

III.C Metal Hydrides

III.C.1 Catalytically Enhanced Hydrogen Storage Systems

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Objectives

- Determine the chemical nature of the titanium species responsible for the enhanced kinetics of Ti-doped NaAlH₄.
- Determine the mechanism of action of the dopants of Ti-doped NaAlH₄ in the dehydrogenation and rehydrogenation processes.
- Apply insights gained from fundamental studies of Ti-doped NaAlH₄ to the design and synthesis of hydrogen storage materials that meet the FreedomCAR 2010 hydrogen storage targets, especially cost, specific energy, and energy density.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- M. Hydrogen Capacity and Reversibility
- N. Lack of Understanding of Hydrogen Physisorption and Chemisorption

Approach

- Characterization of Ti dopants through electron paramagnetic resonance (EPR) studies.
- Studies of the effects of doping on hydrogen bonding interactions through infrared spectroscopy, nuclear magnetic resonance (NMR) spectroscopy and inelastic neutron scattering.
- Determination of the influence of doping on bulk hydride thermodynamic properties of equilibrium hydrogen plateau pressures.
- Elucidation of the mechanism of the hydrogen cycling process through kinetic measurements and modeling.
- Determination of the influence of doping on structure and detection of minor phases through synchrotron X-ray and neutron diffraction studies.
- Design, synthesis, and evaluation of advanced complex hydrides suggested by the insight gained by fundamental studies.

Accomplishments

- Detection of $\text{Al}_{0.93}\text{Ti}_{0.07}$ in Ti-doped NaAlH_4 after 7 cycles of dehydrogenation-rehydrogenation by synchrotron X-ray diffraction (XRD) studies.
- Identification of a Ti(0) species that replaces a Ti(III) species as the predominate Ti species within 3 cycles of dehydrogenation/rehydrogenation through EPR spectroscopy.
- Detection of significant **bulk** structural changes in the local environment of the $[\text{AlH}_4]^-$ units upon doping **or** only ball milling NaAlH_4 through infrared spectroscopy.
- Detection of decrease in the crystal domain size and increase in anisotropic strain mainly along the *c* axis upon doping **or** only ball milling NaAlH_4 through XRD studies.
- Confirmation of the success of our proprietary method for the extraction of the by-product from “ $\text{Ti}_{x/3}\text{Na}_{1-x}\text{AlH}_4$ ” through X-ray diffraction studies.
- Synthesis of an advanced complex hydride with a potentially higher reversible H_2 capacity than Ti-doped NaAlH_4 at relevant temperatures and reasonable kinetics.

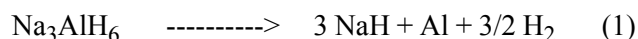
Proposed Future Work

- Tandem EPR, X-ray absorption fine structure and XRD studies (collaboration with University of Denver and GE Global Research). These studies will a) verify our earlier conclusions about the changes in the oxidation state of the titanium occurring during cycling; b) provide information about the local chemical environment of titanium; and c) allow the quantification of the amount of titanium that is present in any segregated phases that arise during cycling.
- Solid-state ^1H nuclear magnetic resonance spectroscopy studies. These are planned to determine the effect of the doping process on the T_1 relaxation of the hydrogen of NaAlH_4 and therefore reveal whether paramagnetic Ti dopants are in close proximity to hydrogen throughout the bulk of the hydride.
- Neutron diffraction structure determination (collaboration with University of Milan) of unmilled NaAlD_4 to determine the structural effects induced by mechanical milling.
- Inelastic neutron scattering studies of unmilled NaAlH_4 (collaboration with National Institute of Standards and Technology) to determine effects on the $[\text{AlH}_4]^-$ units induced by mechanical milling.
- TOM-SIMS depth profiling of Ti distribution in doped NaAlH_4 (collaboration with GE Global Research).
- Determination of hydrogen storage capacity and hydrogen cycling kinetics of “ $\text{Ti}_x\text{Na}_{1-x}\text{AlH}_4$ ”, “ $\text{Ti}_{x/3}\text{Na}_{1-x}\text{AlH}_4$ ”, and novel complex hydrides.
- Preparation and evaluation of other novel complex hydrides.

