RISK MITIGATION STRATEGIES FOR HYDROGEN STORAGE MATERIALS

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ABSTRACT

Hydrogen is seen as an ideal energy carrier for stationary and mobile applications. However, the use of high energy density materials such as hydrides comes with the drawback of risks associated to their high reactivity towards air and water exposure. We have developed novel strategies to mitigate these risks. These strategies were evaluated using standard UN tests and isothermal calorimetric measurements. Cycling experiments were conducted to assess the impact of the mitigants on the modified materials derived from $8LiH \bullet 3Mg(NH_2)_2$ system. In some cases, our results show an improvement in kinetics when compared to the unmodified material. Effective mitigants were also discovered for aluminum hydride (alane) and lithium borohydride, completely inhibiting ignition.

1.0 INTRODUCTION

Hydrogen is generally perceived as an ideal candidate to be an energy carrier while at the same time reducing the environmental effects typically caused by petroleum-based products such as gasoline. Hydrogen storage is one of the leading challenges that must be met for the realization of a hydrogen economy. There has been significant interest in understanding the chemical and hydrogen properties in intermetallics (e.g. $LaNi_5$), metal hydrides [1] complex metal hydrides such as alanates [2-4], borohydrides [5-7], amides [8-10], and adsorbents [11-16]. Although there is an increased interest in the use of this technology for stationary as well as mobile applications, there is limited knowledge on the details involving potential environmental reactivity risks associated with these materials, and even less on how to reduce the risks associated with the environmental exposure of hydrogen storage materials.

This work presents a thorough study on the amelioration of risks associated with Li-Mg-N-H, alane and lithium borohydride systems. Several strategies were developed at Savannah River National Laboratory in an attempt to either reduce or eliminate the potential for vigorous reaction either with air or water. All the materials in this study showed a significantly higher reactivity towards water rather than air. The focus of this paper will be directed towards the reactivity upon exposure to water. For this reason, the water drop test was selected as the test to assess the effectiveness of different modifiers to lower or mitigate completely the reactivity towards air and water. The conceptualized methods for reducing these risks are: Lewis/Acid bases as stabilizers, heat sink materials, and the incorporation of low-melting endothermic compounds. In addition other additives involving combination of the aforementioned strategies or chemical modifications were also attempted. In addition to the strategies developed, this paper includes the results from some commonly used flame retardants (e.g brominated compounds, aluminum trihydrate, etc.)

EXPERIMENTAL

Materials

The lithium hydride – magnesium amide 8:3 mol ratio mixture was received from Kuriyama (AIST). The material preparation has been described elsewhere [17]. The samples were prepared by Spex milling the materials with its respective modifiers for approximately 5 minutes. The modifiers (which were used as risk mitigants) used were triphenyl phosphate, magnesium stearate, sodium hydroxide, hydrotalcite, decabromodiphenyl ether, were all spex milled separately before subsequent ball milling with $8LiH \cdot 3Mg(NH_2)_2$.

Alane was sourced from Dow Chemical. Aurin tricarboxylic acid ammonium salt was purchased in its powder form from Aldrich. Alane was Spex milled for approximately 10 minutes. The ball to sample weight ratio was 10:1.

Lithium borohydride 90% purity (from Aldrich) was ballmilled for 1 hour. Modifiers (i.e. lithium hydroxide, lithium carbonate, lithium metaborate) were all purchased from Alfa Aesar and Spex milled for 1 hour before use. The lithium borohydride modified samples were prepared by physical mixing for approximately 15 minutes using the appropriate amounts.

Methods

Water Drop Test

The UN standardized Water Drop Test was used to study the reactivity of the samples to water exposure. More details can be found in ref [18]. The test material was formed into a small pile approximately 20 mm high and a 30 mm diameter with a hollow at the top. A few drops of water were added to the hollow. If spontaneous ignition occurred at any time, the substance was classified as a water reactive material emitting flammable gases. No further testing is necessary within the frame of the U.S. standardized test.

Calorimetry

To quantify the heat released through contact with dry and humidified air, oxidation and hydrolysis studies were performed in a Calvet calorimeter. The heat flow (mW) was normalized with respect to the mass of hydride and plotted versus time. Controlled humidity air reaction measurements were conducted at 40 °C and 30% relative humidity. For these measurements, the calorimeter equipped with a flow cell utlilizing either argon or air as the carrier gas with a flow rate of 10 ml/min reacting with 5-10 mg of solid. The reference cell contained an equivalent amount of mitigant in order to correct for the thermal properties of the modifier by itself.

RESULTS AND DISCUSSION

There were three systems selected for study for developing These systems were $8LiH \cdot 3Mg(NH_2)_2$, alane and lithium borohydride. Due to the excessively high reactivity of $8LiH \cdot 3Mg(NH_2)_2$ towards air and water [17] and the increasing interest in amide-containing systems for vehicle applications, the system was more thoroughly tested for the development of risk amelioration methods. This material was received from AIST.

