CATALYTICALLY ENCHANCED SYSTEMS FOR HYDROGEN STORAGE

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Abstract

Values for the $\Delta H^\ddagger$ of dehydrogenation NaAlH$_4$ to Na$_3$AlH$_6$/Al and Na$_3$AlH$_6$ to NaH/Al and the reverse hydrogenation reactions have been determined through kinetic studies of 2 mol % Ti and Zr doped hydride. We find that the experimentally determined values of $\Delta H^\ddagger$ closely match those predicted by the reaction profile diagrams. This demonstrates that the kinetics of both hydrogenation reactions are limited by the micro-reverse, of the fundamental, Al-H bond breaking process. Solid state $^1$H NMR studies have revealed that there are two distinguishable populations of hydrogen in both doped and undoped NaAlH$_4$. The extremely narrow signal (1-2 kHz) that is observed for one of the hydrogen species establishes that it has unusually high solid state mobility. The results of our studies also demonstrate that doping the hydride results in a bulk effect on Al-H bonding and changes structure of the hydride. On the basis of these and X-ray diffraction studies, we developed a new “Na$^+$ substitution” model of the doped hydride, which is strongly supported by ESR studies. The arsino pincer complex, IrH$_2$(C$_6$H$_3$-2,6-(CH$_2$AsBu$_3^+2$)$_2$) has been found to be an active catalyst for the dehydrogenation of a variety of cycloalkanes to arenes as well as the reverse hydrogenation reaction. However, development of a hydrogen storage system based on this technology seems impractical as only a maximum, 20 % conversion to the arene can be achieved.

Introduction

A major obstacle to the conversion of the world to a “hydrogen economy” is the problem of onboard hydrogen storage. Despite decades of extensive effort no material has been found which has the combination of high gravimetric hydrogen density, adequate hydrogen dissociation energetics, long-term cyclability, and low cost required for commercial vehicular
application. A priori, sodium aluminum hydride, NaAlH\textsubscript{4} would seem to be viable candidate for application as practical onboard hydrogen storage material. It has a high weight percent available hydrogen content (5.6 %); low cost ($70/kg); and is readily available in bulk. However, thermal activated evolution of hydrogen from NaAlH\textsubscript{4} 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 the recent finding that the dehydrogenation of anionic aluminum hydrides can be kinetically enhanced and rendered reversible under moderate conditions in the solid state upon doping with selected transition metals [Bogdanovic and Schwickardi 1997]. We have developed methods of doping of sodium aluminum hydride, NaAlH\textsubscript{4} with titanium, zirconium that have resulted in considerable practical improvements in its hydrogen storage properties. It now appears that the doped hydride could possibly be developed as a viable means for the onboard storage for an onboard PEM fuel cell [Zidan et al. 1999; Bogdanovic et al. 2000; Jensen and Gross 2001; Gross et al. 2002; Sandrock et al. 2002].

