

CATALYTICALLY ENHANCED SYSTEMS FOR HYDROGEN STORAGE

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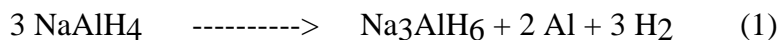
Abstract

A new catalyst has been discovered for the rehydriding of NaH and Al to NaAlH₄. The kinetics of this process in the presence of this catalyst is improved by a factor of ~5 over that of Ti/Zr doped hydride. The problem of hydrocarbon contamination of the hydrogen evolved from catalytically enhanced NaAlH₄ can be eliminated by doping the hydride with TiCl₄ in place of Ti(OBu)₄. Partial substitution of sodium cation by potassium results in a lowering of the plateau pressure associated with the dehydriding of X₃AlH₆ to XH and Al.

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 et. al., 1975). This process is thermodynamically mically favorable at moderate



temperatures. However, it is characterized by very slow kinetics (Dymova et. al., 1975) and reversibility only under severe conditions (Dymova et. al., 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 dehydriding 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 dehydriding 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 material that undergoes rapid dehydriding at temperatures as low as 100 °C and proceeds at an appreciable rate even at 80 °C (Jensen et al., 1999; Zidan et al., 1999). 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 NaAlH₄ is also kinetically enhanced by doping the hydride with zirconium through our procedure (Jensen et al., 1999; Zidan et al., 1999). 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. We have found that titanium and zirconium can act in concert to optimize dehydriding/rehydriding kinetics while achieving a 4.5 wt % cyclable hydrogen capacity. These findings represented a breakthrough in the application of this class of hydrides to hydrogen storage and suggested that our materials might be developed as practical onboard hydrogen carriers. In order to assess this possibility, we have extended our studies to large scale (100 g) hydrogen cycling tests that are being conducted in collaboration with Sandia National Laboratory. Additionally, Honda, General Motors, Toyota, Japan Steel Works and Motorola have expressed interest in the commercial application of these materials. However, further kinetic enhancement, especially for the rehydriding 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 dehydriding of NaAlH₄ could be achieved by other catalysts. Additionally, there is a thermodynamic limitation on the release of hydrogen from sodium aluminum hydride at the 80-100°C temperatures that can be supplied from the exhaust of a PEM fuel cell. The 3.6 wt % hydrogen released by first dehydriding reaction (in which NaAlH₄ is converted to Na₃AlH₆ and Al) establishes a practical plateau pressures in the range of 3-10 atm. However, in this temperature range the plateau pressure of the second reaction, in which (Na₃AlH₆ is converted to NaH and Al) is insufficient for utilization in a PEM fuel cell system. In order to harness the additional 1.9 wt % hydrogen available from this reaction

at moderate temperatures, sodium must be at least partially substituted by an alternate cationic species that would favorably alter the thermodynamics of hydrogen release.

Results

Screening of Advanced Catalysts. We have explored the dehydriding and rehydriding kinetics of NaAlH_4 doped with a variety of potential catalysts and catalyst precursors. The catalytic enhancement resulting from doping the hydride with the vanadium alkoxide complex, $\text{V}(\text{O})(\text{OPr}^i)_3$, Ti_3Al , and TiAl , were inferior in all respects to that produced by the titanium and zirconium catalyst precursors. We have, however, found two catalyst precursors that significantly improve the reversible dehydriding process. Most notably, we have discovered a new catalyst (composition can not be disclosed at this time due to proprietary reasons) whose principal effect is to vastly improve rehydriding kinetics. As seen in Figure 1, the kinetics of hydrogen uptake by dehydrided material are vastly

