Catalyzed Complex Metal Hydrides

Borislav Bogdanović and Gary Sandrock

Abstract

Complex hydrides are mixed ionic–covalent compounds that can serve as reversible H_2 storage media only when they are catalyzed by a transition metal such as Ti. As the prime example, the phenomenology of Ti-catalyzed sodium alanate ($NaAlH_4$) is reviewed from a historical perspective. Dehydriding yields a theoretical 5.6 wt% H_2 during two-step decomposition, $NaAlH_4 \rightarrow Na_3AlH_6 \rightarrow NaH + Al$, although 100% recovery of that H_2 is not currently possible. H_2 can be discharged and recharged at practical rates at 125°C. More work is needed on the alanates, in particular, as well as the identification and optimization of the catalytic mechanism and a broad extension of the concept to other than Na-based alanates. The possibility of an even further extension of the concept to other complex hydrides (e.g., the borohydrides and transition-metal complexes) is discussed.

Keywords: *hydrogen storage, kinetic properties, metal hydrides.*

Introduction

There is a practical need for improved H_2 storage methods with high inherent gravimetric capacity, for example, to carry hydrogen for fuel-cell vehicles. The history and potential of rechargeable metal hydrides for this purpose are presented elsewhere in this issue, clearly showing that we in the hydride field have been hampered by fundamental thermodynamic and kinetic limitations. On the one hand, interstitial hydrides that are easily reversible around room temperature (e.g., those based on V or the AB, AB_2, and AB_5 intermetallic compounds) represent essentially metallic H bonding and are limited to only about 1.5–2.5 wt% reversible gravimetric H capacity. At the other extreme, we have reversible hydrides that exhibit strong covalent or ionic H bonding (e.g., MgH_2 and LiH, respectively) that can provide good gravimetric H capacity (7–13 wt%), but unfortunately require temperatures greater than 250°C to release the bound H. This basic dilemma has existed for many years.

Bogdanović et al. suggested a new and different approach, starting in 1996, namely, the use of catalyzed alkali metal alanates, for example, Ti-doped $NaAlH_4$ and Na_3AlH_6.[1,2] Because this approach offers the clear potential of achieving >5 wt% H storage capability at temperatures that are only modestly greater than ambient (e.g., 50–100°C), past thermodynamic barriers were considered to be breached. Early

work at the Max-Planck-Institut für Kohlenforschung in Mülheim, Germany (MPI—Mülheim), was quickly confirmed by other investigators and has resulted in the generation of a great deal of worldwide interest (both fundamental and practical) over the past five years. It is our purpose here to briefly review the fundamentals of the catalyzed alanates and the recent practical progress made and then to comment on the need for future research and development in this area. In particular, we will suggest that the catalyzed alanate complex hydrides may have more general applicability to other complex hydrides. We do not cover here the aqueous complex hydride solutions (e.g., $NaBH_4$) that are catalytically hydrolyzed to generate H_2 gas.[3]

Chemistry and Thermodynamics of $NaAlH_4$ and Na_3AlH_6

The $NaAlH_4$ and Na_3AlH_6 mixed ionic–covalent complex hydrides have been known for many years. As shown schematically in Figure 1, $NaAlH_4$, for example, consists of a Na^{1+} cation and a covalently bonded $[AlH_4]^{1-}$ complex. In the case of Na_3AlH_6, there is a related $[AlH_6]^{3-}$ complex. These alanates have been synthesized by both indirect and direct methods and used as chemical reagents (see Reference 2 for a historical review of alanate synthesis). However, the practical key to

using the Na alanates for hydrogen storage is to be able to easily accomplish the following reversible two-step dry-gas reaction:

$$NaAlH_4 \rightleftharpoons 1/3Na_3AlH_6 + 2/3Al + H_2$$
$$\rightleftharpoons NaH + Al + 3/2H_2. \qquad (1)$$
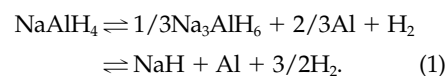
Stoichiometrically, the first step consists of 3.7 wt% H_2 release, and the second step 1.9 wt% H_2 release, for a theoretical net reaction of 5.6 wt% reversible gravimetric H storage. Although Dymova et al. showed that the reversibility of Reaction 1 was possible,[4,5] the conditions required were impractical in their severity. For example, the formation of $NaAlH_4$ from the elements required temperatures of 200–400°C (i.e., above the 183°C melting point of the tetrahydride) and H_2 pressures of 100–400 atm. Fortunately, the addition of a Ti catalyst makes the reversibility of Reaction 1 profoundly easier, as we shall show, and thus much more practical for H storage.

