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Accelerated thermal decomposition of AlH_3 for hydrogen-fueled vehicles

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ABSTRACT The potential for using aluminum hydride, AlH_3, for vehicular hydrogen storage is explored. It is shown that particle-size control and doping of AlH_3 with small levels of alkali-metal hydrides (e.g. LiH) results in accelerated desorption rates. For AlH_3–20 mol % LiH, 100 °C desorption kinetics are nearly high enough to supply vehicles. It is highly likely that 2010 gravimetric and volumetric vehicular system targets (6 wt % H_2 and 0.045 kg/L) can be met with onboard AlH_3. However, a new, low-cost method of off-board regeneration of spent Al back to AlH_3 is needed.

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1 Introduction

Interest in hydrogen-fueled vehicles is rapidly growing. The major challenge is on-board hydrogen storage [1]. Compressed H_2 gas and cryogenic liquid H_2 have practical volume and other technical limitations. Solid adsorbents (carbon) and absorbents (metal hydrides) have possibilities [2, 3], but none yet approach the US Department of Energy 2010 storage system goals at 6.0 weight percent gravimetric and 0.045 kg/L volumetric H capacities [4]. For reversible metal hydrides, the greatest potential and activity seem to be in the alkali-metal alanates [5, 6] and Li-based amides [7], where reversible gravimetric capacities of at least 5 wt % H seem to be possible, but not necessarily at desorption temperatures < 100 °C, i.e. at predominant fuel cell or internal combustion engine waste heat temperature levels.

It has long been assumed that hydride recharging would be done on board, with a 2010 target recharge rate of 1.5 kg H_2/min (3.3 min for a 5 kg H_2 tank) [4]. But it is an immense problem to remove the exothermic heat of hydriding at that charging rate. For example, if we charged H_2 at 1.5 kg/min into a vehicular storage tank based on $NaAlH_4$ ($\Delta H = -37$ kJ/mol H_2 [5, 6]), we would have to remove heat at the rate of 450 kW! This would require very substantial and costly heat-exchange means and would seem to practically eliminate the possibility of quick on-board recharging. If off-board recharging is really to be the paradigm, then we should expand our hydride search to materials that may not be considered easily reversible. In this paper we reconsider the long-overlooked (and not easily recharged) elemental hydride AlH_3 (aluminum hydride, alane).

2 Basics of aluminum hydride

AlH_3 is a covalent binary hydride known for more than 60 years [8]. It often takes polymeric $(AlH_3)_n$ forms. There are at least six structures of AlH_3 [9], not to mention other solvated versions [10]. In principle, the following simple desorption reaction would generate 10.1 wt % H_2 and common, nontoxic Al powder:

$$AlH_3 \rightarrow Al + 3/2H_2 \,. \qquad (1)$$

For thermodynamic reasons, this reaction is highly favorable and not easily reversed. H_2 gas pressures above 2.5 GPa are needed to rehydride Al powder back to AlH_3 [11, 12]. So, we are really proposing a lightweight, low-volume hydride source of vehicular fuel that must be recharged off-board after its use by a new, yet to be developed, process. Here we consider only the desorption properties of α-AlH_3.

In spite of its very large dissociation pressure, AlH_3 is metastable at room temperature. It can be easily handled in air, inert gas and vacuum without decomposition. This metastability is generally assumed to be due to the presence of an Al_2O_3 layer surrounding each AlH_3 particle and serving to effectively encapsulate the contained hydrogen. It is clear that AlH_3 can be decomposed by modest heating, typically in the 60–200 °C range, depending on the form and structure [8–17]. It was the principal purpose of our work to improve the H_2-desorption properties of α-AlH_3 over those reported nearly 25 years ago [16, 17]. In particular, we show below that the use of particle-size control and 'doping stimulants' can result in AlH_3 decomposition kinetics at 100 °C that are nearly adequate to supply H-fueled vehicles.

3 Experimental

The AlH_3 we used is the α (trigonal/rhombohedral, $R\overline{3}c$) version made by Dow Chemical in 1975 from $LiAlH_4$ and $AlCl_3$ by a wet (ether solvent) chemical process [9, 10]. It is the

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most stable form [9] and is virtually solvent free. It is the same batch used in the 1980 kinetic studies of Herley et al. [16, 17]. When it was received more than a quarter-century ago, it contained 8.3 wt % H, i.e. somewhat lower than the 10.1 wt % expected of pure AlH_3. However, in an impressive testimony to its shelf life in air, the hydride still contains 8.0 wt % H. The sample consists of translucent, approximately 50–100-μm cuboidal particles [17].