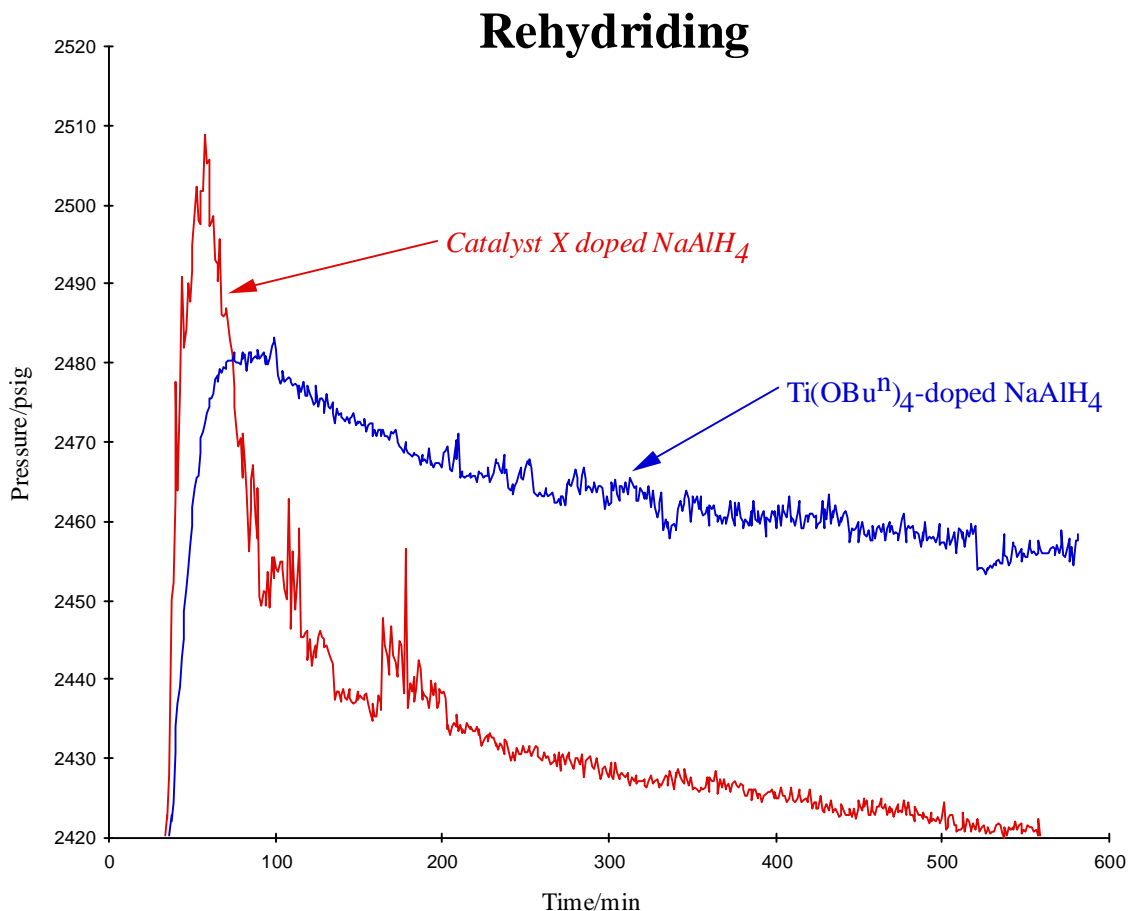


Figure 1. Comparison of hydrogen uptake by mixture of NaH + Al doped with “catalyst X” vs. $\text{Ti}(\text{OBu})_4$.

improved in material doped with “catalyst X” beyond those resulting from doping with Ti/Zr. In the presence of the new catalyst, hydrogen recharging occurs in less than 2 h at

150 °C under 170 atm of hydrogen as opposed to the 10 h required for NaAlH₄ that is doped with the titanium and/or zirconium alkoxide catalyst precursors. The combined benefit of the new, Ti, and Zr catalysts have been realized in a sample of NaAlH₄ that was doped with a ternary mixture of catalysts.

As mentioned above, large scale hydrogen cycling tests of Ti/Zr doped NaAlH₄ are being conducted in collaboration with Sandia National Laboratories. These studies have shown that the hydrogen evolved from hydride doped with Ti(OBu)₄ and/or Zr(Oi-Pr)₄ contaminated with the gaseous hydrocarbons, butane and propane. Concerns that such contamination of hydrogen might impair the operation of a fuel cells lead us to explore the doping of the hydride with the inorganic catalyst precursor, TiCl₄. As seen in Figure 2, the catalytic enhancement of the dehydriding process was seen to be similar, and in fact slightly improved when TiCl₄ was used in place of Ti(OBu)₄. Thus the problem of hydrocarbon contamination of the hydrogen evolved from catalytically enhanced NaAlH₄ has been eliminated.