The thermodynamics of Reaction 1 are classic and comparable with many other metallic, ionic, and covalent hydrides. As shown in Figure 2, typical low-hysteresis, two-plateau absorption and desorption isotherms can be measured.[2] Temperature dependencies of the plateau pressures P are related to the van't Hoff equation

$$\ln P = \Delta H/RT - \Delta S/R, \qquad (2)$$

where ΔS is the entropy change, R is the gas constant, and the enthalpy changes ΔH for the $NaAlH_4$ and Na_3AlH_6 decompositions are about 37 kJ/mol H_2 and 47 kJ/mol H_2, respectively. This allows the direct comparison of the Na-alanate thermodynamic properties with those of other typical hydrides by means of the van't Hoff diagram of Figure 3. We see that $NaAlH_4$ has thermodynamics comparable to those of classic low-temperature (LT) hydrides $LaNi_5H_6$ and TiFeH—that is, in the range useful for a near-ambient-temperature hydrogen store. Na_3AlH_6 requires about 110°C for H_2 liberation at atmospheric pressure and is therefore less convenient
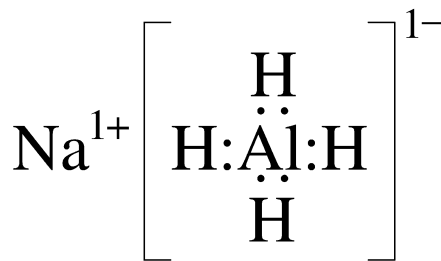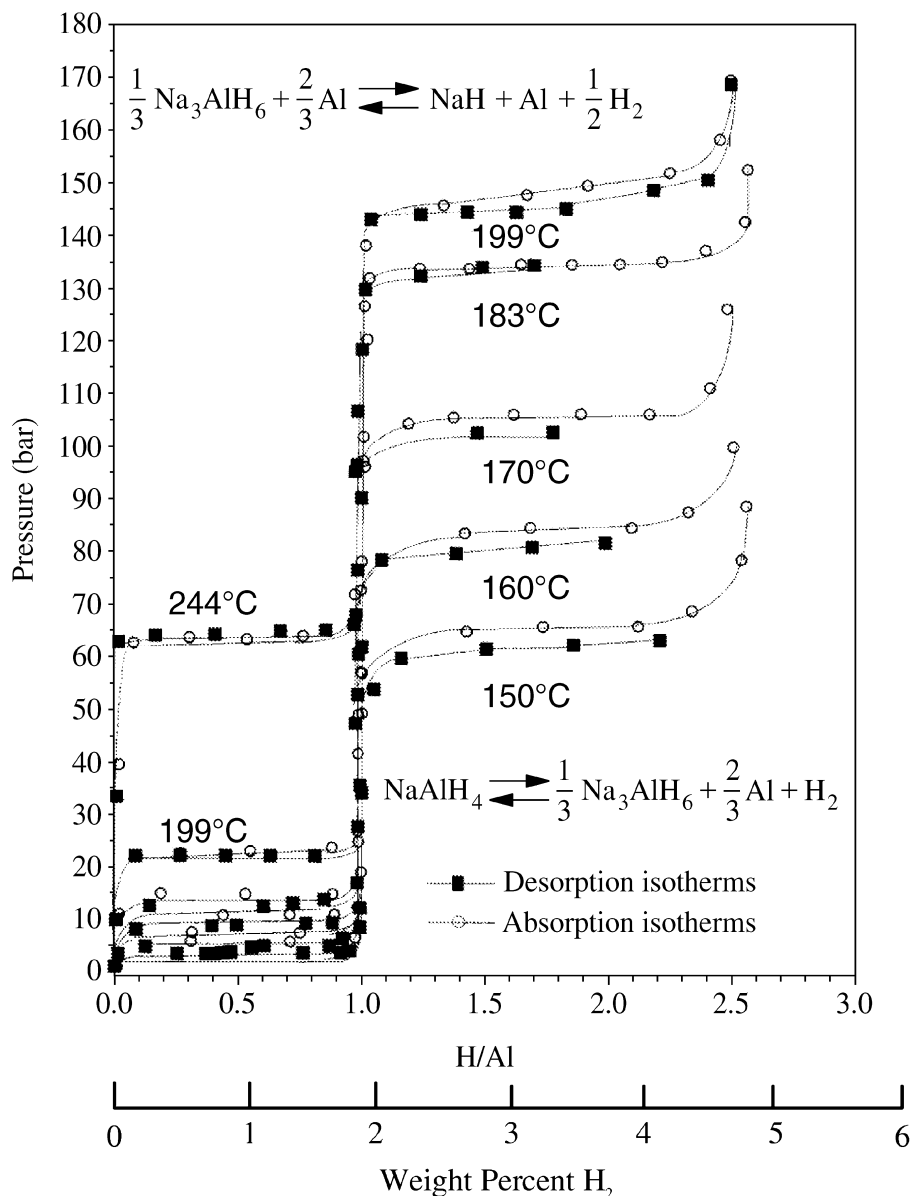