Introduction

We have developed methods of doping sodium aluminum hydride, NaAlH_4 , with titanium and/or zirconium that give rise to state-of-the-art hydrogen storage materials. However, less than ~5 weight percent hydrogen can be reversibly released from these materials under conditions that are required for the practical operation of an onboard fuel cell. Additionally, the rate and equilibrium plateau pressures of the second dehydrogenation reaction, seen in equation 1, are impractical for hydride that is doped with titanium, and improved variations of this

material must be produced to achieve commercial viability.



It was initially speculated that the remarkable enhancement of the hydrogen cycling kinetics in doped NaAlH_4 was due to surface-localized catalytic sites. However, we obtained X-ray diffraction data that revealed that the doping of the hydride results in bulk lattice distortions. These observations led us to develop a new model of the doped hydrides in which Ti is substituted into the bulk hydride lattice. More recently, evidence in support of our “substitution

model” of doped NaAlH_4 was obtained through EPR spectroscopic studies of the Ti dopants in the hydride (conducted in collaboration with Prof. Eaton of the University of Denver). Additionally, experimental and modeling kinetic studies (conducted in collaboration with Dr. Kiyobayashi of the National Institute of Advanced Science and Technology, Osaka, Japan) established that the kinetics of dehydrogenation and rehydrogenation are highly sensitive to the distribution of the dopant rather than differences in the Al-H bonding interactions.

Approach

To guide our development of advanced complex hydrides, we are conducting fundamental studies to determine the nature of the Ti dopant and the structural effects it exerts on NaAlH_4 . In this effort, we are employing a wide variety of techniques, including electron paramagnetic resonance (collaboration with Prof. S. Eaton, University of Denver); synchrotron X-ray and neutron diffraction (collaborations with Dr. H. Brinks and Prof. B. Hauback, Institute for Energy Research, Kjeller, Norway, and Prof. Alberto Albinati, University of Milan); inelastic neutron scattering (collaboration with Dr. T. Udovic, National Institute of Standards and Technology); X-ray diffraction and infrared spectroscopy (collaboration with Prof. Klaus Yvon, University of Geneva); and solid-state NMR spectroscopy.

The doping process generates by-products that constitute “dead weight” in the kinetically enhanced hydride. For example, doping with TiCl_3 or TiCl_4 results in the formation of segregated NaCl by-product. Our newer model suggests that removal of “dead weight” doping by-product might lead to materials having both increased hydrogen capacity as well as the highly acceptable kinetics that are achieved at high doping levels. Additionally, the “substitution” model, unlike the Redox model, predicts that plateau pressure, a thermodynamic property, should be significantly altered at high doping levels. Thus, we are probing the effect of doping on the equilibrium plateau pressures of the hydride. We are also developing methods of removing the inert, “dead weight” by-products that are generated in the doping process and measuring the hydrogen cycling capacities and kinetics of these

purified materials. Finally, guided by our substitution model of the doped hydride, we are synthesizing and testing novel complex hydrides with potentially much higher reversible hydrogen capacities.

Results

Infrared Spectroscopy. Strong experimental evidence for our substitution model of the doped hydride has been obtained through infrared (IR) spectroscopic studies carried out in collaboration with the University of Geneva. Doping the hydride results in a shift of the IR line for the ν_3 asymmetric stretching mode to $\sim 15 \text{ cm}^{-1}$ higher frequency. Also, one part of the ν_4 asymmetric bending mode shifts by $\sim 20 \text{ cm}^{-1}$ to lower frequency. The broad ν_3 bands also become sharpened, and a new vibration appears at 710 cm^{-1} . These findings suggest **bulk** structural changes in the local environment of the $[\text{AlH}_4]^-$ units. Mechanical milling of the hydride alone produces similar effects.

X-ray Diffraction Studies. Studies carried out with the University of Geneva have revealed both a decrease in the crystal domain size and an increase in anisotropic strain. Doping and milling have also been found to influence structure parameters such as the axial ratio c/a , cell volume and atomic displacement amplitudes. These observations support the idea that some Ti diffusion and substitution into the alanate lattice does occur, in particular during cycling, and that this provides the mechanism through which Ti doping enhances kinetics during re-crystallisation. Synchrotron X-ray diffraction studies conducted with the Institute for Energy Research have shown that a solid-solution of Ti in Al of approximate composition $\text{Al}_{0.93}\text{Ti}_{0.07}$ can be detected in the hydride after 7 cycles of dehydrogenation/rehydrogenation.