We have also been investigating hydrogen storage through the reversible dehydrogenation of cycloalkanes to arenes. Cycloalkanes are cheap and abundant. The dehydrogenation of cycloalkanes to arenes releases approximately 7 weight percent hydrogen. Such a storage system also meets criteria of low cost and high hydrogen density required for practical applications. However, it is, generally considered to be impractical as their dehydrogenation occurs at adequate rates only in the presence of high loadings of heterogeneous, precious metal catalysts at temperatures in excess of 300 °C. We found that the PCP pincer complex, IrH\textsubscript{2}\{C\textsubscript{6}H\textsubscript{3}-2,6-(CH\textsubscript{2}PBu\textsubscript{t}\textsubscript{2})\textsubscript{2}\} (1) is a uniquely active and robust catalyst for aliphatic dehydrogenations [Gupta et al. 1996; Gupta, Hagen et al.1997; Gupta, Kaska et al. 1997; Xu et al. 1997; Liu et al. 1999; Jensen 2000]. In contrast to most catalysts that have been reported thermochemical dehydrogenation of alkanes, the pincer catalyst does not require a sacrificial hydrogen acceptor. Thus in the presence of the pincer catalyst, alkanes are efficiently dehydrogenated to alkenes with the direct evolution of H\textsubscript{2} [Xu et al 1997; Jensen 2000]. The pincer catalyst is also the first reported homogeneous catalyst for the dehydrogenation of cycloalkanes to arenes [Gupta, Hagen et al. 1997]. Unlike the heterogeneous catalysts that are known for this reaction, it shows appreciable activity at temperatures as low as 100 °C and very low catalyst loadings [Gupta, Hagen et al. 1997; Jensen 2000]. 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 based on the reversible dehydrogenation of a cycloalkane to its arene analog, such as the methycyclohexane/toluene system seen in Scheme 1. Temperatures in excess of 200 °C are thermodynamically required to achieve a usable pressure of hydrogen from the dehydrogenation of alkanes. However, unlike solid hydrogen storage materials, liquid cycloalkanes can be easily transported within a system. Thus a small portion can be continuously feed into a small hot tube at a rate that insures an adequate supply of hydrogen for the onboard application. This system is also attractive since it is compatible with the existing gasoline infrastructure.
Scheme 1

Current Year Objectives

Task 1. Determination of Minimum Catalyst Doping Levels Required for Practical Hydrogen Storage Performance of NaAlH₄.

Doping NaAlH₄ with titanium, greatly accelerates the initial dehydrogenation reaction seen in equation 1. We have determined that

\[
\text{NaAlH}_4 \rightarrow \frac{1}{3} \text{Na}_3\text{AlH}_6 + \text{Al} + \text{H}_2
\] (1)

following mechanically doping the hydride with 2 mol % titanium, a hydrogen flow rate of 0.01 g H₂/s per kg can be achieved at 100 °C against a pressure of 1 atm. This performance is adequate to meet the demands of a fuel cell operating under practical conditions. We have also found that NaH and Al doped with 2 mole percent Zr(OPr)₄ will absorb 4.4 weight percent hydrogen within 15 at 120°C under 125 atm of hydrogen. Despite this progress, it has not yet been demonstrated that ~5 weight percent hydrogen can be reversible released from these materials under conditions that are required for the practical operation of an onboard fuel cell. Most notably, the rates of the second dehydrogenation reaction, seen in equation 2, are

\[
\text{Na}_3\text{AlH}_6 \rightarrow 3 \text{NaH} + \text{Al} + 3/2 \text{H}_2
\] (2)

