

HYDROGEN STORAGE VIA CATALYTICALLY ENHANCED METAL HYDRIDES

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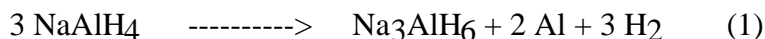
Abstract

The dehydrogenation kinetics of NaAlH_4 are significantly enhanced upon doping with zirconium through homogenization with 2 mole % Zr(OPr)_4 . TPD measurements show that zirconium is inferior to titanium as a catalyst for the dehydriding of NaAlH_4 to Na_3AlH_6 and Al but a superior catalyst for the dehydriding of Na_3AlH_6 to NaH and Al. The benefit of both catalytic effects can be realized in materials containing a combination of both titanium and zirconium catalysts. After the initial dehydriding/rehydriding cycle, NaAlH_4 which is doped with titanium and/or zirconium are stabilized with a greater than **4 wt %** cyclable hydrogen capacity. The onset of rapid dehydriding occurs in the titanium containing materials at temperatures below **100 °C**. A 100 g sample of the Ti/Zr doped NaAlH_4 has been successfully prepared and loaded into modular test beds at SNL.

Introduction

For decades, hydrogen has been targeted as the utopian fuel of the future due to its abundance and environmental friendliness. A major difficulty in the utilization of hydrogen as a fuel 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. Metallic hydrides (Sandrock et al. 1992; Sandrock 1995), activated charcoal (Carpetis and Peshka, 1980; Agarwal et al., 1987) and carbon nanotubes (Dillon et al., 1997) have been investigated as hydrogen carriers. Unfortunately, despite decades of extensive effort, especially in the area of metallic hydrides, no material has been found which has the combination of a high gravimetric hydrogen density, adequate hydrogen dissociation energetics, and low cost required for commercial vehicular application (Suda and Sandrock, 1994).

The dehydrogenation of NaAlH₄ is known to occur by a multistep process involving the reactions seen in equations 1 and 2 (Dymova, 1975). This process is thermodynamically



favorable at moderate temperatures. However, it is characterized by very slow kinetics (Dymova, 1975) and reversibility only under severe conditions (Dymova, 1974). Thus despite favorable thermodynamics and a high available hydrogen weight percentage, NaAlH₄ was precluded from consideration as a potential hydrogen storage material until it was recently discovered that titanium doping of NaAlH₄ significantly enhances the kinetics of hydrogen desorption and renders the dehydrating process reversible under moderate conditions (Bogdanovic and Schwickardi, 1997; Jensen et al., 1999; Zidan et al., 1999). Bogdanovic found that the onset of the initial dehydrating was lowered by 50 °C upon titanium doping by evaporation of an ether suspension of NaAlH₄ which contained 2 mol % of titanium tetra-*n*-butoxide, Ti(OBuⁿ)₄ (Bogdanovic and Schwickardi, 1997). We subsequently found that homogenization of NaAlH₄ with Ti(OBuⁿ)₄ resulted in a lowering of the dehydrating temperature by 75 °C and markedly improved cyclable hydrogen capacities (Jensen et al., 1999). These findings represented a breakthrough in the application of this class of hydrides to hydrogen storage. However, further kinetic enhancement of the dehydrating process is required to produce a material that is suitable for practical vehicular applications. It was therefore of interest to investigate whether further improvement of the kinetics of the reversible dehydrating of NaAlH₄ could be achieved by other transition metal catalysis. During the past year we have screened a variety of other transition metal complexes as catalyst precursors. We have found that the dehydrogenation kinetics of NaAlH₄ are also significantly enhanced upon doping with zirconium through homogenization with Zr(OPr)₄. While zirconium was found to enhance the dehydrating kinetics of NaAlH₄, the catalytic action is seen to be different than that of titanium. Furthermore, we have found that the differing catalytic effects of titanium and zirconium can be carried out in concert. In order to evaluate the feasibility of a hydrogen storage system based on this type of material, we have prepared a 100 g sample of the Ti/Zr doped NaAlH₄ which is being studied in modular test beds at Sandia National Laboratory.

Results

Catalytic Effect of Zirconium.

