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Catalytically Dehydrating Sodium Aluminum Hydride

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Introduction

A major obstacle to the conversion of the world to a “hydrogen economy” is the problem of onboard hydrogen storage. High pressure and cryogenic hydrogen storage systems are impractical for vehicular applications due to safety concerns and volumetric constraints. This has prompted an extensive effort to develop solid hydrogen storage systems for vehicular application. Metal hydrides [1,2], activated charcoal [3,4] and advanced carbons [5-7] have been investigated as hydrogen carriers. Unfortunately, despite decades of extensive effort, no material has been found that has the combination of a high gravimetric hydrogen density, adequate hydrogen dissociation energetics, reliability, and low cost required for commercial vehicular application [8-10].

A priori, sodium aluminum hydride, NaAlH₄, would seem to be a viable candidate for application as a practical onboard hydrogen storage material. It has a high weight-percent available hydrogen content (5.6 %), low cost, and is readily available in bulk. Complex aluminum hydrides have, in fact, been utilized in “one pass” hydrogen storage systems in which hydrogen is evolved from the hydride upon contact with water. However, these reactions are highly irreversible and could not serve as the basis for a rechargeable hydrogen storage system. Thermal activated evolution of hydrogen from NaAlH₄ occurs at appreciable rates only at temperatures well above its melting point of 183°C. Additionally, this process can be reversed only under severe conditions. Thus, until recently, complex aluminum hydrides were not considered as rechargeable hydrogen carriers. This situation was changed by Bogdanovic and Schwickardi, whose pioneering studies demonstrated that, upon doping with selected titanium compounds, the dehydrogenation of anionic aluminum hydrides could be kinetically enhanced and rendered reversible under moderate conditions in the solid state [11]. This project followed on this breakthrough discovery. We have developed improved catalysts for the dehydrating of NaAlH₄ [12,13].

Results

The hydrogen capacities of the original materials prepared by Bogdanovic and Schwickardi were found to quickly diminish upon cycling. Following the initial desorption, only 4.2 of the lost 5.6 wt % could be restored under the moderate conditions employed in these studies. The hydrogen capacity was further diminished to 3.8 wt % after the second dehydrating cycle [11]. These materials were prepared by evaporation of suspensions of NaAlH₄ in diethyl ether solutions of the soluble titanium compounds Ti(OBuⁿ)₄, and β-TiCl₃. We subsequently found that catalytic enhancement of NaAlH₄ also occurs upon mechanically mixing the titanium catalyst precursors with the aluminum hydride host [12]. The materials resulting from this mechanical process have kinetic and cycling properties that are much closer to those required for a practical hydrogen storage medium [12,13]. The kinetic improvement is illustrated in Figure 1, which compares the thermal programmed desorption (TPD) spectrum of undoped NaAlH₄ with hydride that was doped with Ti(OBuⁿ)₄ by both methods. It can be seen that the onset of rapid kinetics for the first dehydrating process occurs at ~150°C for the hydride that is doped by the original solution method of Bogdanovic and at a much lower, ~120°C, temperature for NaAlH₄ that is doped by the mechanical process. The discontinuity that occurs after elimination of ~3.5 wt % hydrogen

reflects the independence of the two dehydriding reactions. It is evident from Figure 1 that the two titanium-doped materials differ primarily in their effectiveness in catalyzing the first dehydriding reaction.

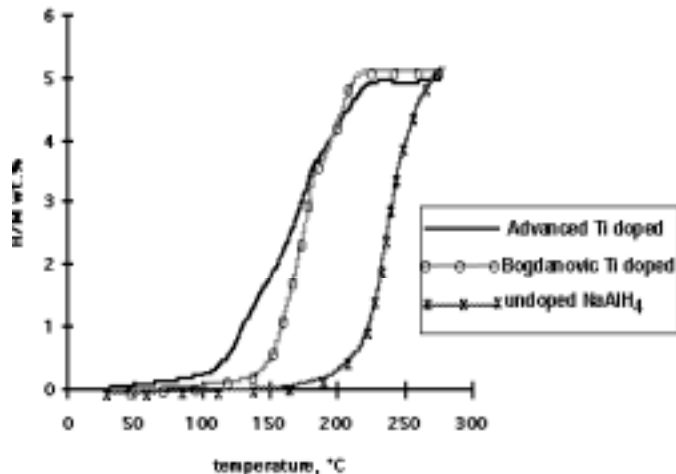


Figure1 - Thermal programmed desorption (2°C/min) of hydrogen from NaAlH₄.

The mechanical milling method is not only a more effective means of charging the hydride with catalyst, but also activates the material through milling (i.e. reduces the average particle size) [12]. However, the introduction of catalysts enhances the kinetics far beyond those that are achieved by reducing the particle size.

