LiAlH ₄ :Mg ₂ NiH ₄	1:1			MgH ₂ , Mg ₂ NiH, Mg ₂ NiH _{0.3} , Al _{1.1} Ni _{0.8}	_,
NaAlH ₄ :Mg ₂ NiH ₄	1:1			SM, NaMgH ₃ , Mg ₂ NiH _{0.3}	
NaAlH ₄ :Mg ₂ NiH ₄ :TiCl ₃	1:1:.04	Mortar pestle		SM, MgH ₂ , Mg ₂ NiH _{0.2}	
NaAlH ₄ :Mg ₂ NiH ₄ :TiCl ₃	1:1:.04	BM 40 min		SM, Al, NaMgH ₃ , Mg ₂ NiH _{0.26}	
Mg2NiH4:NaH Mg2NiH4:LiH	1:1.2 1:9.9	Mortar pestle BM 40 min		SM, MgH ₂ , Mg ₂ NiH _{.26} SM, MgH ₂ , Mg ₂ NiH _{.26}	

SM denotes starting materials. BM denotes ball mill(ing). MSP denotes molten state processing.

(2)

When the mixture is further reacted with MSP conditions at 170 °C, the reaction yields mixed metal products as follows. Weight percent values from whole pattern XRD fitting are provided for the six products in the line below Eq. (2), with the estimated standard deviations given in parentheses, where weight percents are rounded off to match the decimal place of the standard deviation.

 $LiAlH_4 + NaAlH_4 + MgH_2 + Cr + Al$

→ (MSP, 170°C)
→
$$Na_2LiAlH_6 + NaMgH_3 + NaH + Al + MgH_2 + Cr$$

8.2 (0.6), 10.2 (0.8), 1.0 (0.3), 38 (2), 19 (1), 23 (2)

Assumptions as to the reactions that took place to form this mix of products are shown below in:

$$LiAlH_4 + 2NaAlH_4 \rightarrow Na_2LiAlH_6 + 2Al + 3H_2$$
(3)

$$NaAlH_4 + MgH_2 \rightarrow NaMgH_3 + Al + 3/2H_2$$
(4)

The product mixture contains evidence of NaH formation as well, with one clear peak in the XRD pattern as shown in Fig. 1. However, the identification of NaH is not definitive as only the 100% peak is observed, and that peak is small. The NaH likely comes from the partial decomposition of Na_2LiAlH_6 , as shown below:

$$Na_2LiAlH_6 \rightarrow 2NaH + LiH + Al + 3/2H_2$$
(5)

No evidence of LiH is seen in the XRD pattern, though it is likely present if NaH is. The probable NaH product is seen with MSP reactions above 60 °C for NaAlH₄:LiAlH₄ mixtures containing Cr, Mn and $V_2H_{1.10}$ as additives.

These Cr mixtures were explored further by varying the ratio of starting materials away from the simple 1:1:1:1 mixtures. The Cr and the MgH₂ mol ratios were varied to see if this would change the reaction products. When the Cr content was doubled, regardless of the MgH₂ content, ball milling resulted in starting materials and Al. When the mol ratio of Cr was increased to 4:1, ball milling alone causes the LiAlH₄ to decompose to Li₃AlH₆. This result is not unexpected, as other researchers have reported that ball milling LiAlH₄ with transition metal additives causes the alanate to decompose [15–17].

The temperature of ball milling was another experimental parameter that was varied. A typical 60 minute ball milling reaction creates enough heat to warm the vials to approximately 60 °C. In order to separate the effect of mechanical mixing from the effect of exothermic heating during mixing, the 1:1:1:1 Cr mixture was ball milled "cold" by cooling the vial every 10 min for a total of 60 min of milling time; the vials did not exceed room temperature during milling with this method. The cold ball



Fig. 1. X-ray diffraction pattern of the 170 °C molten state processing products of the quaternary mixture NaAlH₄:LiAlH₄:MgH₂:Cr with mole ratios of 1:1:1:1.

milling prevented the decomposition of LiAlH₄ and only the starting materials were observed in the XRD pattern, where regular ball milling showed the presence of starting materials and aluminum. The cold ball milled mixture, and the regular ball milled mixture, were further reacted under MSP conditions at a low temperature of 60 °C (usually done at 170 °C or higher). The low temperature MSP yields starting materials, Al, and Li₃AlH₆ regardless of ball milling conditions. Note that in this case the Li₃AlH₆ is present in the XRD pattern. The Al peak is much more intense after the MSP than after the ball milling, so presumably the three hour heating provides energy for grain growth of Al and Li₃AlH₆, and/or the quantity of products has increased with heat, to a level of Li₃AlH₆ detectable by XRD.