Particle-size reduction was accomplished and dopants were introduced by high energy planetary ball milling (Fritsch Pulverisette 6 at 200 rpm), using a 250-cm^3 stainless steel vial, seven 15-mm-diameter balls and 1.5-g samples (64:1 ball:powder ratio, by mass). The ball-mill vial is equipped with a pressure transducer and a thermometer, which allow instantaneous radio transmission of pressure and temperature data during milling. Samples were evaluated by temperature programmed desorption (TPD), whereby the sample being tested is heated at a constant rate (2 °C/m) and the desorbed H_2 collected in a previously evacuated volume. Pressure during desorption ranged from 0 to 60 kPa. The specimen reactor was a 13-mm-diameter stainless steel tube (electrically heated by wrapped resistive tape) containing a Type K thermocouple in the center of the sample bed. Arrhenius kinetic analysis was done using a stepped temperature technique [18]. Ball milled sample particle sizes were roughly estimated from scanning electron microscope (SEM) examination. X-ray diffraction (XRD) studies were performed on as-ball-milled, partially desorbed and fully desorbed samples.

4 Results and discussion

The first series of experiments looked at the effect of reduction of particle size by high-energy ball milling (BM). Figure 1 shows the TPD curves for as-received (∼ 100 μm), 1 h BM (∼ 1 μm) and 3 h BM (∼ 0.3 μm) powder. It is clear that particle-size reduction does effectively lower the desorption-temperature range. Whereas the as-received AlH_3 powder desorbs in the temperature range of 175–200 °C, one hour of ball milling reduces the temperature range to 125–175 °C. The levels of desorbed H_2 shown in Fig. 1 (7–8 wt %) are not matched by any easily reversible hydride at < 200 °C, as far as we know. Because the first hour of BM is reasonably effective, this period was used for subsequent doping experiments.

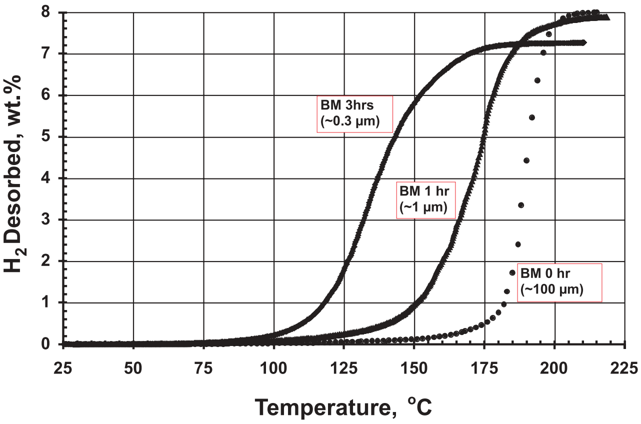

FIGURE 1 Effect of ball-milling time (and particle size) on temperature programmed desorption (TPD) scans of AlH_3. Scan rate = 2 °C/min

The second series of experiments on AlH_3 used doping additions that would be expected to alloy with Al, thus facilitating the breaking of Al–H bonds. Well-known examples from the phase-diagram literature include Ni and Ti. But neither had any measurable effect. We also tried CaH_2 as a potential reductant of the Al_2O_3 surface oxide. Again, there was little or no beneficial effect.

What did give very positive results was the addition of alkali-metal hydrides such as LiH, NaH, KH, $LiAlH_4$, etc. Figure 2 shows the effects of the addition of 10–50 mol % LiH to AlH_3 on the TPD curves. The desorption temperatures of the 10 and 20% LiH doped samples were reduced 40–50 °C from the pure 1-h BM AlH_3 sample. The 20% doped sample even shows significant desorption starting below 100 °C, albeit at an ultimate capacity of less than 7 wt %. We are performing X-ray diffraction (XRD) studies to better understand why the alkali-metal hydrides are such good stimulants. These studies so far indicate that small quantities of fine alanate particles form during ball milling (e.g. $LiAlH_4$ in the LiH case, or $NaAlH_4$ and $KAlH_4$ in the NaH and KH doping cases). The most likely mechanism of doping then is the formation of surface layers or islands of alanate that serve as ‘windows’ for hydrogen egress from the decomposing AlH_3.