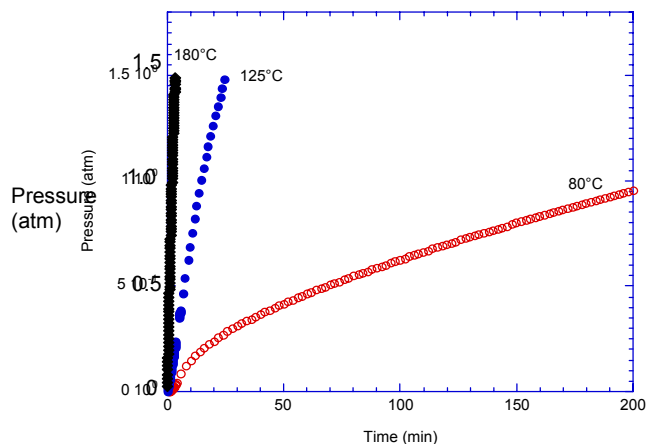


Figure 2 - Progression of hydrogen desorption from NaAlH₄ doped with 2 mol % Ti(OBuⁱ)₄ in the course of time at constant temperatures.

A more detailed kinetic study was carried out in which the release of hydrogen from samples of NaAlH₄, which was doped with Ti(OBuⁱ)₄ through the homogenization method, was monitored at constant temperatures. As seen in Figure 2, the material undergoes rapid dehydriding at 120°C and proceeds at an appreciable rate even at 80°C.

After the initial dehydriding, over 4.0 wt% hydrogen can be restored at 170°C under 150 atm of hydrogen. The cyclable hydrogen capacity is also improved in materials that are doped with $\text{Ti}(\text{OBU}^n)_4$ by the mechanical milling method. Unlike solution-doped material, the hydrogen capacity is undiminished through 10 dehydriding/rehydriding cycles. As seen in Figure 3, the TPD spectrum of the second and third dehydridings is virtually superimposed [13]. It can also be seen that the temperature required for rapid dehydrogenation is further lowered to 100°C after the preliminary cycle. The finding of rapid dehydriding at 100°C in conjunction with a stable, hydrogen-cycling capacity of over 4.0 wt % suggests the application of these materials as hydrogen carriers for onboard fuel cells.

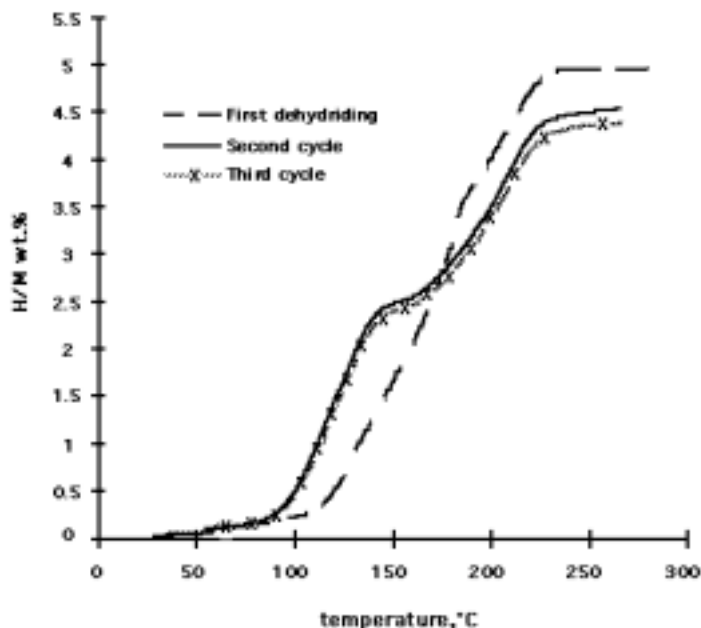


Figure 3 - Effect of dehydriding/rehydriding cycles on thermal programmed desorption (2°C min^{-1}) of hydrogen from NaAlH_4 doped with $\text{Ti}(\text{OBU}^n)_4$ through mechanical milling.

We also explored the effect of doping NaAlH_4 through mechanical milling with $\text{Zr}(\text{OPr}^n)_4$ under an atmosphere of argon [13]. Hydrogen evolution from samples of the zirconium-doped hydride was studied by TPD. Plots of the desorbed hydrogen weight percentage as a function of temperature are seen in Figure 4. In contrast to the titanium-doped material, the catalytic effect is most pronounced for the second rather than the first dehydriding process. In view of the closely related chemistry of titanium and zirconium, it is surprising that their primary catalytic effects are exerted on different reactions in the dehydriding process. As observed for the titanium-doped material, rehydriding can be achieved at 170°C and 150 atm of hydrogen pressure and the dehydriding behavior shows excellent reproducibility after the preliminary cycle of dehydriding/rehydriding. As seen in Figure 4, the temperature required for dehydriding is consistently 20°C lower than observed for the first cycle. The hydrogen capacity of these materials drops to 4.5 wt % in the second cycle, but is also stabilized by the third cycle [13].