Lithium Hydride-Magensium amide (8:3 ratio)

Figure 1 shows the results from the test conducted with triphenyl phosphate (TPP) as modifier. The unmodified sample ignites upon contact with one water droplet. A sustained flame is generated that last a couple of minutes. In contrast, the sample modified with 20 wt. % TPP did not exhibit ignition when in contact with water. The sample started having a reaction with water, changing in temporarily to a dark violet color while charring. Additional drops were added in attempt to increase the contact of water with the material, but no ignition was observed. Also, the material turned into a hard brittle crust while reacting to water. TPP has been previously reported to have flame retardancy effects [19-22]. It has been found that among phosphorus-based flame retardants, TPP and its analogs are the most effective for many polymers including acrylonitrile-butadiene-styrene co-polymer (ABS) [23]. Also TPP, has a waxy texture that will potentially coat the particles inhibiting direct contact to water. One important characteristic of this modifier is that it possesses a low melting of 48-52°C and a relatively high boiling point at 247-250°C [24]. This is a property that can potentially further reduce the possibility of an ignition event by the endothermic effects these phase changes possess. A sample containing 10 wt. % TPP was also tested and exhibited lower reactivity towards water as it took a longer time to have an ignition event and lasted a shorter period of time compared to the unmodified sample.

The $8LiH \cdot 3Mg(NH_2)_2$ system was also tested with magnesium stearate, due to the low melting point of this additive. This additive is widely used in the food and pharmaceutical industry because of its lubricating properties, as well as for its low cost. Magnesium stearate is the magnesium salt of stearic acid that melts at 88 °C, property that was thought to be advantageous for this application. The rationale behind using this additive was first to provide a coating to the hydride particles and to absorb part of the heat released through the heat of fusion as the magnesium stearate melts. This is a concept that can be extended further using other additives, but the obvious advantages of low cost, and benign

nature of this material in terms of health effects, made magnesium stearate our model additive. The modified sample containing this additive however did not showed any difference to the control sample, igniting upon contact with a water droplet. Although this additive proved to be unsuccessful avoiding the ignition event in the $8LiH \cdot 3Mg(NH_2)_2$ system, it is thought as a promising additive for other systems.

Another additive tested was the conventional Mg/Al hydrotalcite. Hydrotalcite is a naturally occurring anionic clay. Hydrotalcite has the exact chemical formula $[Mg_6Al_{12}(OH)_{16}CO_3 \cdot 4H_2O]$. LDH's, also known as hydrotalcite-like compounds, are positively charged metal mixed hydroxide layers stacked together. In order to maintain overall charge neutrality, the presence of interlayer anions is required. These materials can either be naturally occurring or be synthesized chemically [25].

LDHs are generally represented by the formula $[M^{2+}_{1-X}M^{3+}_X(OH)_2]^{x+}(A_{x/n})^{n-} \cdot mH_2O]$ where the divalent $M^{2+} = Ca^{2+}$, Mn^{2+}, Zn^{2+}, etc., and the trivalent $M^{3+} = Al^{3+}$, Cr^{3+}, Mn^{3+}, etc., where "x" is the ratio of $(M^{3+}/ M^{2+} + M^{3+})$, which ranges between x = 0.2-0.4) and A^{n-} is charge balancing anions. The overall electrical neutrality is maintained by anions in the interlayers such as CO_3^{2-} and NO_3^{2-}. The remaining space is occupied by water molecules during the crystallization process. Hydrotalcites are being proposed as alternatives to inorganic hydroxides, such as Aluminum trihydrate, $Al(OH)_3$, and magnesium hydroxide, $Mg(OH)_2$ [26]. These are very commonly used flame retardants that work by suppressing smoke through the release of steam [27, 28]. Recently, Camino et al [29] showed that hydrotalcite is a better flame retardant than Aluminum trihydrate and magnesium hydroxide, attributing part of its improved effectiveness to the layered structure. One positive aspect of these modifiers (i.e. inorganic hydroxides and LDH's) is that the remaining products after reaction are essentially harmless. Hydotalcite was marginally effective as mitigant reducing slightly the time of sustained ignition.

Auminum trihydrate was used as mitigant due to its acidity as well as it is one of the most commonly used flame retardants. The effectiveness of this compound as flame retardant is related to its endothermic decomposition that takes place between 180 and 200 °C leading to the release of steam which dilutes flammable gases and promotes the formation of thermal insulating protective coating of alumina [20].

$$2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O \quad \Delta H = 73 \text{ kJ/mol}$$
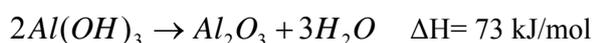
The aluminum trihydrate sample showed no differences in reactivity compared to the pristine sample. Thus, this mitigant proved to be ineffective. It is still uncertain if the production of steam derived from this mitigant is affecting the effectiveness due to inherent reactivity of the hydride material to water.