3.1.2. Mixtures with Mn metal

The quaternary mixture of both alanates, MgH₂ and Mn is interesting in that it yields MnH_{0.07} with just ball milling, in addition to the non-Mn starting materials and Al. The hydrogen originates from LiAlH₄ decomposition with ball milling. When this mixture is heated via MSP, the MnH_{0.07} decomposes leaving Mn along with other products shown in Eq. (6) below. Weight percent values from whole pattern XRD fitting are provided for the six products in the line below Eq. (6). The information present for NaMgH₃ and NaH in the XRD is limited, so the least squares program was unable to determine estimated standard deviations for these two phases.

3.1.3. Mixtures with $V_2H_{1.1}$

The quaternary mixture of NaAlH₄:LiAlH₄:MgH₂:V₂H_{1.1} at 1:1:1:1 forms starting materials and Al with ball milling. The MSP reaction of this mixture at 170 °C results in the product mixture shown below in Eq. (7); the XRD pattern of the MSP product for the quaternary V₂H_{1.1} mixture is shown in Fig. 2.

$$\begin{split} \text{LiAlH}_4 + \text{NaAlH}_4 + \text{MgH}_2 + \text{V}_2\text{H}_{1.1} + \text{Al} \\ &\rightarrow (\text{MSP}, 170\ ^\circ\text{C}) \\ &\rightarrow \text{Na}_2\text{LiAlH}_6 + \text{NaMgH}_3 + \text{NaH} \\ &\quad + \text{Al} + \text{MgH}_2 + \text{V}_2\text{H}_{1.1} + \text{LiAlH}_4 \\ &\quad 20\ (2), 12\ (2), 2\ (2), 33\ (3), 14\ (1), 5 \end{split}$$



Fig. 2. X-ray diffraction pattern of the 170 °C molten state processing products of the quaternary mixture NaAlH₄:LiAlH₄:MgH₂:V₂H_{1.1} with mole ratios of 1:1:1:1.

Note that the LiAlH₄ seen is a high temperature-pressure phase for which the structure has not been solved, so the weight percent could not be found with least squares-this is an estimate of the upper limit based on the relative peak intensities of this phase. When the transition metal additive contains vanadium, LiAlH₄ remains in the product mixture, while it does not for either Cr or Mn. This suggests that the $V_2H_{1,1}$ is catalyzing the decomposition of the alanates to a lesser extent than the Cr and Mn reactants, which are in the elemental state. However, the product phase Na₂LiAlH₆ does show the highest weight percent for the V₂H_{1.1} mixture relative to Cr and Mn, indicating that the vanadium catalyzes the decomposition to a greater extent than the Cr and Mn reactants. Given that only the crystalline phases appear in the XRD patterns, and sample pyrophoricity prevents examination by complementary techniques on our electron microscopes, we note that there is a difference in the reaction of the vanadium versus the chromium and manganese guaternary samples and further investigation is needed to better characterize this subtle variance.

3.2. Mixtures of alanates and Mg₂NiH₄

The Mg₂NiH₄ was ball milled with: (1) LiAlH₄, (2) NaAlH₄, and (3) NaAlH₄ with 4 mol% TiCl₃ to explore the affect of the Ni component on the alanate materials. The mixture with LiAlH₄ results in the starting Mg compound completely decomposing with ball milling to form four products: MgH₂, Mg₂NiH, Mg₂NiH_{0.3} and Al_{1.1}Ni_{0.9}. The Mg₂NiH₄ partially disproportionated to MgH₂ and Ni. No crystalline Li species are present, and it is likely that the LiAlH₄ has decomposed to some extent, providing the Al metal which then combines with the Ni to form the aluminum rich AlNi phase.