impractical for titanium doped hydride. We have found that the rate of this process is greatly enhanced in zirconium doped hydride [Zidan et al., 1999]. These studies also indicated that the titanium and zirconium dopants could act in concert to yield a material with adequately enhanced kinetic performance through both dehydrogenation reactions. However, the addition of two dopants significantly reduces the cyclable hydrogen weight percentage of the hydride. Therefore, one of our objectives during the past year has been to determine the minimum levels of dopants that are required to adequately enhance the kinetics of NaAlH₄ under the practically relevant conditions.
Task 2. Characterization of “mobile hydrogen” and identification of the “Active Catalyst” by NaAlH₄ by Solid State NMR Spectroscopy. Following Bogdanovic’s disclosure of the discovery of the remarkable effect of dopants on the hydrogen cycling kinetics of NaAlH₄, it was anticipated that alternative dopants and counter ions for the [AlH₄]⁻ complex could be identified that would further improve the dehydrogenation kinetics and thermodynamic properties. While significant improvements have been made in the engineering of a practical hydrogen storage system based on titanium doped NaAlH₄ [Jensen and Gross 2001; Gross et al. 2002; Sandrock et al. 2002], no dopant precursors have been found that give a greater kinetic enhancement than those cataloged in Bogdanovic’s original 1995 patent. Similarly, only the sodium and mixed sodium, lithium salts of the alanates have been found undergo largely reversible dehydrogenation under moderate conditions upon doping. This lack of progress is surprising in view of the recent “gold rush” flurry of activity that has been direct towards the development of alanates as practical onboard hydrogen carries [Bogdanovic and Schwickardi 1997; Jensen et al. 1999; Zidan et al. 1999; Bogdanovic et al. 2000; Zaluska et al. 2000; Gross et al. 2000; Jensen and Gross 2001; Bogdanovic and Schwickardi, 2001; Gross et al. 2002; Sandrock et al. 2002; Meisner et al. 2002]. Clearly, these efforts have been handicapped by the dearth in the understanding of the nature and mechanism of action the dopants. In order to elucidate the structural changes that occur upon doping the hydride, we have conducted solid state ¹H NMR studies. It was initially speculated that the remarkable enhancement of the hydrogen cycling kinetics in doped NaAlH₄ was due to surface-localized catalytic sites [Bogdanovic and Schwickardi 1997; Bogdanovic et al. 2000; Gross et al. 2000; Thomas et al. 2002]. However, we have obtained X-ray crystallographic data that reveals that the doping of the hydride results in bulk lattice distortions [Sun et al., 2002]. We have conducted solid-state ¹H NMR experiments on samples of doped NaAlH₄ in order to gain insight into the chemical environment of the hydrogen. Our data has shown that there are at least two bulk populations of hydrogen in doped NaAlH₄, one of which has extraordinary mobility for hydrogen in a solid state material. Further solid-state ¹H NMR studies have been conducted in order to determine the relationship between the relative amount of “mobile hydrogen” and the levels of titanium and/or zirconium dopants. Experiments have also been carried out with the objectives of characterizing the “mobile hydrogen” and “active catalyst” that are present in the doped hydride.

Task 3. Testing of Arsino Pincer as Catalyst for Alkane Dehydrogenation. The major drawback to homogenous, pincer complex catalyzed systems is that pronounced product inhibition occurs after dehydrogenation of about 10% of the cycloalkane to arene. The dissociation of the arene products from the catalyst is apparently reversible and, at high concentrations, they effectively compete with alkanes for coordination to complex. In an attempt to eliminate this problem, we synthesized the novel iridium complex, IrH₂{C₆H₃-2,6-(CH₂AsBu)₂} in which the phosphorous donor atoms are substituted by arsenic. The altered electronic environment at the metal center improves the alkane/arene binding selectivity and significantly improved levels of conversion methylcyclohexane to toluene can be achieved with the arsino complex. The catalytic dehydrogenation of methylcyclohexane to toluene proceeds to >20% compared to the only 10 % conversion that obtained with the phosphino catalyst. This result verified our hypothesis that the σ-donor strength of the ligand greatly influences the attainable conversion level in the catalytic system. Unfortunately, the conversion level is still far short of practically significant, >90 % mark. We reasoned that arene product of increased steric bulk such as naphthalene and biphenyl might have a weaker interaction with the iridium center and therefore allow higher conversion levels. In order to test this hypothesis, we have determined the maximum percent conversions of other cycloalkanes decalin and dicyclohexyl to the corresponding arenes that can be obtained through catalytic dehydrogenation by the arsino pincer catalyst.
Results

Task 1. Determination of the Minimum Catalyst Doping Levels Required for Practical Hydrogen Storage Performance of NaAlH₄. Our studies of the dehydrogenation and re-hydrogenation of duel titanium/zirconium doped hydride revealed very complicated kinetics. It was unclear whether the reaction rates were limited by the rate of formation of Al-H bonds or instead by rate of contact between particles of aluminum hexahydride complex ion and aluminum metal. This question was addressed by charting the reaction-enthalpy profile of the reversible dehydrogenation of NaAlH₄.