Aluminum powder (17 μm) was tested as additive on the system. The rationale behind using this material as risk mitigant was its high specific heat capacity of approximately 0.91 kJ/kg. Thus it would potentially work as a heat sink. Based on this, it was expected that aluminum particles would be able to absorb a significant amount of the heat released during the oxidation and hydrolysis reaction of the material. Samples were prepared by physical mixing with various amounts of aluminum ranging from 5 to 30 wt %. The results from our UN water drop tests suggest that the effect of the additive is negligible until 30 wt. % where inconsistent results were obtained. The inconsistency of these results might be due to a poor dispersion of the modifier in the mixture. However, even in such a situation that the dispersion is greatly enhanced by the use of this additive at amounts larger than 30 wt. % the use of this additive will not be feasible for practical purposes.

The use of sodium hydroxide and lithium hydroxide was also tested and found to be marginally effective. Samples required high loadings, ~30 wt% in order to inhibit an ignition event. However, results from calorimetric measurements suggest hydroxides are particularly useful for decreasing the heat released when in contact with humid atmospheric conditions. This result is of particular interest,

since the fire suppressing action of these hydroxides involves the release of steam. A detailed discussion on calorimetry results is included in the next section.

Although brominated compounds have been subject of the debate because of its potential toxicity to the nervous and endocrine systems [30-35], it is undisputable that these compounds have excellent flame retardancy effects. Decabromodiphenyl ether, better known as Deca-BDE, is the most commonly flame retardant used commercially, mostly in polymer applications. In general halogenated compounds have been shown be effective flame retardants, being brominated compounds the most commonly used not only because of its effectiveness, but also because of its thermal stability. Green et al [36]proposed the following working mechanism, in which HBr competes for the radical species OH· and H·. These two active species are crucial for the propagation of the flame.

$$H^\bullet + HBr \rightarrow H_2 + Br^\bullet$$

$$^\bullet OH + HBr \rightarrow H_2O + Br^\bullet$$
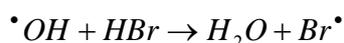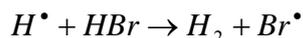
Thus the active radical species responsible for the flame propagation (i.e. OH· and H·), are replaced by Br·, which is considerably less active, slowing the rate of energy production which eventually results in extinguishing the flame. In practical applications, Deca-BDE is rarely used by itself. It is commonly used in combination with antimony oxide (Sb_2O_3) in 2:1 to 3:1 halogen/antimony ratio. Although antimony oxide does not provide any flame inhibition properties by itself, it has a synergistic effect on halogen compounds. The action of antimony oxide consists on the formation of antimony oxyhalides and trihalides in the condensed phase, by reacting with the halogenated flame retardant (e.g. Deca-BDE). This will ease the transfer of halogen and antimony to the gas phase where they do actually work.

Water drop test on the $8LiH\cdot 3Mg(NH_2)_2$ system was performed using Deca-BDE and the combination of Deca-BDE with antimony oxide. Both samples showed a more vigorous reaction towards water than the control sample. The increase in reactivity is hypothesized to be associated with the side reactions leading to the formation of lithium bromide and magnesium, which are highly exothermic. The use of antimony oxide did not improve the effectiveness of the modifier, further supporting our hypothesis.

Calorimetry

Calorimetric studies under humid conditions (30% RH) at 40 °C were conducted in samples containing TPP, sodium hydroxide and iron oxide as potential risk mitigants. Figure 2 shows the results for the calorimetric measurements for the mitigant-containing samples. With the exception of the sample containing sodium hydroxide, all samples released comparable heat rates, as can be easily observed by the areas under the heat flow vs. times curves. These results suggest that neither TPP nor iron oxide affect the release of hydrogen under the experimental conditions. The total heat released by the sample containing sodium hydroxide, is significantly reduced compared to the unmodified sample.

Since the occurrence of an ignition event is not solely dependent on the amount of heat released, but also on how quick the heat is released, the first derivative of heat flow with respect to time in all sample was analyzed (shown in Figure 2, right side). The heat release rate results showed that iron oxide achieves the highest release rate and in slightly less time, suggesting that a catalytic effect might be present in the modified sample. The unmodified and TPP-modified samples showed similar heat release rates whereas the sodium hydroxide-modified sample shows significantly slower heat release rate.

Effect of Mitigant on Cyclic Performance

Isothermal cyclic measurements were performed using a Sieverts apparatus (HyEnergy) on samples at 200 °C, 100 bar for absorption and 1 bar for desorption. All samples were prepared by adding 20 wt.% of the mitigant followed by high-energy (Spex) ballmilling using a 10:1 ball to sample weight ratio for 5 minutes. Figure 3 shows the average hydrogen desorption capacities for all samples up to the fourth cycle, discarding the data from the first desorption. The unmodified samples showed an average capacity of ~3.2 wt. % H_2. Surprisingly, none of the mitigants significantly had a negative impact on the amount of hydrogen desorbed from the sample. Actually, TPP had comparable desorption capacity to the unmodified sample whereas the hydrotalcite-modified sample shows an improvement from 3.2 for the unmodified sample, to 3.7 wt % H_2.