The sweeping TPD data of Figs. 1 and 2 are good for screening purposes, but do not give a good kinetic picture relative to the requirements of a vehicle fuel supply. For this purpose, we determined isothermal desorption curves for the 80% AlH_3–20% LiH composition. The 100 °C results are shown in

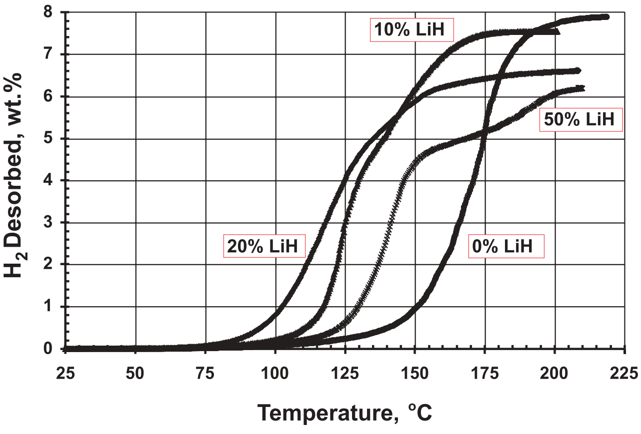

FIGURE 2 Effect of LiH doping on the TPD scans of one-hour-ball-milled AlH_3–LiH mixtures. LiH levels expressed in mol percent. Scan rate = 2 °C/min

Fig. 3. As implied by the 20% LiH TPD curve in Fig. 2, there are two desorption stages: relatively rapid kinetics for the first four hours (about 4 wt % H_2) and then significantly lower kinetics after a short transition period. The temperature dependences of both stages were determined and the results are shown in Fig. 4 as Arrhenius plots of rate (on a logarithmic scale) vs. reciprocal absolute temperature. The exponential fit of the rate data show that the desorption kinetics of both stages follow thermally activated behavior of the form

$$\text{Rate} = k_0 \exp(-Q/RT), \quad (2)$$

where the rate is in wt %/h, k_0 is the rate constant, Q is the thermal activation energy (J/mol H_2), R is the gas constant (8.315 J mol^{-1} K^{-1}) and T is absolute temperature (K). Values of k_0 and Q for the two stages of 1-h-ball-milled 80% AlH_3–20% LiH are listed in the Fig. 4 caption.

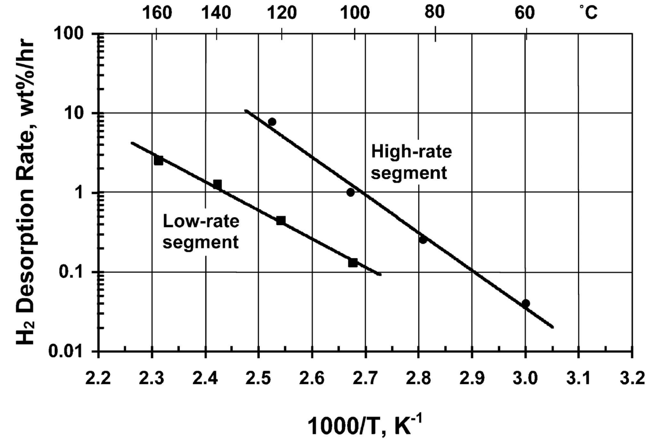

FIGURE 4 Arrhenius desorption plots of 80 mol % AlH_3–20 mol % LiH for the high-rate and low-rate segments (cf. Fig. 3). High-rate data taken from 0–1 wt % H_2 desorbed and low-rate data from 0–6.5 wt %. *Straight lines* show data are exponential with reciprocal temperature and obey the Arrhenius equation: rate (wt %/h) $= k_0 \exp(-Q/RT)$. For the high-rate segment, $k_0 = 6.5 \times 10^{12}$ and $Q = 91.3$ kJ/mol H_2. The fit for the lower-rate stage gives $k_0 = 5.4 \times 10^8$ and $Q = 68.2$ kJ/mol