Figure 1. Schematic formula for $NaAlH_4$.

$$\frac{1}{3}\,Na_3AlH_6 + \frac{2}{3}\,Al \rightleftharpoons NaH + Al + \frac{1}{2}\,H_2$$

199°C

183°C

170°C

244°C

160°C

150°C

$$NaAlH_4 \rightleftharpoons \frac{1}{3}\,Na_3AlH_6 + \frac{2}{3}\,Al + H_2$$

199°C

••–■– Desorption isotherms
∘∘–∘– Absorption isotherms

Pressure (bar) — vertical axis
H/Al — horizontal axis
Weight Percent H$_2$ — secondary horizontal axis

Figure 2. Pressure–composition isotherms for NaAlH₄ and Na₃AlH₆.[2]

for, say, supplying a fuel cell that provides waste heat (<80°C) that is not suitable for supplying the required enthalpy of H$_2$ desorption. On the other hand, the Na$_3$AlH$_6$ van't Hoff line falls between the LT intermetallic hydrides and the high-temperature (HT) Mg and Mg-alloy hydrides, thus filling a moderate-temperature (MT) gap that might be useful for non-fuel storage applications such as heat pumping and heat storage.[2]

The Importance of Catalysis

The practical use of Reaction 1 requires catalysis for achieving good kinetics. Our first work on catalyzed alanates at MPI—

Mülheim was derived from studies that used transition-metal catalysts for the preparation of MgH$_2$. We doped NaAlH$_4$ with Ti by solution-chemistry techniques whereby nonaqueous liquid solutions or suspensions of NaAlH$_4$ and either TiCl$_3$ or the alkoxide Ti(OBu^n)$_4$ [titanium(IV) n-butoxide] catalyst precursors were decomposed to precipitate solid Ti-doped NaAlH$_4$.[1,2] An alternate approach was taken by Jensen et al. and Zidan et al. at the University of Hawaii, whereby the liquid Ti(OBu^n)$_4$ precursor was simply ball-milled with the solid NaAlH$_4$.[6,7] They also added Zr(OPr^i)$_4$ (where Pr^i indicates the isopropyl group) to help stimulate the ki-

netics of the second step (Na$_3$AlH$_6$ decomposition) of Reaction 1. Zaluska et al. also obtained positive results by ball-milling with carbon (i.e., not using a transition-metal catalyst).[8] Ball-milling with alkoxide catalyst precursors does result in *in situ* decomposition during at least the first several hydriding/dehydriding cycles, resulting in significant contamination of the H$_2$ with hydrocarbons; using the inorganic TiCl$_3$ catalyst precursor is clearly better if one wishes to use the ball-milling catalyst-doping approach.[9] More detailed reviews of the recent history of catalyzed alanate work are available.[10,11]