The use of TPP as mitigant not only arose from the fact that it is a very efficient flame retardant but also as an attempt for enhancing the kinetics of the material. Recently, Wang et al [37]reported a remarkable kinetic enhancing effect in the similar $2LiH \cdot Mg(NH_2)_2$ mixture, where the results indicate that dehydrogenation and hydrogenation can be successfully achieved at temperatures below 150 °C. They found that TPP reacts with LiH and $Mg(NH_2)_2$ exothermically during the ball-milling process to form a stable compound that does not change during the cycling process. An effect was also observed on the durability of the material upon cycling, suggesting that TPP not only affects the system kinetics but also the thermodynamics, through the persistence of amorphous $Mg(NH_2)_2$. The nature of the interaction is believed to take place between the benzene ring and LiH or $Mg(NH_2)_2$, as the FTIR results suggest.

Figure 4 shows the desorption measurements obtained on a Sieverts apparatus for $8LiH \cdot 3Mg(NH_2)_2$ and the TPP-modified sample. Similar to the findings on the $2LiH \cdot Mg(NH_2)_2$ mixture, TPP shows an enhancing effect in the desorption kinetics. Although some of the cycles shown in Figure 4 are not in equilibrium, it is evident that the pristine material is suffering degradation as the cycling proceeds whereas the TPP-modified sample remained essentially unaffected. The sample was cycled for 15 cycles and there was no measured decrease in performance.

Lithium borohydride

Lithium borohydride, a hydride with acidic character, reacts with a strong base and becomes neutralized. Figure 5 shows the results of the water drop test of pure lithium borohydride and 5 mol% (5.5 wt.%) LiOH/LiBH4. Pure lithium borohydride reacts vigorously upon in contact with a water droplet, giving of some sparks followed by a sustained flame that last for a few minutes. In contrast, the samples modified with lithium hydroxide showed diminished reactivity towards water even at very low contents, as the 1 mol % LiOH/LiBH4 ignited after being in contacts with nine water droplets. No ignition was observed in the 5 mol% $LiOH/LiBH_4$ sample. This presents a quick, simple and scalable technique to modify a sample, without compromising the hydrogen storage capacity of a material.

Other modifiers such as lithium carbonate and lithium metaborate were also tested. Lithium carbonate was marginally effective at high loadings, making it not practical. Lithium metaborate showed no effect in the reactivity of the sample.

Alane

Alane is generally thought to be a metastable material that shows no reactivity towards air. However, one the main safety concerns with this material is at the time the material is either on fully or partially dehydrogenated state, since the presence of pure bare aluminum metal will potentially cause a vigorous reaction under the presence of air or water. So in order to simulate these conditions, chemically synthesized (from Dow Chemical) alane was ballmilled in a high-energy Spex 8000 mill for 10 minutes in order to activate the material. Aurin tricarboxylic acid ammonium salt, most commonly referred as Aluminon was used as mitigant for alane. Aluminon is traditionally used as indicator of the presence of aluminum in aqueous solutions in colorimetric analytical methods. The bright red color is obtained with the intensity being dependent of the amount of Al(III) species

coordinated, pH and presence of interfering species (e.g. Fe). A detailed review on the application and limitations of aluminon as reagent for the detection of aluminum species is found in [38]. Figure 6 shows the water drop test for the pristine and modified samples with aluminon.

The unmodified alane sample ignited upon in contact with a water droplet. The flame and sparks were very bright white and intense. The modified sample, which contains 20 wt. % aluminon showed no reactivity towards water. XRD measurements (Figure 7) were conducted to determine any crystallographic changes upon modifying the sample; however changes in the pattern are very subtle, indicating no impact on the crystal structure.

The TGA results, shown in Figure 8 showed no impact of the mitigant (aluminon) on alane, as both samples follow the identical behavior, starting the weight loss at about 130 °C and ending at about 155°C. The total weight loss obtained for the modified sample was approximately 80 % of the loss obtained for the pristine sample, further indicating that the mitigant by itself does not hinder the desorption of hydrogen on alane. Thus the aluminon modification represents a low-cost strategy to modify alane.