Electron Paramagnetic Spin Studies. As mentioned above, our EPR studies have established that the predominant titanium species arising upon Ti doping of NaAlH_4 is spin-isolated Ti(III). However, more recent studies have revealed changes in the population of the Ti(III) species upon cycling. Collaborative EPR studies with the University of Denver have revealed that over 75% of the Ti in the doped hydride is converted to Ti(0) within 5 cycles, and virtually all Ti is present as Ti(0) after 15 cycles.

It is surprising that despite this change in the oxidation state of the titanium during the first 5 cycles, there is very little change in the dehydrogenation and rehydrogenation kinetics of the doped hydride.

Effect of Doping Level on Plateau Pressures.

Our initial studies of the equilibrium hydrogen pressures of Ti-doped NaAlH₄ were conducted with samples of NaAlH₄ that were doped with 1.3-2.0 mole % Ti(OBu)₄. The plateau pressure was seen to increase from 3.0(2) to 4.7(2) MPa over the range of doping levels. However, we soon found that different plateau pressures were obtained at the same doping levels if different dopant precursors were used. During the past quarter, we have found similar variation even among samples that are doped to the same level with the same dopant precursor. This finding is consistent with several reports that the exceptionally flat isotherms reported by Bogdanovic et al. cannot be reproduced. We and several other groups have instead observed plateaus that are severely sloped. Thus, accurate determination of plateau pressures is impossible. We have also found significant variation among the pressures observed at the same points in the dehydrogenation of identically prepared samples. We have therefore terminated experimental work in this area.

Purification of “Ti_{x/3}Na_{1-x}AlH₄”. A proprietary method has been developed for the removal of the contaminant sodium salts resulting upon Ti doping of NaAlH₄. The removal of doping by-products from Ti-doped NaAlH₄ by our process was verified this quarter as part of a research collaboration with the Institute for Energy Research. It was also shown that the extract contains the by-product. However, the extract was also seen to contain an appreciable amount of NaAlH₄. Thus, a solvent with improved selectivity for the doping by-product must be identified.

Synthesis of an Advanced, Novel Complex Hydride. A novel, partially substituted complex hydride (formulation is proprietary information) was synthesized. It has showed extremely promising dehydrogenation and rehydrogenation behavior.

Conclusions

In addition to the earlier EPR and kinetic evidence, we have now obtained IR and XRD results supporting our “substitution” model of Ti-doped NaAlH₄. It is clear from both the EPR and synchrotron X-ray studies that the majority Ti species changes from Ti(III) to an AlTi alloy during the first few cycles of dehydrogenation/rehydrogenation. It is striking that, despite this change, only a minor change in the hydrogen cycling kinetics occurs. This would seem to suggest that the enhanced hydrogen cycling kinetics are due to a Ti species that is present in only a relatively minor amount. The slight kinetic improvement that is observed beyond the third cycle is similar to those observed when the hydride is ball milled without dopant. The finding that a significant amount of the AlTi alloy arises after the third cycle then suggests that the alloy is responsible for this minor kinetic enhancement and acts as an anti-sintering agent. Our adoption of the “substitution” model has guided us to the preparation of “Ti_{x/3}Na_{1-x}AlH₄”, “Ti_xNa_{1-x}AlH₄”, and a novel complex hydride. The evaluations of the hydrogen storage performance of these materials that are currently underway will provide a true test of the validity and value of the “substitution” model of doped complex hydrides.

FY 2004 Publications

1. Kinetic Study and Determination of the Enthalpies of Activation of Titanium and Zirconium Doped NaAlH₄ and Na₃AlH₆. T. Kiyobayashi, S.S. Srinivasan, D. Sun, and C.M. Jensen; *J. Phys. Chem. A* **2003**, *107*, 7671.
2. Rehydrogenation of Dehydrogenated NaAlH₄ at Low Temperature and Pressure. D. Sun, S.S. Srinivasan, T. Kiyobayashi, N. Kuriyama, and C.M. Jensen; *J. Phys. Chem. B* **2003**, *107*, 10176.
3. Diffraction Studies of Alanates. H.W. Brinks, B.C. Hauback, D. Blanchard, C.M. Jensen, M. Fichtner, and H. Fjellvåg; *Advanced Materials for Energy Conversion II*, **2004**, 153.