Zirconium doped NaAlH₄ was prepared by homogenizing freshly recrystallized hydride with Zr(OPr)₄ under an atmosphere of argon. Hydrogen evolution from samples of the zirconium doped hydride was studied by thermal programmed desorption (TPD). Plots of the desorbed hydrogen weight percentage as a function of temperature are seen in Figure 1. The discontinuity in the desorption curves reflects the difference in activation energies of the dehydrating reactions seen in equations 1 and 2. In contrast to the titanium doped material, the catalytic effect is most pronounced for the dehydrating of Na₃AlH₆ to NaH and Al (equation 2) rather than the dehydrating of NaAlH₄ to Na₃AlH₆ and Al (equation 1). 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 dehydrating process.

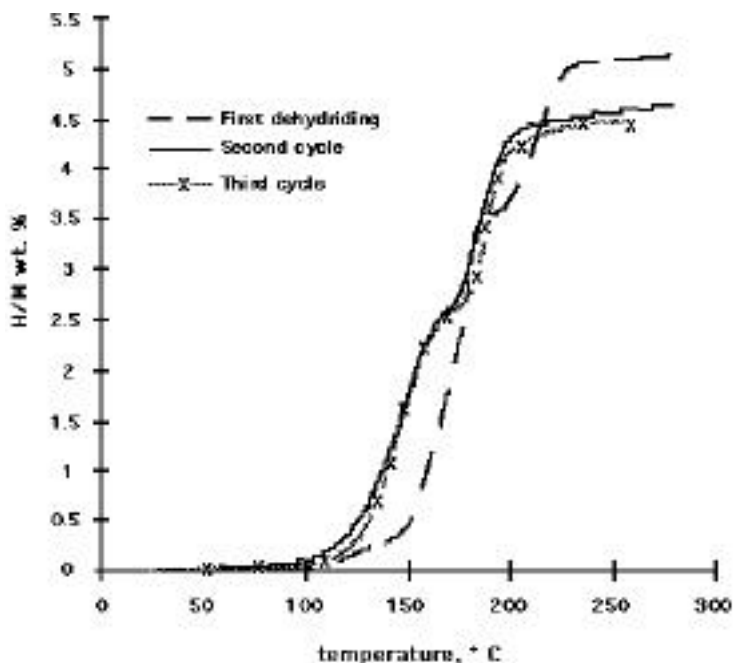


Figure 1 - Effect of dehydrogenating/rehydrogenating cycles on thermal programmed desorption ($2\text{ }^{\circ}\text{C min}^{-1}$) of hydrogen from NaAlH_4 doped with zirconium by the homogenization method.

The rehydrogenation is also catalyzed by the zirconium doping. As observed for titanium doped NaAlH_4 (Bogdanovic and Schwickardi, 1997; Jensen et al., 1999), recharging of the dehydrogenated materials can be achieved at $170\text{ }^{\circ}\text{C}$ and 150 atm of hydrogen pressure.

Cycling Studies

After the preliminary cycle of dehydrogenating/rehydrogenating, the TPD spectra of the zirconium containing materials showed excellent reproducibility. As seen in Figure 1, the temperature required for dehydrogenating is consistently $20\text{ }^{\circ}\text{C}$ lower than for the first cycle. Similar behavior was observed in a parallel study of materials doped with 2 mol % titanium through our homogenization technique. As seen in Figure 2, the temperature required for the dehydrogenating reactions is lowered by $20\text{ }^{\circ}\text{C}$ after the preliminary dehydrogenating/rehydrogenating cycle. The onset of rapid dehydrogenation at $100\text{ }^{\circ}\text{C}$ in the titanium doped material is noteworthy as it suggests the application of these materials as hydrogen carriers for onboard fuel cells.

The hydrogen capacity of these materials drops to 4.5 wt % in the second cycle but is also stabilized by the third cycle. We previously noted similar stabilization of the hydrogen storage capacity in titanium doped NaAlH_4 which was prepared through our homogenization technique (Jensen et al., 1999).