CONCLUSIONS

Risk amelioration methods for $8LiH \cdot 3Mg(NH_2)_2$, lithium borohydride and alane were developed. Due to the high reactivity of these materials to water rather than air exposures, the modified materials were evaluated using UN Water Drop Test. TPP proved to be an effective mitigant with enhanced effects on the kinetics and durability upon cycling. Aluminon-modified alane did not show any reactivity to water, as shown through the Water Drop Test and XRD. For the case of Li-OH-lithium borohydride, the sample undergoes reaction and dissolves. The mitigating effect on lithium borohydride is observed even at very low contents of the mitigant (~1%).
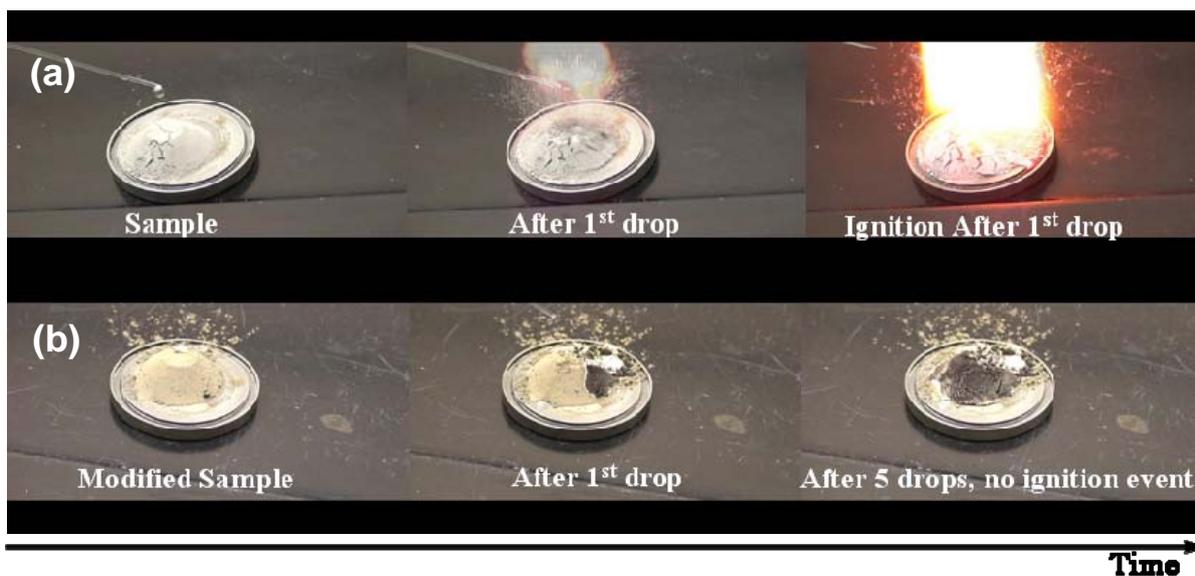
Figure 1. Water Drop Test for (a) 8LiH·3Mg(NH$_2$)$_2$ and (b) TPP-modified sample.
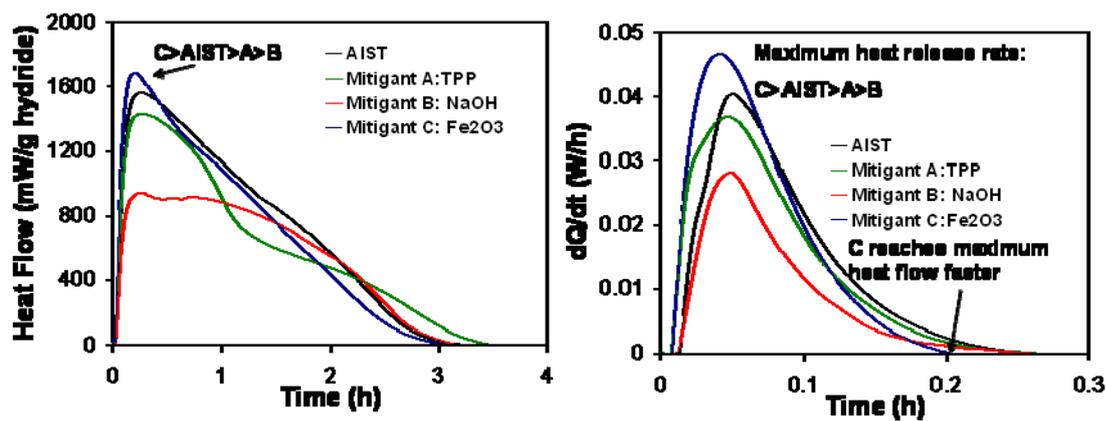
Figure 2. Calorimetry results for modified samples of 8LiH·3Mg(NH$_2$)$_2$ (left) heat flow as function of time; and (right) first heat derivative with respect to time.
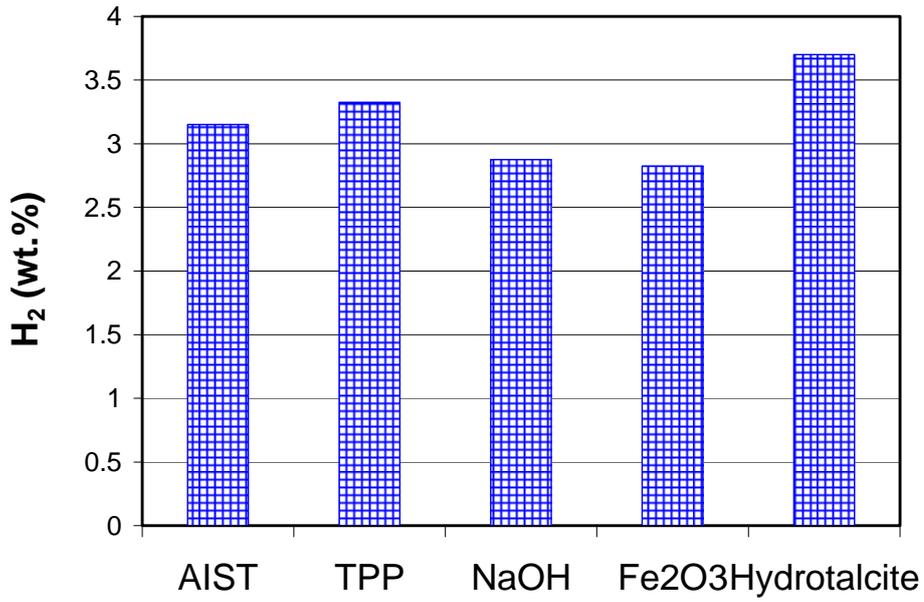
Figure 3. Average desorption capacities of 8LiH·3Mg(NH$_2$)$_2$, shown as AIST, and mitigant-containing samples. TPP; sodium hydroxide; iron oxide; and Hydrotalcite.
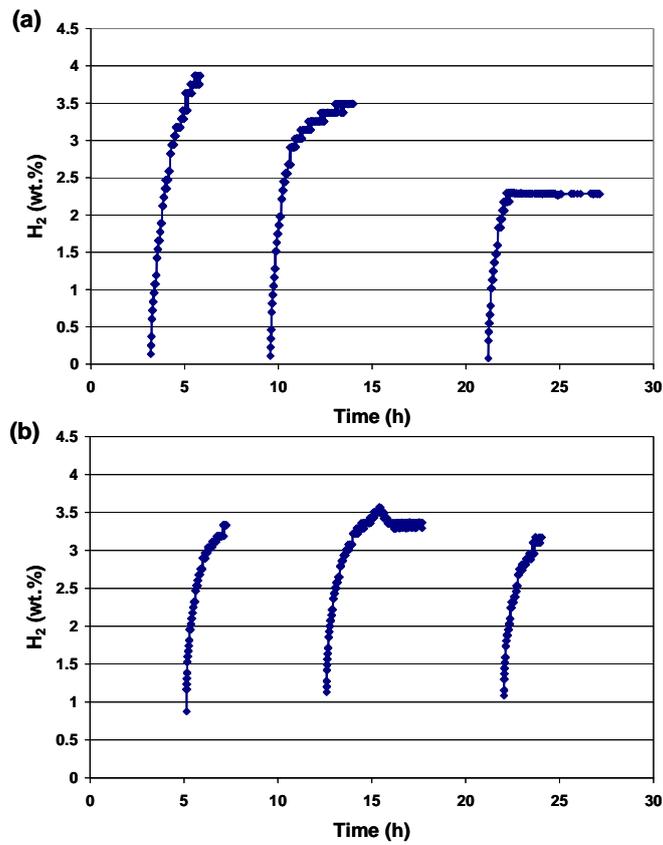
Figure 4 Hydrogen desorption measurement of (a) 8LiH·3Mg(NH$_2$)$_2$ and (b) TPP-modified sample.