4. Dehydrogenation Process of Titanium and Zirconium Doped Aluminates. T. Kiyobayashi, S. Akita, S.S. Srinivasan, D. Sun, S. Sangawa, C.M. Jensen and N. Kuriyama; *Advanced Materials for Energy Conversion II*, **2004**, 157.
5. Rehydrogenation and Cycling Studies of Dehydrogenated NaAlH₄. D. Sun, S.S. Srinivasan, G. Chen and C.M. Jensen; *J. Alloys and Compd.*, **2004**, 373, 265.
6. Synchrotron X-ray and Neutron Diffraction Studies of NaAlH₄ Containing Ti Additives. H.W. Brinks, C.M. Jensen, S.S. Srinivasan, B.C. Hauback, D. Blanchard, and K. Murphy; *J. Alloys Compd.* **2004**, 376, 215.
7. Long Term Cycling Behavior of Titanium Doped NaAlH₄ Prepared through Solvent Mediated Milling of NaH and Al with Titanium Dopant Precursors. S.S. Srinivasan, H.W. Brinks, B.C. Hauback, D. Sun and C.M. Jensen, *J. Alloys and Compd.* **2004**, 377, 283 .
8. Dehydrogenation of Alkanes Catalyzed by an Iridium-Phosphinito PCP Pincer Complex. D. Morales-Morales, R. Redón, C. Yung, and C.M. Jensen; *Inorg. Chim. Acta* **2004**, 357, 2953 (invited contribution for topical volume on Rhodium and Iridium Chemistry).
9. Method for Preparing Ti-doped NaAlH₄ Using Ti Powder: Observation of Unusual Reversible Dehydrogenation Behavior. P. Wang and C.M. Jensen; *J. Alloys and Compd.* **2004** in press.
10. Structure and Hydrogen Dynamics in Ti-doped Sodium Aluminates. J. Iniguez, T. Yildirim, T.J. Udovic, M. Sulic, and C.M. Jensen; *Phys. Rev. B* **2004**, 70, 60101.
11. Effects of Milling, Doping and Cycling of NaAlH₄ Studied by Vibration Spectroscopy and X-ray Diffraction. S. Gomes, G. Renaudin, H. Hagemann, K. Yvon, C.M. Jensen, M.P. Sulic; *J. Alloys Compd.* **2004** in press.
12. Preparation of Ti-doped Sodium Aluminum Hydride from Mechanical Milling of NaH/Al with Off-the-shelf Ti Powder. P. Wang and C.M. Jensen; *J. Phys. Chem. B* **2004** in press.
13. EPR Studies of Titanium Doped NaAlH₄: Fundamental Insight to a Promising New Hydrogen Storage Material. S.S. Eaton, M. Kuba, K. Murphy, and C.M. Jensen; submitted to *J. Am. Chem. Soc.*

FY 2004 Invited Presentations

1. European Materials Research Society 2003 Meeting, Symposium on Nanoscale Materials for Energy, Strasbourg, France, 6/11/03.
2. GE Global Research Center, Niskayuna, New York, 7/11/03.
3. Gordon Research Conference on Hydrogen-Metal Systems, Waterville, Maine, 7/15/03.
4. XII International Materials Research Congress, Cancun, Mexico, 8/17/03.
5. International Workshop on the Present Status of Hydrogen Technologies, Mexican Institute of Petroleum, Mexico City, Mexico, 8/20/03.
6. OSTEC Committee on Hydrogen Absorbing Materials, Osaka, Japan, 3/2/04.
7. Symposium on the Fundamentals of Advanced Materials for Energy Conversion II, 2004 meeting of the Minerals, Metals, and Materials Society, Charlotte, North Carolina, 3/14/04.
8. Session on Perspectives on Hydrogen Storage, annual meeting of the American Physical Society, Montreal, Canada, 3/22/04.
9. Symposium on Hydrogen Storage Materials, 205th meeting of the Electrochemical Society, San Antonio, TX, 5/10/04.