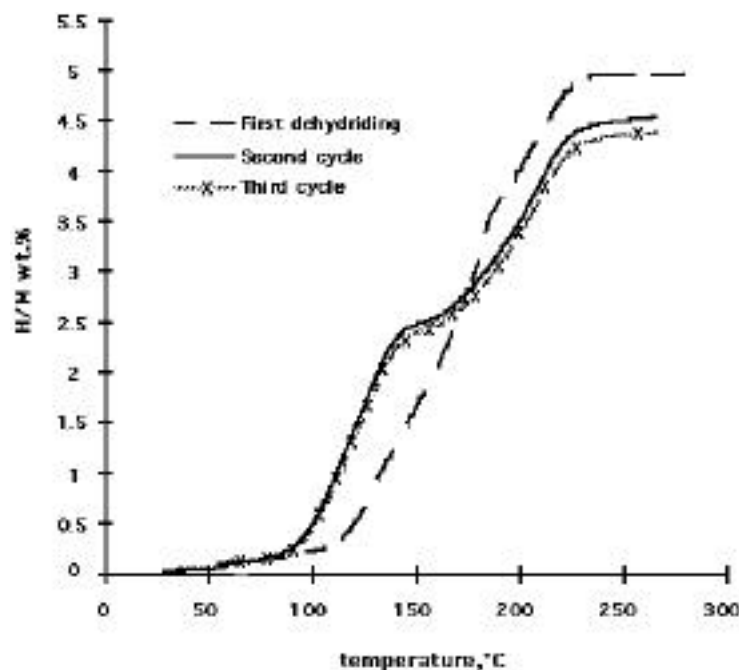


Figure 2 - Effect of dehydrating/rehydrating cycles on thermal programmed desorption ($2\text{ }^{\circ}\text{C min}^{-1}$) of hydrogen from NaAlH_4 doped with titanium through the homogenization (advanced) method.

Tandem Titanium/Zirconium Catalysis

The chain of advancement in the development of metal catalyzed NaAlH_4 is illustrated through comparison of the TPD spectra of the third dehydrating cycle of variety of doped materials. As seen in Figure 3, hydride which was doped with titanium through the method of Bogdanovic has a cyclable hydrogen capacity of 3.2 wt % and dehydrating behavior that is markedly improved over undoped NaAlH_4 . Titanium doping through our homogenization technique further enhances the kinetics of the first dehydrating reaction and improves the cyclable hydrogen capacity to 4.0 wt %. The zirconium doped material shows enhancement of the kinetics of the second dehydrating reaction and a further improved cyclable hydrogen capacity of 4.5 wt %. However, the kinetics of the first dehydrating reaction in this material are inferior to those of material that is doped with titanium through this method.

In order to determine the compatibility of the catalytic action of zirconium and titanium, a sample was prepared in which NaAlH_4 homogenized with 1 mol % of both $\text{Zr}(\text{OPr})_4$ and $\text{Ti}(\text{O}i\text{Bu})_4$. The sample was then stabilized by 3 dehydrating/rehydrating cycles. As seen in Figure 3, the TPD spectrum of the titanium/zirconium doped material is a virtual superposition 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 dehydrating/rehydrating behavior of NaAlH_4 .

Large Scale Synthesis of Titanium/Zirconium Doped NaAlH_4 .

The discovery that Ti/Zr doped NaAlH_4 undergoes reversible loss of observed >4 weight percent hydrogen at temperatures as low as $100\text{ }^{\circ}\text{C}$ is very encouraging. However, a