Figure 5. Water Drop Test of (a) LiBH$_4$, and (b) 5 mol % LiOH-LiBH$_4$.
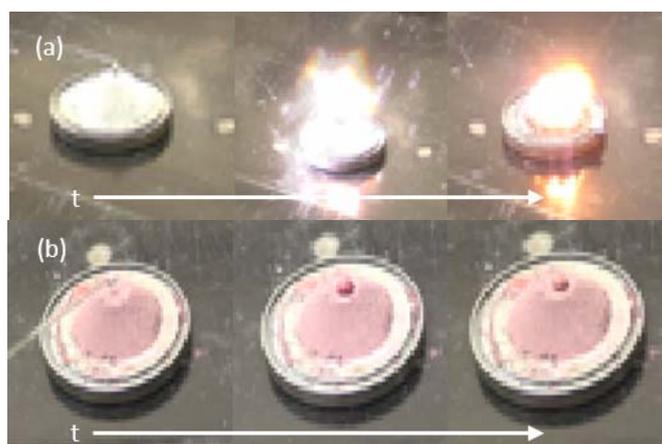
Figure 6. Water Drop Test of (a) unmodified and (b) modified alane with 20 wt% aluminon.
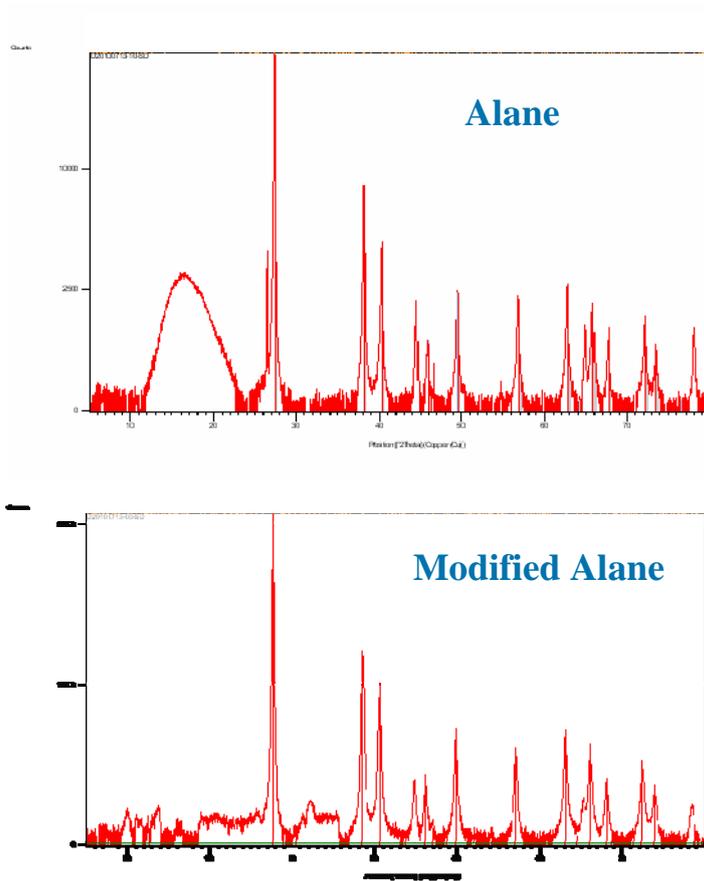
Figure 7. X-ray diffractograms of alane (top); and 20 wt.% Aluminon-alane.
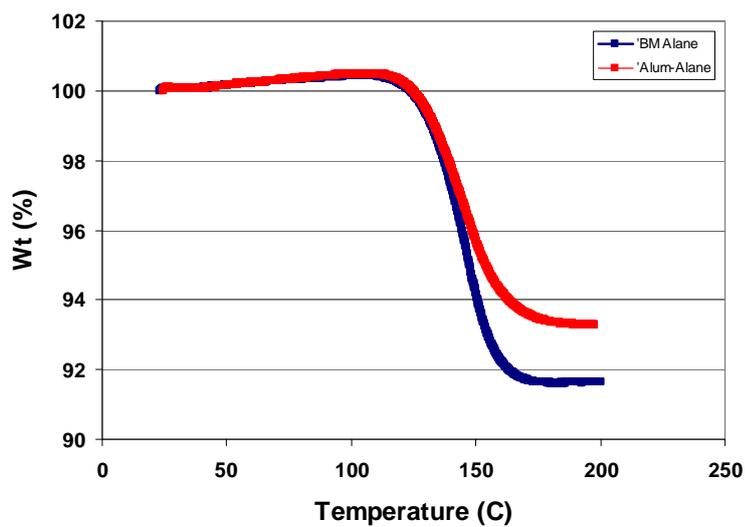
Figure 8. TGA results for Alane (blue); and Aluminon-alane (red).