Figure 4, and the related equation (2), offer a convenient basis to judge the desorption kinetics of 80% AlH_3–20% LiH relative to vehicle-supply requirements. If we have an 8–10 wt % H-storage medium and assume a five-hour driving time, then we need desorption rates on the order of 1.6–2 wt %/h. From Fig. 4, 2 wt %/h would require about 107 °C for the initial (0–3.5 wt %) portion of the decomposition curve and about 151 °C for the low-rate (> 4 wt %) portion. Thus the initial part of the AlH_3 desorption curve comes close to vehicle requirements if we have 100 °C waste heat available for decomposition. But the later part of the curve will require further improvements in kinetics. The two-stage desorption behavior may represent incomplete grinding of the AlH_3 particles and mixing of the dopant, and can hopefully be eliminated by optimization of the grinding process.

Although Ti doping of AlH_3 alone did not have benefit, we should mention that we have had positive results in that direction by combining LiH and Ti dopants, even to the point of achieving significant desorption rates at room temperature (to be published). So, the beneficial effects of Ti and other direct alanate dopants [5, 6] apparently carry over to AlH_3 containing surface alanate particles.

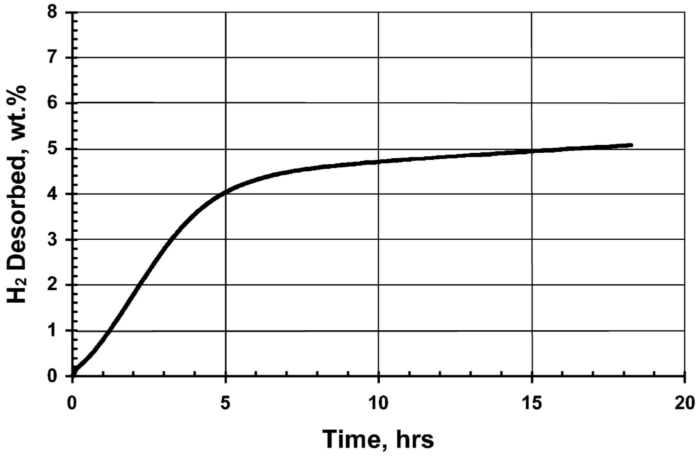

FIGURE 3 100 °C isothermal desorption curve of 80 mol % AlH_3–20 mol % LiH. Note the initial, high-rate desorption segment (0–3.5 wt % H_2 desorbed) and the later low-rate segment (> 4.5 wt % H_2 desorbed). Sample not carried to complete second-stage desorption

5 System weight, volume and safety considerations

This preliminary work clearly suggests that doped AlH_3 has a very good chance of reaching the 2010 gravimetric system goal (6 wt % H_2) [4], especially if we can make more pure AlH_3 with an initial capacity closer to the theoretical 10 wt % H. In addition, there are a few unusual 'engineering' considerations that should help in minimizing system weight relative to storage-medium weight, i.e. allowing thin-walled containers, minimal heat exchange and minimal desorption waste heat requirements from the fuel cell or internal combustion engine:

1. Even though it is thermodynamically quite unstable, doped AlH_3 can be stored near atmospheric pressure. During service, H_2 desorption would be controlled by temperature.
2. The endothermic heat of H_2 desorption from α-AlH_3 is unusually low, only about 7.6 kJ/mol H_2 [15], a fraction of that of the sodium alanates (37 and 47 kJ/mol H_2 for $NaAlH_4$ and Na_3AlH_6, respectively [5, 6]).
3. The decomposition of AlH_3 to Al and H_2 does not seem to result in any significant decrepitation (particle-size reduction), as also noted earlier by Herley et al. [17]. Because the spent Al will be recharged off-board, there are no special onboard container accommodations required for cyclic decrepitation and expansion.

Detailed safety studies surely need to be done. After all, like the alanates and borohydrides, one considered application of AlH_3 is as an additive to solid rocket fuel [19]. The Na alanates (especially Na_3AlH_6) are considered to be pyrophoric or highly flammable [20]. For comparison, air exposures were made of 1-h-ball-milled 80% AlH_3–20% LiH. It was not spontaneously pyrophoric after ball milling, but was after H removal. Undoped AlH_3 was not found to be pyrophoric in the 1- or 3-h-ball-milled states, before or after dehydriding.