The dramatic effects of Ti catalyst level (using the dry TiCl$_3$-NaAlH$_4$ ball-milling/doping technique[12]) on 125°C hydriding kinetics and capacity are shown in the hydriding curves of Figure 4. The kinetics are dramatically increased and capacity decreased with increasing catalyst level. Nearly identical catalyst effects are seen with desorption experiments, although the two steps of Reaction 1 are more clearly sequential in desorption.[12,13] So, it is very clear that catalysis affects both of the reaction directions of Reaction 1 as well as both steps. The capacity is decreased with increasing catalyst level because the catalyst precursor reacts with some of the Na as part of its process to produce the catalyst itself:[12]

$$(1 - x)NaAlH_4 + xTiCl_3 \rightarrow$$
$$(1 - 4x)NaAlH_4 + 3xNaCl + xTi$$
$$+ 3xAl + 6xH_2. \quad (3)$$
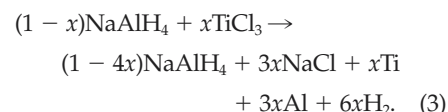
Reaction 3 is at least partly hypothetical. It is clear from x-ray diffraction (XRD) studies that the Cl does react with the Na component of the alanate to form NaCl,[13] but the final form of the Ti catalyst is not clear.[14] We think it is probably metallic, as shown, but rather than being elemental, it may be in the form of an alloy or intermetallic compound (e.g., with Al). Another possibility, recently suggested from lattice-parameter studies, is that the transition-metal dopant (e.g., Ti) actually acts not as a classic surface "catalyst" on NaAlH$_4$, but rather enters the entire Na$^+$ sublattice as a variable valence species to produce vacancies and lattice distortions, thus aiding the necessary short-range diffusion of Na and Al atoms.[15] Ti, derived from the decomposition of TiCl$_4$ during ball milling, seems to also promote the decomposition of LiAlH$_4$ and the release of H$_2$.[16]