References

[1]   Sakintuna B, Lamari-Darkrim F, Hirscher M. Metal hydride materials for solid hydrogen storage: A review. International Journal of Hydrogen Energy 2007;32:1121.
[2]   Anton DL. Hydrogen desorption kinetics in transition metal modified NaAlH4. Journal of Alloys and Compounds 2003;356-357:400.
[3]   Walters RT, Scogin JH. A reversible hydrogen storage mechanism for sodium alanate: the role of alanes and the catalytic effect of the dopant. Journal of Alloys and Compounds 2004;379:135.
[4]   Bogdanovic B, Felderhoff M, Germann M, Härtel M, Pommerin A, Schüth F, Weidenthaler C, Zibrowius B. Investigation of hydrogen discharging and recharging processes of Ti-doped NaAlH4 by X-ray diffraction analysis (XRD) and solid-state NMR spectroscopy. Journal of Alloys and Compounds 2003;350:246.
[5]   Züttel A, Wenger P, Rentsch S, Sudan P, Mauron P, Emmenegger C. LiBH4 a new hydrogen storage material. J Power Sources 2003;118:1.
[6]   Züttel A, Rentsch S, Fischer P, Wenger P, Sudan P, Mauron P, Emmenegger C. Hydrogen storage properties of LiBH4. Journal of Alloys and Compounds 2003;356-357:515.
[7]   Au M. Hydrogen Storage Reversibility of LiBH4 Based Materials. Presentation at the Fall 2005 MRS Meeting, Boston, MA, 2005.
[8]   Pinkerton FE. Decomposition kinetics of lithium amide for hydrogen storage materials. Journal of Alloys and Compounds 2005;400:76.
[9]   Song Y, Yang R. Decomposition mechanism of magnesium amide Mg(NH2)2. Int J Hydrogen Energy 2009;34:3778.
[10]   Lu J, Choi YJ, Fang ZZ, Sohn HY. Effect of milling intensity on the formation of LiMgN from the dehydrogenation of LiNH2-MgH2 (1:1) mixture. J Power Sources;195:1992.
[11]   Chen X-W, Su DS, Hamid SBA, Schlogl R. The morphology, porosity and productivity control of carbon nanofibers or nanotubes on modified activated carbon. Carbon 2007;45:895.
[12]   Dillon AC, Gilbert, K.E.H., Parilla, P.A., Horbacewicz, C., Alleman, J.L., Jones, K.M., Heben, M.J. Hydrogen Storage in Carbon Single-wall Nanotubes. Hydrogen, Fuel Cells, and Infrastructure Technologies 2003.
[13]   Schlichtenmayer M, Streppel B, Hirscher M. Hydrogen physisorption in high SSA microporous materials - A comparison between AX-21_33 and MOF-177 at cryogenic conditions. International Journal of Hydrogen Energy;36:586.
[14]   Yürüm Y, Taralp A, Veziroglu TN. Storage of hydrogen in nanostructured carbon materials. International Journal of Hydrogen Energy 2009;34:3784.
[15]   Züttel A, Sudan P, Mauron P, Kiyobayashi T, Emmenegger C, Schlapbach L. Hydrogen storage in carbon nanostructures. International Journal of Hydrogen Energy 2002;27:203.
[16]   Thomas KM. Hydrogen adsorption and storage on porous materials. Catalysis Today 2007;120:389.
[17]   Tanaka H, Tokoyoda K, Matsumoto M, Suzuki Y, Kiyobayashi T, Kuriyama N. Hazard assessment of complex hydrides as hydrogen storage materials. International Journal of Hydrogen Energy 2009;34:3210.
[18]   United Nations Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, 3rd revised edition, 1999.
[19]   Xiao J, Hu Y, Yang L, Cai Y, Song L, Chen Z, Fan W. Fire retardant synergism between melamine and triphenyl phosphate in poly(butylene terephthalate). Polymer Degradation and Stability 2006;91:2093.
[20]   Laoutid F, Bonnaud L, Alexandre M, Lopez-Cuesta JM, Dubois P. New prospects in flame retardant polymer materials: From fundamentals to nanocomposites. Materials Science and Engineering: R: Reports 2009;63:100.
[21]   Kim J, Lee K, Lee K, Bae J, Yang J, Hong S. Studies on the thermal stabilization enhancement of ABS; synergistic effect of triphenyl phosphate nanocomposite, epoxy resin, and silane coupling agent mixtures. Polymer Degradation and Stability 2003;79:201.

