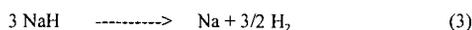
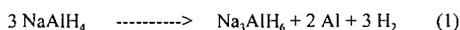


Catalytically Enhanced Sodium Aluminum Hydride as a Hydrogen Storage Material. Craig M. Jensen, Kevin Magnuson, Ragaay A. Zidan, Satoshi Takara, Allan G. Hee, Nathan Mariels, and Chrystel Hagen, Department of Chemistry, University of Hawaii, Honolulu, HI 96822.

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 [1,2] activated charcoal [3,4] and carbon nanotubes [5] have been investigated as hydrogen carriers. Unfortunately, despite decades of extensive effort, especially in the area of metal 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 [6].

The dissociation of hydrogen from sodium aluminum hydride, NaAlH₄, is not a single concerted process. It has been found to occur by the series of discrete reactions seen in equations 1, 2, and 3 [7-9]. Their independence is verified by the observation of a series



of equilibrium plateau pressures. The first two of these reactions are thermodynamically favorable at moderate temperatures and liberate 1.8 and 3.6 weight percent, wt %, hydrogen. However, NaAlH₄ has generally been discounted from consideration as a potential hydrogen storage material due to slow dehydriding kinetics [9] and the severe conditions required for its rehydriding [10]. Thus this material has not been developed as a rechargeable hydrogen carrier despite its high gravimetric hydrogen density and favorable dehydriding thermodynamics at moderate temperatures.

In 1996, Bogdanovic reported [11,12] that doping of NaAlH₄ with a few mole percent of titanium significantly enhanced the kinetics of the dehydriding and rehydriding processes. The temperature required for rapid dehydriding of NaAlH₄ was found to be

lowered from 200 °C to 150 °C. The conditions required for rehydriding were also dramatically reduced to 170 °C and 150 atm. It was also noted that these materials showed the application-relevant properties of no hysteresis on cycling and negligible plateau slopes. Unfortunately, the hydrogen capacities of the materials produced by Bogdanovic quickly diminish upon cycling. Following the initial dehydriding of the titanium doped material, only 4.2 of the lost 5.6 wt % could be restored under the moderate conditions employed in these studies. The hydrogen capacity is further diminished to 3.8 wt % after the second dehydriding cycle and reduced to only 3.1 weight percent after 31 cycles. This lack of stability along with the still unacceptably high (150 °C) temperature required for their rapid dehydriding, precludes them from consideration as viable onboard hydrogen carriers. This work, however, suggested that sodium aluminum hydride might be adapted for application as a practical hydrogen storage material.

The Bogdanovic materials were prepared by evaporation of suspensions of NaAlH_4 in solutions of titanium precursors. We recently found that titanium doping of NaAlH_4 also occurs upon mechanically mixing the liquid catalyst precursor, titanium tetra-*n*-butoxide, $\text{Ti}(\text{O}i\text{Bu})_4$, with the aluminum hydride host [13]. The resulting purple materials are visually very distinct from the brown powders obtained through Bogdanovic's procedure. While our homogenization technique is equivalent to ball milling of the material, there is compelling evidence that a chemical reaction also transpires in the process.

The materials resulting from our homogenization process have kinetic and cycling properties that are much closer to those required for a practical hydrogen storage medium [13]. The material undergoes rapid dehydriding at 120 °C and proceeds at an appreciable rate even at 80 °C. The temperature required for rapid kinetics in the first dehydriding is further lowered to 100 °C after the preliminary dehydriding-rehydriding cycle. The cyclable hydrogen capacity is also improved in the advanced titanium doped material. Over 4.0 wt % hydrogen can be evolved through 10 dehydriding-rehydriding cycles.

We have found that the dehydriding of NaAlH_4 is also kinetically enhanced upon doping with zirconium through our procedure [14]. The zirconium doped material has a further improved, 4.5 wt % cyclable hydrogen capacity. In contrast to the titanium doped material, the catalytic effect is most pronounced for the second rather than the first dehydriding process and inferior kinetics are observed for the first dehydriding reaction.

We have found that titanium and zirconium can act in concert to optimize dehydrogenating/rehydrogenating kinetics while achieving a 4.5 wt % cyclable hydrogen capacity.

The chain of advancement in the development of metal catalyzed NaAlH_4 is illustrated by comparison of the thermal programmed desorption spectra of the third dehydrogenating cycle of the various doped materials. As seen in Fig 1, hydride that was doped with titanium through the method of Bogdanovic has a cyclable hydrogen capacity of 3.2 wt % and dehydrogenating behavior that is markedly improved over undoped NaAlH_4 . Titanium doping through our homogenization technique further enhances the kinetics of the first dehydrogenating reaction and improves the cyclable hydrogen capacity to over 4.0 wt %. The zirconium doped material shows improved kinetics for the second dehydrogenating process and a cyclable

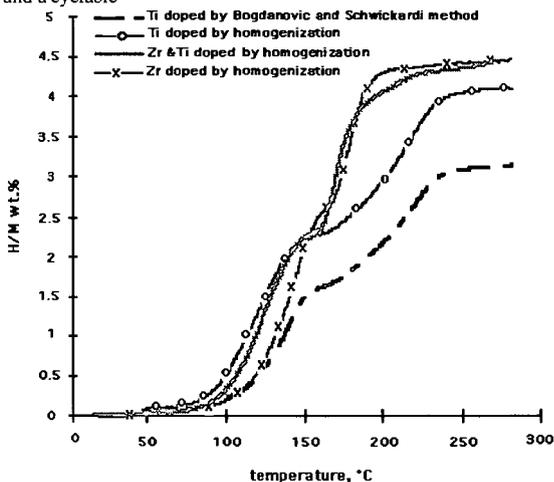


Fig. 1. Thermal programmed desorption (2 C min^{-1}) of hydrogen from various doped samples NaAlH_4 after 3 cycles of dehydrogenating/rehydrogenating.

hydrogen capacity of 4.5 wt %. Finally the titanium/zirconium doped material exhibits dehydrogenating behavior that is a virtual superpositioning of the behavior of homogenized titanium doped material for the first dehydrogenating process and the zirconium doped material for the second dehydrogenating process while maintaining a cyclable hydrogen capacity of 4.5 wt %. The finding of rapid dehydrogenating at 100 °C in conjunction with a stable, hydrogen cycling capacity of 4.5 wt % suggests the application of these materials as hydrogen carriers for onboard fuel cells.

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