In order to understand the role of the catalyst, Sandrock et al. have performed detailed desorption-kinetics studies (forward reactions, both steps, of Reaction 1) as a function of temperature and catalyst
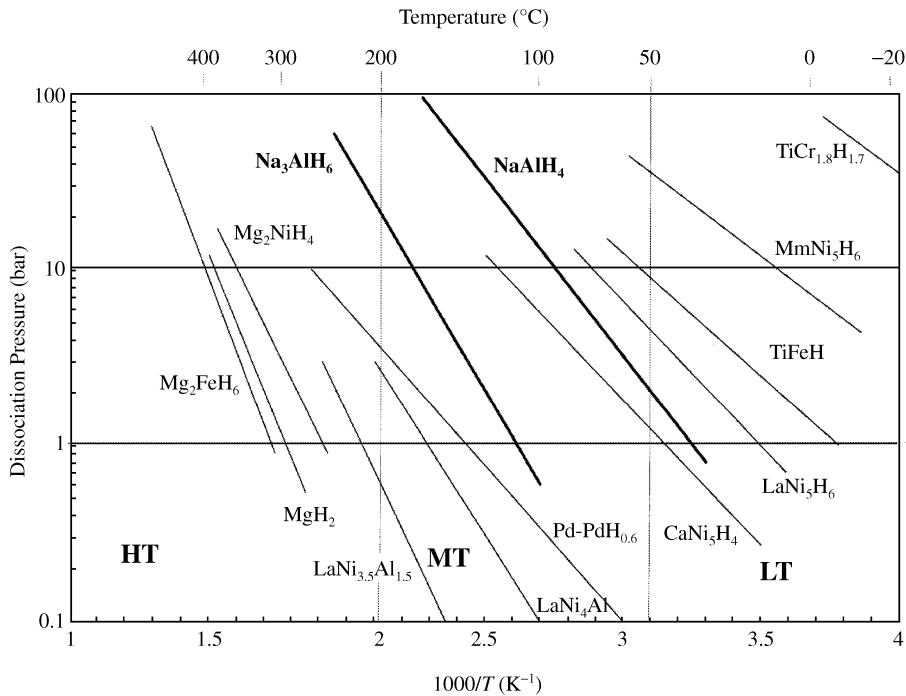
Figure 3. A van't Hoff diagram comparing NaAlH₄ and Na₃AlH₆ dissociation pressures with those of other well-known hydrides.[2] HT, MT, and LT stand for high-, medium-, and low-temperature hydrides, respectively. Mm in MmNi₅H₆ is misch metal, a low-cost mixture of rare-earth elements.
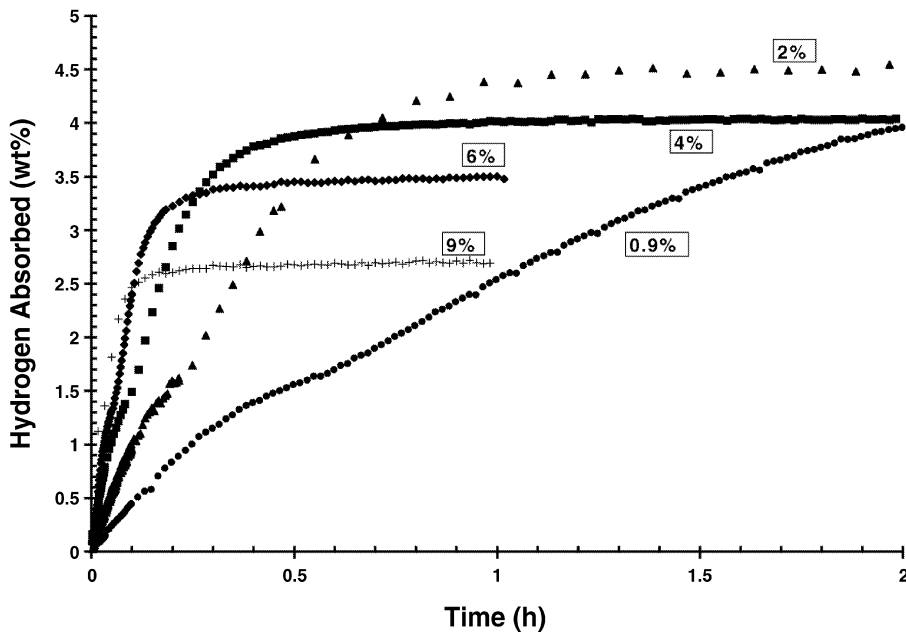

Figure 4. H_2 absorption curves starting from NaH + Al (dehydrided NaAlH₄), as a function of added $TiCl_3$ catalyst precursor (expressed in mol%). Initial temperature $T_i = 125°C$. Applied hydrogen pressure $P_{H_2} = 81–90$ atm.[12]

level.[12] Both the $NaAlH_4$ and Na_3AlH_6 decomposition reactions obey classic, thermally activated behavior consistent with the Arrhenius equation

$$Rate = k \exp(-Q/RT), \qquad (4)$$

where k is the pre-exponential rate constant and Q is the activation energy. For example, the Arrhenius plots for undoped and 4 mol% Ti-doped Na alanate are shown in Figure 5. Catalysis results in multiple order-of-magnitude increases in kinetics for both reactions. This important practical result of catalysis is a combined result of both changes in slopes (Q) and intercepts (k) of the Arrhenius lines. If one plots the activation energy Q as a function of catalyst loading, as shown in Figure 6, it is very clear that the smallest Ti addition (0.9 mol%) has marked effects on lowering Q for both steps of Reaction 1. However, further increases in Ti level have no effects, at least not on Q. The dramatic decrease in Q indicates a major discontinuous change in the thermally activated mechanism. Further increases in desorption kinetics accrue with further increases in Ti level, but only through increases in the pre-exponential rate constant k.[12]

Work Yet Needed on the Alanates

It has been an interesting and exciting five years since the first publication showing the potential for catalyzed $NaAlH_4$ and Na_3AlH_6.[1] Data generated on these materials thus far show levels of $NaAlH_4$ charging and discharging rates that approach practical viability at temperatures suitable for fuel-cell vehicles and other applications. The Na_3AlH_6 decomposition rates and temperatures are not quite adequate yet. But most would agree that the practical possibilities for a new low-temperature generation of 5 wt% hydrides have been shown with this class of materials. But there is much yet to do. We herewith summarize our opinions on the R&D and engineering activities yet needed.