[22]   Lee K, Kim J, Bae J, Yang J, Hong S, Kim H-K. Studies on the thermal stabilization enhancement of ABS; synergistic effect by triphenyl phosphate and epoxy resin mixtures. Polymer 2002;43:2249.

[23]   Anderson CE, Ketchum DE, Mountain WP. Fire Science 1998;6:390.

[24]   Triphenyl Phosphate MSDS No. L08130 Alfa Aesar 2009.

[25]   Rives V. Layered Double Hydroxides: Present and Future Nova Science Pub Inc 2001.

[26]   Wang L, Su S, Chen D, Wilkie CA. Variation of anions in layered double hydroxides: Effects on dispersion and fire properties. Polymer Degradation and Stability 2009;94:770.

[27]   Almeida Pinto U, Visconte LLY, Gallo J, Nunes RCR. Flame retardancy in thermoplastic polyurethane elastomers (TPU) with mica and aluminum trihydrate (ATH). Polymer Degradation and Stability 2000;69:257.

[28]   Zhang X, Guo F, Chen J, Wang G, Liu H. Investigation of interfacial modification for flame retardant ethylene vinyl acetate copolymer/alumina trihydrate nanocomposites. Polymer Degradation and Stability 2005;87:411.

[29]   Camino G, Maffezzoli A, Braglia M, De Lazzaro M, Zammarano M. Effect of hydroxides and hydroxycarbonate structure on fire retardant effectiveness and mechanical properties in ethylene-vinyl acetate copolymer. Polymer Degradation and Stability 2001;74:457.

[30]   Darnerud PO. Toxic effects of brominated flame retardants in man and in wildlife. Environment International 2003;29:841.

[31]   Hakk H, Letcher RJ. Metabolism in the toxicokinetics and fate of brominated flame retardants--a review. Environment International 2003;29:801.

[32]   Legler J. New insights into the endocrine disrupting effects of brominated flame retardants. Chemosphere 2008;73:216.

[33]   Legler J, Brouwer A. Are brominated flame retardants endocrine disruptors? Environment International 2003;29:879.

[34]   Messer A. Mini-review: Polybrominated diphenyl ether (PBDE) flame retardants as potential autism risk factors. Physiology & Behavior;100:245.

[35]   Sjödin A, Patterson DG, Bergman Å. A review on human exposure to brominated flame retardants--particularly polybrominated diphenyl ethers. Environment International 2003;29:829.

[36]   Green J. Mechanisms for Flame Retardancy and Smoke suppression -A Review. Journal of Fire Sciences 1996;14:426.

[37]   Wang J, Hu J, Liu Y, Xiong Z, Wu G, Pan H, Chen P. Effects of triphenyl phosphate on the hydrogen storage performance of the Mg(NH2)2–2LiH system. Journal of Materials Chemistry 2009;19:2141.

[38]   Clark RA, Krueger GL. Aluminon:Its Limited Application as a Reagent for the Detection of Aluminum Species. The Journal of Histochemistry and Cytochemistry 1985;33:729.