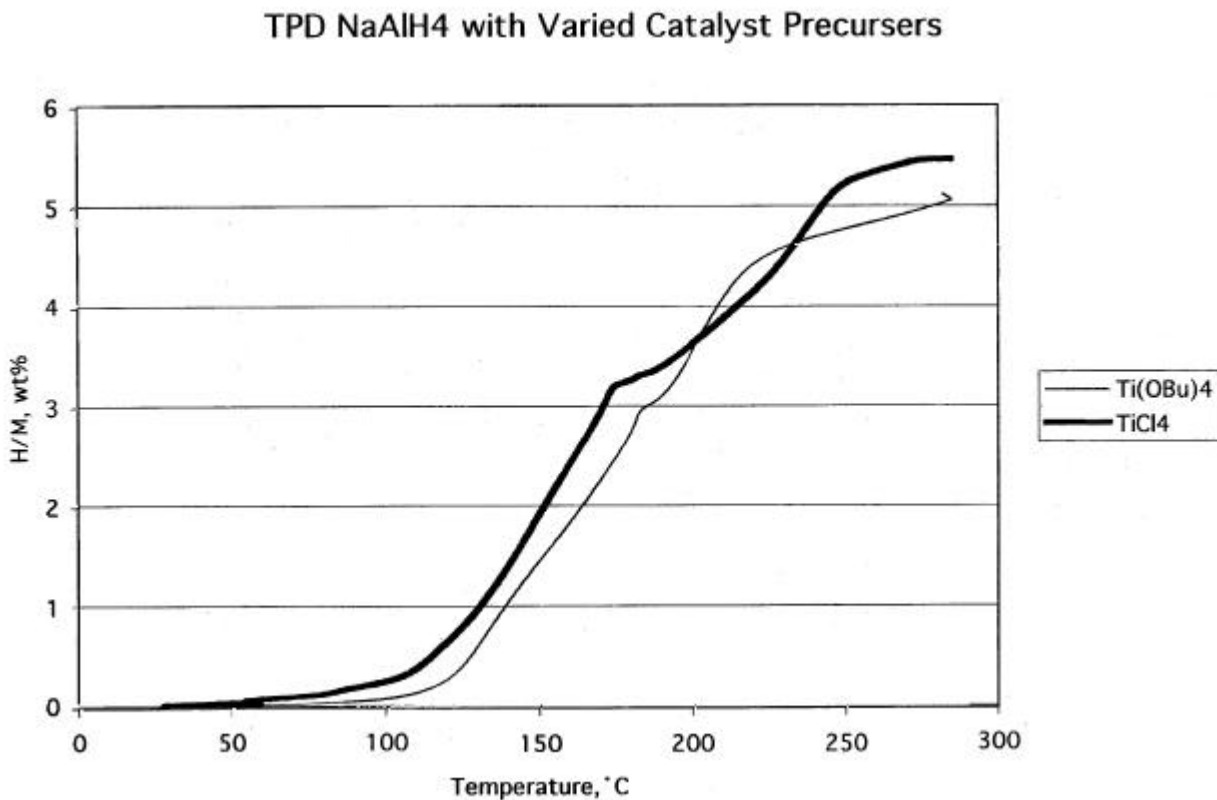


Figure 2. Comparison of the thermal programmed desorption (2 °C min⁻¹) of hydrogen from NaAlH₄ doped with TiCl₄ vs. Ti(OBu)₄.

Synthesis and Evaluation of Salts with Partial Substitution of the Sodium Cation. We have synthesized Na₂KAlH₆ through the mechanical alloying of a stoichiometric combination of KH and NaAlH₄. Unfortunately, we have found that the

potassium substitution results in an increase of the hydrogen desorption temperature to about 170 °C and decreases the hydrogen capacity by about 50%. Similar attempts to prepare the magnesium substitution compound were unsuccessful. Our studies revealed that the material resulting from energetic mechanical alloying of either MgH₂ or Mg powder with NaAlH₄ is simply a mixture of MgH₂ and NaAlH₄.

Conclusions

Two important advances have been made in the development of improved catalysts for the reversible dehydriding of NaAlH₄. We have discovered a new catalyst for the rehydriding of NaH and Al to NaAlH₄. The kinetics of this process in the presence of this catalyst is improved by a factor of ~5 over that of Ti/Zr doped hydride. Thus the time required to recharge dehydrided material has been reduced from 10 h to 2 h. Additionally, we have found that the problem of hydrocarbon contamination of the hydrogen evolved from catalytically enhanced NaAlH₄ can be eliminated by doping the hydride with TiCl₄ in place of Ti(OBu)₄.

We have determined that partial substitution of sodium cation by potassium results in a lowering rather than the hoped for raising of the plateau pressure associated with the dehydriding of X₃AlH₆ to XH and Al. Our attempts to prepare NaMgAlH₆ through mechanical alloying techniques were unsuccessful. These results, in conjunction those previously obtained for Na₂LiAlH₆ (Bogdanovic and Schwickardi, 1997), indicate that the partial substitution of sodium by alkali metal or alkaline earth cations are not a means of raising the plateau pressure the 1.9 wt % hydrogen available from this reaction such that it could be utilized for fuel cell applications below 100 °C.

Future Work

Further improvement in the rates of the dehydriding and, more crucially, the rehydriding of NaAlH₄ are required in order for this material to achieve commercial viability. With this goal in mind, we plan to test a variety of bimetallic, aluminum-transition metal hydride complexes as catalysts for these processes. Our search for improved catalysts would be greatly aided by the characterization of the active catalysts in our materials and a fundamental understanding to of the mechanism of the fundamental dehydriding and rehydriding reactions. In order to gain such insight, we propose to study the reversible dehydriding of NaAlH₄ by solid state nuclear magnetic resonance spectroscopy.

We have also found a class of catalysts that could provide the key to a practical hydrogen storage system based on the reversible dehydrogenation of cycloalkanes to arenes. Such a system meets the criteria of low cost and high hydrogen density (~7.0 wt %). The PCP pincer complex, IrH₂{C₆H₃-2,6-(CH₂PBu^t)₂} is the first reported homogeneous catalysts for the dehydrogenation of cycloalkanes to arenes (Gupta et. al., 1997). Unlike the heterogeneous catalysts for this reaction, it shows appreciable activity at low concentrations at temperatures as low as 100 °C. We have also found that the pincer complex also catalyzes the hydrogenation of arenes to cycloalkanes under

moderate (10 atm) pressures of hydrogen. The two-way, hydrogenation/dehydrogenation activity of the catalyst suggests its application in a hydrogen storage system. The major obstacle to the practical application of the pincer catalyst is that pronounced product inhibition occurs after about 10% dehydrogenation of cycloalkanes. In order to eliminate this problem we plan to synthesize and test an improved catalyst, $\text{IrH}_2\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{AsBu}^t_2)_2\}$.

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