Finally, how close will AlH_3 come to meeting the 2010 volumetric DOE H-capacity target (0.045 kg H_2/L) [4]? The density of α-AlH_3 is 1.48 g/cm^3 (1.48 kg/L) [21]. If we assume full 10 wt % gravimetric H capacity, then crystalline AlH_3 has a volumetric capacity of 0.148 kg H_2/L, more than double that of liquid H_2. If we further assume that 50% of the system volume must be left for void space, internal heat exchangers, primary container and other components, we still have a volumetric capacity of 0.074 kg H_2/L, more than 60% higher than the 2010 target.

6 Conclusions

We believe that this preliminary work has set the stage for serious consideration of dopant-stimulated, microcrystalline α-AlH_3 for onboard vehicular hydrogen supply. More work needs to be done to optimize capacity and H_2 desorption kinetics via doping species and techniques, as well as to understand the fundamentals. We need to closely examine structural forms of AlH_3 other than the α-phase. Finally, and most importantly, we need to develop off-board techniques for the economic rehydriding of spent Al back to AlH_3, e.g. by electrolytic means. All these R&D activities are continuing at DOE's Brookhaven, Sandia and Savannah River National Laboratories. In addition, we pose these challenges to the hydride and materials science R&D communities.

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REFERENCES

1 L. Schlapbach, A. Züttel: Nature **414**, 353 (2001)
2 M. Hirscher: Appl. Phys. A **72**, 129 (2001)
3 L. Schlapbach: MRS Bull. **27**, 675 (2002)
4 Anon.: 'Hydrogen Storage Draft'. In: *Multi-year Research, Development, and Demonstration Plan Planned Activities for 2003–2010*, US DOE Hydrogen, Fuel Cells & Infrastructure Technologies Program, 2003 [http://www.eere.energy.gov/hydrogenandfuelcells/mypp/]
5 B. Bogdanovic', G. Sandrock: MRS Bull. **27**, 712 (2002)
6 C.M. Jensen, K.J. Gross: Appl. Phys. A **72**, 213 (2001)
7 P. Chen, Z. Xiong, J. Luo, J. Lin, K.L. Tan: Nature **420**, 302 (2002)
8 B. Siegel, G. Libowitz, G.G. Libowitz: in *Metal Hydrides*, ed. by W.M. Mueller, J.P. Blackledge, G.G. Libowitz (Academic, New York 1968) p. 545
9 F.M. Brower, N.E. Matzek, P.F. Reigler, H.W. Rinn, C.B. Roberts, D.L. Schmidt, J.M. Snover, K. Terada: J. Am. Chem. Soc. **98**, 2450 (1976)
10 A.E. Finholt, A.C. Bond, H.I. Schleshinger: J. Am. Chem. Soc. **62**, (1947)
11 B. Baranowski, M. Tkacz: Z. Phys. Chem. NF **135**, 27 (1983)
12 S.K. Konovalov, B.M. Bulychev: Inorg. Chem. **34**, 172 (1995)
13 P. Claudy, B. Bonnetot, J.M. Letoffe: J. Therm. Anal. **15**, 129 (1979)
14 P. Claudy, B. Bonnetot, J. Etienne, J. Turck: J. Therm. Anal. **8**, 255 (1975)
15 G.C. Sinke, L.C. Walker, F.L. Oetting, D.R. Stull: J. Chem. Phys. **47**, 2759 (1967)
16 P.J. Herley, O. Christofferson, R. Irwin: J. Phys. Chem. **85**, 1874 (1981)
17 P.J. Herley, O. Christofferson, J.A. Todd: J. Solid State Chem. **35**, 391 (1980)
18 G. Sandrock, K. Gross, G. Thomas: J. Alloys Compd. **339**, 299 (2002)
19 V. Lindner: in *Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 10*, 4th edn., ed. by J.I. Kroschwiz, M. Howe-Grant (Wiley, New York 1993) p. 69
20 D. Anton: 'High Density Hydrogen Storage System Demonstration Using $NaAlH_4$ Based Complex Compound Hydrides'. In: *2004 Annual Program Review*, US DOE Hydrogen, Fuel Cells & Infrastructure Technologies Program, 2004 [http://www.eere.energy.gov/hydrogenandfuelcells/2004_annual_review.html]
21 J.W. Turley, H.W. Rinn: Inorg. Chem. **8**, 18 (1969)