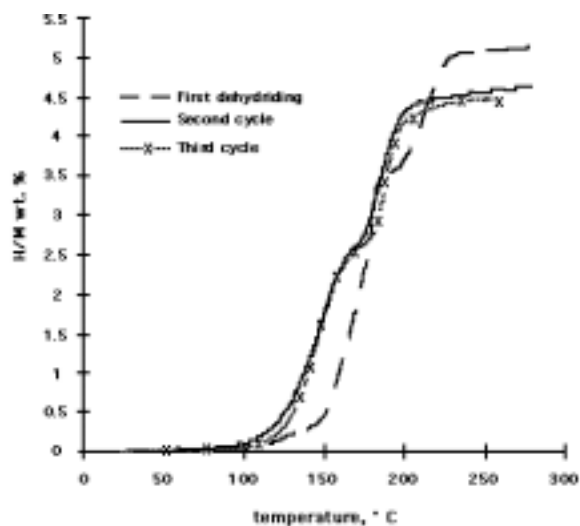


Figure 4 - Effect of dehydriding/rehydriding cycles on thermal programmed desorption ($2^{\circ}\text{C min}^{-1}$) of hydrogen from NaAlH_4 doped with $\text{Zr(OPr}^n)_4$ by the mechanical milling method.

It has been found that titanium and zirconium catalysts are quite compatible and can exert their differing catalytic roles in concert to optimize the dehydriding/rehydriding behavior of NaAlH_4 [13]. The TPD spectrum of hydride that was mechanically doped with 1 mol % of both $\text{Zr(OPr}^n)_4$ and $\text{Ti(OBu}^n)_4$ and then stabilized by 3 dehydriding/rehydriding cycles is seen in Figure 5. The spectrum is a virtual superpositioning of the first segment of the curve for the titanium doped material and the second segment of the zirconium doped material. Thus, titanium and zirconium can act in concert to optimize the dehydriding/rehydriding behavior of NaAlH_4 .

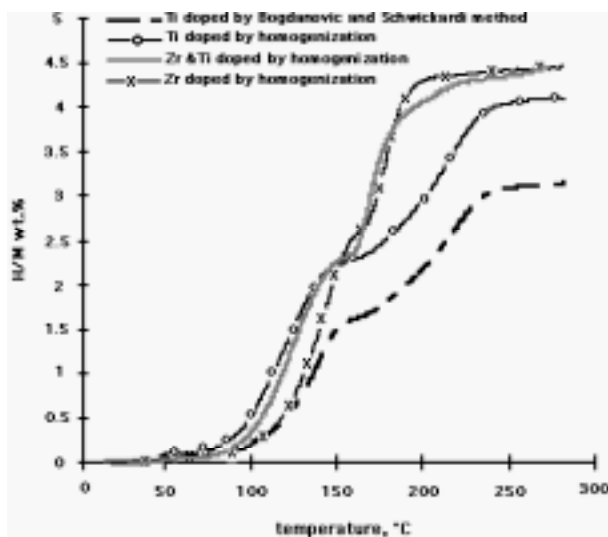


Figure 5 - Thermal programmed desorption ($2^{\circ}\text{C min}^{-1}$) of hydrogen from various doped samples NaAlH_4 after 3 cycles of dehydriding/rehydriding.

The chain of advancement in the development of metal catalyzed NaAlH₄ is illustrated by comparison of the TPD spectra of the third dehydriding cycle of a variety of doped materials. As seen in Figure 5, hydride that was doped with titanium through the solution method has a cyclable hydrogen capacity of 3.2 wt % and dehydriding behavior that is markedly improved over undoped NaAlH₄. Doping with Ti(OBuⁿ)₄ through the mechanical milling technique further enhances the kinetics of the first dehydriding reaction and improves the cyclable hydrogen capacity to over 4.0 wt %. The material that was mechanically doped with Zr(OPrⁿ)₄ shows enhancement of the kinetics of the second dehydriding reaction and a further improved cyclable hydrogen capacity of 4.5 wt %. Finally, enhanced kinetics of both dehydriding reactions and the maximized hydrogen capacity are observed in a sample that was mechanically milled with both dopants.

Conclusion

Our studies of these catalytically enhanced hydrides indicate that we may be on the threshold of producing hydrogen storage materials that can be utilized for the practical onboard storage of hydrogen.

Acknowledgements

Funding for this project was provided by the by the U.S. Department of Energy Hydrogen Program. We wish to acknowledge the valuable contributions of Don Meeker of Sandia National Laboratories, as well as Nathan Mariels and Allan Hee of the University of Hawaii for their technical contributions to these studies.

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