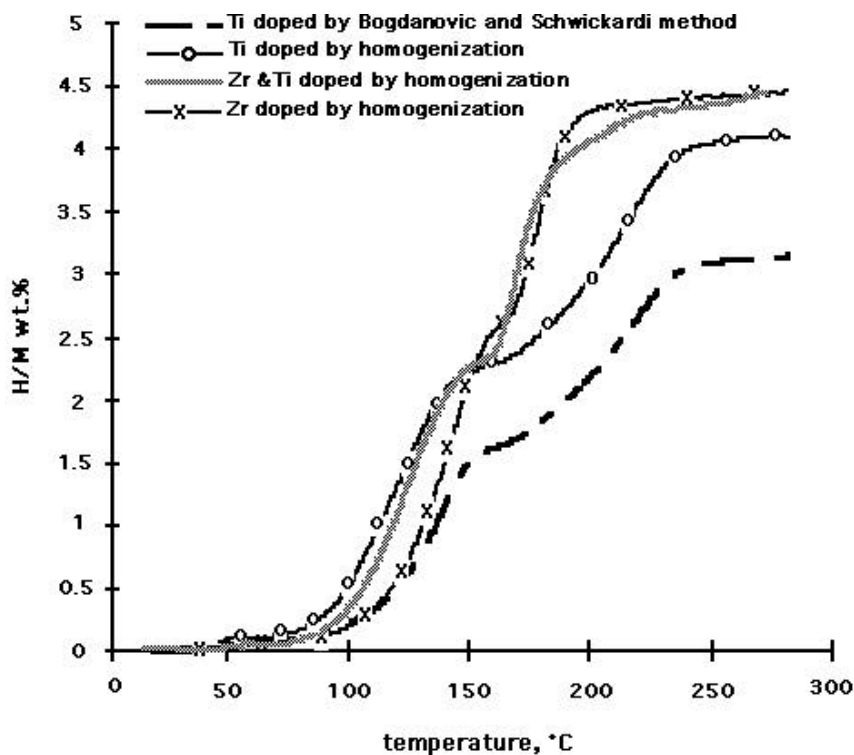


Figure 3 - Thermal programmed desorption ($2\text{ }^{\circ}\text{C min}^{-1}$) of hydrogen from various doped samples NaAlH_4 after 3 cycles of dehydrogenating/rehydrogenating.

hydrogen storage system based on this material is feasible only if long term cycling stability can be maintained in bulk. Thus long term cycling studies have been planned in collaboration with Sandia National Laboratory. A 100 g sample of the Ti/Zr doped NaAlH_4 has been successfully prepared and loaded into modular test beds at SNL. The material will be monitored through 100 dehydrogenation/rehydrogenation cycles in order to determine its long term stability.

Conclusions

While zirconium is inferior to titanium as a catalyst for the dehydrogenating of NaAlH_4 to Na_3AlH_6 and Al, it is a superior catalyst for the dehydrogenating of Na_3AlH_6 to NaH and Al. Our studies show that the benefit of both catalytic effects can be realized in materials containing a combination of both titanium and zirconium catalysts. After the initial dehydrogenating/rehydrogenating cycle, NaAlH_4 which is doped with titanium and/or zirconium are stabilized with a nearly 4.5 wt % cyclable hydrogen capacity.

We have found that the dehydrogenating kinetics of NaAlH_4 are significantly enhanced through zirconium doping. While zirconium is inferior to titanium as a catalyst for the dehydrogenating of NaAlH_4 to Na_3AlH_6 and Al, it is a superior catalyst the dehydrogenating of Na_3AlH_6 to NaH and Al. The benefit of both catalytic effects can be realized in materials containing a combination of both titanium and zirconium catalysts. After the initial dehydrogenating/rehydrogenating cycle, NaAlH_4 that is doped with titanium and/or zirconium is stabilized with a greater the 4 wt % cyclable hydrogen. The occurrence of rapid dehydrogenating in the titanium containing materials at temperatures below $100\text{ }^{\circ}\text{C}$ suggests their application as hydrogen carriers for onboard fuel cells.

Future Work

Thermodynamic and kinetic parameters the dehydriding and rehydriding processes are required to calculate the optimum temperatures and pressures for hydrogen storage systems based on catalytically enhanced NaAlH₄. In order to obtain these values, we will determine PCT curves and carry out kinetic measurements of Ti/Zr doped NaAlH₄ in the 80-130 °C temperature range. The sensitivity of the materials to the trace hydrogen contaminants: O₂, CO, CO₂, and H₂O will also be investigated. Ternary hydrides in which the sodium of NaAlH₄ is partially substituted by potassium, alkaline earth metals, and transition metals will also be synthesized. The PCT curves of these materials will be determined in order to gauge the effect of the substitutions on the plateau hydrogen pressures.

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