Identity and Mechanism of the Ti Catalyst

We do not yet know the identity of the effective catalyst, nor how it works in such a dramatic manner. XRD and microscopic analyses have not led to its identification, probably because it is amorphous, too fine,[13,14] or is substitutionally located in the alanate lattice itself.[15,16] Our own attempts to mechanically blend various hypothetical catalyst species have failed. Can we produce effective catalysts only by the *in situ* decomposition of a precursor? How does the catalyst really work to ease the thermal activation process? We need to
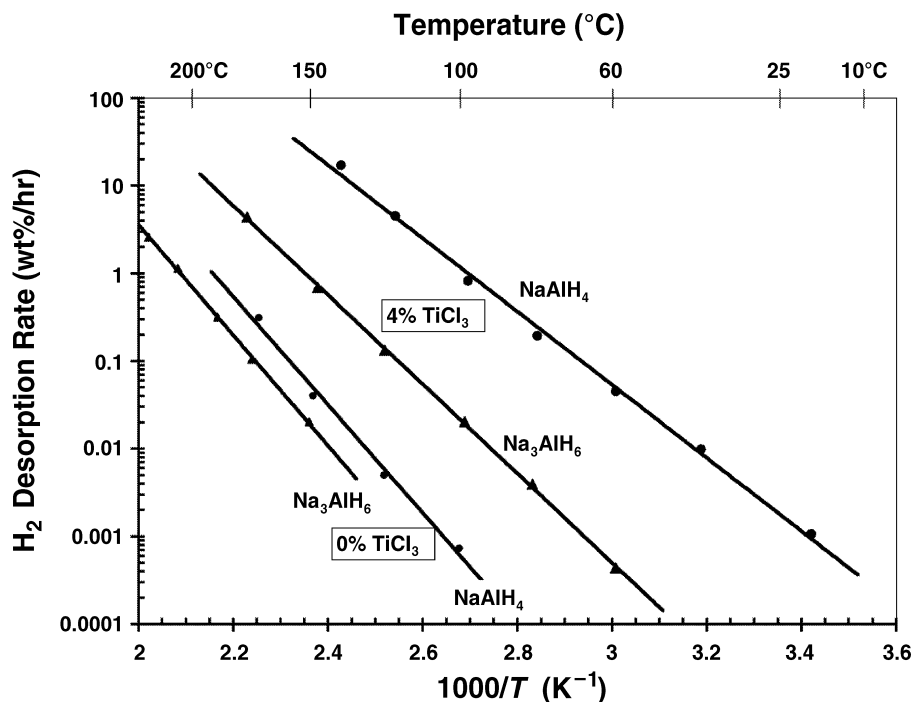
Figure 5. Arrhenius lines for NaAlH$_4$ and Na$_3$AlH$_6$ decompositions for 0 mol% and 4 mol% added catalyst precursor TiCl$_3$.[12]

Figure 6. Activation energies Q for NaAlH$_4$ and Na$_3$AlH$_6$ decompositions as a function of added TiCl$_3$.[12]

answer such key questions if we are to effectively perform the next step, the full optimization of the catalyst.

Optimization of the Catalyst

Most catalyst work thus far has concentrated on the transition metals Ti, Zr, and Fe, along with the nonmetal carbon. Surely we have not optimized the catalyst through these limited investigations. What is the best catalyst for NaAlH$_4$? Is there something better than Ti? Is there something better than Ti or Zr for the problematic Na$_3$AlH$_6$ decomposition?