The ball milled mixture with NaAlH₄ has only one product in common with the LiAlH₄ mixture, and that is Mg₂NiH_{0.3}. There are also starting materials present after ball milling, as well as the previously known mixed metal hydride NaMgH₃. When 4 mol% TiCl₃ is added in addition to NaAlH₄, Mg₂NiH_{0.26} is formed along with NaMgH₃ and Al, and starting materials remain. If the mixture with TiCl₃ is hand ground in a mortar and pestle (much lower energy than a ball mill) the mixed metal hydride NaMgH₃ does not form, which suggests that the energy and/or heat associated with ball milling is required for this reaction to take place.

3.3. Mixtures of LiAlH₄ and binary hydrides

Mixtures of LiAlH₄, 4 mol% Ti, and the binary hydrides: (1) KH, (2) MgH₂ and (3) CaH₂ were investigated. Ball milling the mixture with KH produced two ion exchange compounds, KAlH₄ and K₃AlH₆, and left unreacted LiAlH₄ which continued the ion exchange with MSP. Ball milling with MgH₂ causes the LiAlH₄ to completely decompose to form Li₃AlH₆ which is an indicator that the MgH₂ has a catalytic effect on LiAlH₄ decomposition. The combination containing CaH₂ produced starting materials, Li₃AlH₆, and Al with ball milling, indicating that the LiAlH₄ partially decomposes while the CaH₂ does not react. When heated with MSP, this mixture forms CaH₂, Al, LiCl and LiH, which are expected products from the decomposition of LiAlH₄ and reaction of the chloride from TiCl₃ with Li decomposition products.

3.4. Mixtures of Mg₂NiH₄ and binary hydrides

The mixed metal compound Mg_2NiH_4 was ball milled with: (1) LiH and (2) NaH. In both cases, the mixtures yielded starting materials, MgH_2 , and $Mg_2NiH_{2.6}$, and in the case of LiH, some Mg was present as well.

4. Conclusion

A wide variety of hydride mixtures, with and without light transition metal additives, were investigated. This work provides insight into the relative chemical stabilities of chemical reactions that take place between four hydride materials that are candidates for transportation applications, if the systems can be modified to overcome either temperature, kinetic or weight percent limitations.

The addition of transition metal elements to NaAlH₄ does not create mixed metal alanates with ball milling, and MSP generally produces a decomposition product, Na₃AlH₆. The addition of elements or other hydrides destabilizes LiAlH₄—when mixed with Cr or Mn, Al is observed, while mixtures with binary hydrides produce the hexahydride, Li₃AlH₆ (or K₃AlH₆ in the case of KH).

NaAlH₄ in combination with Mg materials often produces NaMgH₃. When the Mg compound used is Mg₂NiH₄, NaMgH₃ forms with just ball milling. Mixtures with MgH₂ do not form the mixed metal hydride unless heated above 60 °C in the MSP step. Two explanations are likely, first that the presence of Ni catalyzes the decomposition of NaAlH₄, and second that Mg₂NiH₄ is less kinetically stable, and therefore more reactive, than MgH₂. The temperature effect is seen in the hexahydride product as well, but for a different reason. Mixtures containing LiAlH₄ and NaAlH₄ form mixed metal Na₂LiAlH₆ with MSP of 170 °C or higher, while Li₃AlH₆ is formed with MSP at 60 °C rather than the mixed metal product. The difference in products is likely due to the fact that at 60 °C, all of the materials are solids, and diffusion in the solid state is very slow. When the reaction temperature is increased above the melting point of LiAlH₄ (125 °C), molten LiAlH₄ can mix with the other ingredients much more easily, and the mixed metal hexahydride Na2LiAlH6 forms.

Quaternary mixtures lead to known mixed metal products Na_2LiAlH_6 and $NaMgH_3$. When the transition metal additive is Cr or Mn, no residual LiAlH₄ reactant remains but residual MgH₂ does, while the transition metal additive $V_2H_{1.1}$ leaves LiAlH₄ reactant remaining in the product mixture, while simultaneously producing a greater weight percent of crystalline Na_2LiAlH_6 relative to Cr and Mn reactions.

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