Hydrogen Capacity and Cyclic Retention

To our knowledge, no one has practically achieved the full cyclic potential of NaAlH$_4$. For example, see Figure 2, which shows that the full capacity of Reaction 1 [ΔH/Al (the change in hydrogen content relative to a fixed amount of Al) = 3, or Δwt% = 5.6] is not quite achieved. Either initial H capacities are low,[8,9,12] or the full capacity is lost after the first cycle by not achieving the full NaAlH$_4$ stoichiometry during charging.[2] Part of the loss is clearly associated with the catalysis process itself (e.g., Reaction 3), but that is not the whole story. We need more cyclic data, along with associated metallography and other analytical techniques, to see

what is physically and chemically happening during cycling.

Engineering Data

Early attempts to look at larger alanate beds from an engineering point of view originated at Sandia National Laboratories[9] and are continuing there and at other laboratories. These results are very preliminary and not necessarily focused on the final and optimum catalyzed material. Like the extensive work done on LT intermetallic hydride beds, we need to learn how to put the alanates into practical, safe configurations. We need to know thermal conductivities and expansion behavior. We need to know if there are potential reactions with container materials. The alanates are well known for their reactivity with water, but we need to carefully quantify water reactivity, pyrophoricity, and other aspects of safety.

Thermodynamic Tailoring of Alanates

The history of intermetallic hydrides is deeply laced with thermodynamic tailoring by means of partial substitution of secondary and higher-order components (see the article by Bowman and Fultz in this issue). Are there such possibilities for the alanates? We know that Li can be partially substituted for Na in NaAlH$_4$,[1,2] but
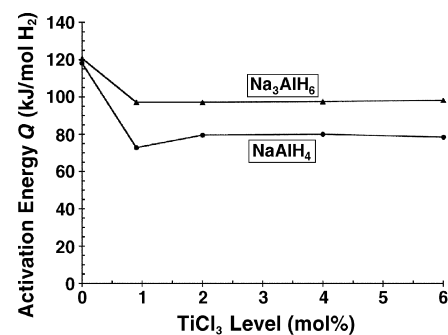
are there other possibilities? Numerous M(AlH$_4$)$_x$ species are known,[17] but their thermodynamic stabilities are largely unknown in more than a qualitative sense. In pure states, which will respond to catalysis? Which can be used for thermodynamic tailoring of NaAlH$_4$, for example? Is there something that will selectively increase the Na$_3$AlH$_6$ plateau pressure without affecting the NaAlH$_4$ plateau pressure or overall H capacity?

Improved Synthesis and Catalyzing Methods

The alanates would seem to have the potential for low cost. In principal, Na and Al are cheap. But NaAlH$_4$ has been made (by direct synthesis) and sold in commercial quantities at rather high cost ($40–50/kg). If our desired end product is a catalyzed alanate, are there combinations of synthesis and catalysis that will make the alanates cheaper than in the past? For example, recent attempts to directly synthesize catalyzed NaAlH$_4$ from powder mixtures of NaH + Al + catalyst precursor[18–20] seem very promising and deserve more attention.

Extension to Other Complex Hydrides
Borohydrides

The alanates have numerous isostructural counterparts in the borohydrides[17] (e.g., NaBH$_4$). The borohydrides tend to be more thermodynamically stable than the alanates, yet less water-reactive. Can the borohydrides be made to respond to catalysis in a manner similar to the alanates? If so, will new problems arise, such as the production of toxic gaseous boranes?

Transition-Metal Complexes

There are a large number of transition-metal complex hydrides that have TMH$_x$ complexes analogous to the [AlH$_4$]$^{1-}$ alanate

complexes, for example, the $[FeH_6]^{4-}$ complex in Mg_2FeH_6.[21] There are numerous such complex hydrides that have been discovered by groups led by Yvon in Geneva,[21] Bronger in Aachen,[22] and Noréus in Stockholm,[23] among others. In most cases, they are reversible only with difficulty, although at least in the case of Mg_2FeH_6, excellent cyclic capacity can be seen, even in the uncatalyzed state.[24] Although some of these hydrides are too stable for low-temperature use, demonstrations of improved (catalyzed) reversibility in the transition-metal complex hydrides would open a new hydride world of opportunities.

Acknowledgments

Supplementary Information

For more information on international cooperative efforts toward solving the H_2 storage problem with metal hydrides and carbon, see URL http://hydpark.ca. sandia.gov/iea.html to view the activities in Task 17 of the International Energy Agency Hydrogen Implementing Agreement.

References

1. B. Bogdanović and M.J. Schwickardi, *J. Alloys Compd.* **253** (1997) p. 1.
2. B. Bogdanović, R.A. Brand, A. Marjanović, M. Schwickardi, and J. Tölle, *J. Alloys Compd.* **302** (2000) p. 36.
3. Millennium Cell Inc. Home Page, http://www.millenniumcell.com (accessed July 2002); H-GeneTech Alliance, http://alliance.hydrogen.co.jp (accessed July 2002).
4. T.N. Dymova, N.G. Eliseeva, S.I. Bakum, and Yu.M. Dergachev, *Dokl. Akad. Nauk SSSR* **215** (1974) p. 1369, Engl. p. 256.
5. T.N. Dymova, Yu.M. Dergachev, V.A. Sokolov, and N.A. Grechanaya, *Dokl. Akad. Nauk SSSR* **224** (1975) p. 591, Engl. p. 556.
6. C.M. Jensen, R.A. Zidan, N. Mariels, A.G. Hee, and C. Hagen, *Int. J. Hydrogen Energy* **24** (1999) p. 461.
7. R.A. Zidan, S. Takara, A.G. Hee, and C.M. Jensen, *J. Alloys Compd.* **285** (1999) p. 119.
8. A. Zaluska, L. Zaluski, and J.O. Ström-Olsen, *J. Alloys Compd.* **298** (2000) p. 125.
9. G. Sandrock, K. Gross, G. Thomas, C. Jensen, D. Meeker, and S. Takara, *J. Alloys Compd.* **330–332** (2002) p. 696.
10. C.M. Jensen and K.J. Gross, *Appl. Phys. A* **72** (2001) p. 213.
11. K.J. Gross, G.J. Thomas, and C.M. Jensen, *J. Alloys Compd.* **330–332** (2002) p. 683.
12. G. Sandrock, K. Gross, and G. Thomas, *J. Alloys Compd.* **339** (2002) p. 299.
13. K.J. Gross, G. Sandrock, and G. Thomas, *J. Alloys Compd.* **330–332** (2002) p. 691.
14. G.J. Thomas, K.J. Gross, and N. Yang, *J. Alloys Compd.* **330–332** (2002) p. 702.
15. D. Sun, T. Kiyobayashi, H.T. Takeshita, N. Kuriyama, and C.M. Jensen, *J. Alloys Compd.* **337** (2002) p. L8.
16. V.P. Balema, K.W. Dennis, and V.K. Pecharsky, *Chem. Commun.* (2000) p. 1665.
17. E.A. Sullivan, in *Kirk-Othmer Encyclopedia of Chemical Technology,* Vol. 13 (John Wiley & Sons, New York, 1995) p. 606.
18. B. Bogdanović and M.J. Schwickardi, *Appl. Phys. A* **72** (2001) p. 221.
19. A. Zaluska, L. Zaluski, and J.O. Ström-Olsen, *Appl. Phys. A* **72** (2001) p. 157.
20. K.J. Gross, G.J. Thomas, E. Majzoub, and G. Sandrock, in *Proc. 2001 DOE Hydrogen Program Review,* NREL/CP-570-30535 (National Renewable Energy Laboratory, Golden, CO, 2001), available from http://www.eren.doe.gov/hydrogen/docs/30535toc.html (accessed July 2002).
21. K. Yvon, *Chimia* **52** (1998) p. 613.
22. W. Bronger, *J. Alloys Compd.* **225** (1995) p. 1.
23. M. Olofsson-Mårtensson, U. Häussermann, J. Tomkinson, and D. Noréus, *J. Am. Chem. Soc.* **122** (2000) p. 6960.
24. A. Reiser, B. Bogdanović, and K. Schlichte, *Int. J. Hydrogen Energy* **25** (2000) p. 425. □