The \( \Delta H \) for the first dehydrogenation reaction has been determined as 37 kJ/mol (Bogdanovic et al. 2000; Gross et al 2002). We have previously determined an activation enthalpy, \( \Delta H^\ddagger \) of 78 kJ/mol for the dehydrogenation of NaAlH₄ doped with 2 mol % titanium to Na₃AlH₆ from the Eyring plot (ln(k/t) vs 1/t) of the dehydrogenation rate over the range 80-120 °C under 1 atm of hydrogen pressure. We have also studied the reverse, re-hydrogenation reaction over the 100-150 °C temperature range under an initial pressure of 100 atm. As illustrated in Figure 1, there is excellent agreement between the activation enthalpy, \( \Delta H^\ddagger \) of 44 kJ/mol that was determined from the Eyring plot of the re-hydrogenation rate data and the 41 kJ/mol value predicted by the different between the \( \Delta H_{\text{dehy}}^\ddagger \) and the \( \Delta H \) of the dehydrogenation reaction. We have also carried out studies of the second dehydrogenation reaction over the 120-150 °C temperature range under 1 atm as well as its reverse over the 100-150 temperature range under an initial pressure of 100 atm. An excellent agreement was again found between the \( \Delta H^\ddagger \) of 109 kJ/mol determined for the second step of dehydrogenation process and the 108 kJ/mol sum of the 93 kJ/mol value we determined for \( \Delta H_{\text{dehy}}^\ddagger \) and the \( \Delta H \) of 15 kJ/mol that was previously determined for the dehydrogenation reaction [Clardy et al 1980]. We concluded that the kinetics of both re-

![Figure 1. Energy-reaction profile for the reversible dehydrogenation of NaAlH₄ to NaH + Al.](image-url)
hydrogenation reactions are limited by the micro-reverse, of the fundamental, Al-H bond breaking process.

We have also conducted analogous kinetic studies and analysis of the dehydrogenation and rehydrogenation of 2 mol % zirconium doped NaAlH₄. Values of 113 and 78 were determined for the $\Delta H^\ddagger$ of the first dehydrogenation reaction and its reverse respectively. The data from our studies of the second dehydrogenation reaction and its reverse gave respective values of 93 and 79 kJ/mol. The excellent agreement between values of $\Delta H^\ddagger_{\text{dehy}}$ and $\Delta H + \Delta H^\ddagger_{\text{rehy}}$ suggests that the kinetics of both the dehydrogenation and hydrogenation reactions of the zirconium are also limited by the micro-reverse, of the fundamental, Al-H bond breaking process. Comparison of the results obtained with the titanium and zirconium doped hydride confirms our earlier conclusion [Zidan et al. 1999] that Ti doping results in the best kinetics for the reversible dehydrogenation of NaAlH₄ to Na₃AlH₆/Al while Zr doping results in the best kinetics the reversible dehydrogenation of Na₃AlH₆ to NaH/Al.

Collaborative X-ray diffraction studies with the National Institute of Advanced Industrial Science and Technology, Osaka, Japan have confirmed the conclusion of solid state NMR studies (see below) that doping results in bulk structural changes rather than generation of surface isolated catalytic sites. The results of these studies have served as the basis of a new model of the doped hydrides. We attribute the structural changes that arise upon doping to the substitution of Na⁺ ions by M⁴⁺ at low (≤2 mol %) doping levels and M³⁺ at higher doping levels and the generation of the requisite number of Na⁺ vacancies in the hydride lattice to maintain charge neutrality [Sun et al. 2002]. Our model is support electron spin resonance (ESR) studies conducted in collaboration with Denver University and Sandia National Laboratory. These studies revealed the presence of Ti³⁺ in samples of NaAlH₄ that were doped with both TiCl₃ and as well as the Ti(IV) precursor, Ti(OBu)₄. This “Na⁺ substitution” model predicts that the dopants should effect dehydrogenation and hydrogenation kinetics only in the local domain of a substitution site. Therefore, the complicated and inadequate overall kinetic performance that was found for the duel Ti/Zr doped hydride [Sandrock et al. 2002] can be understood. The [AlH]₆⁻ anions that are proximal to titanium cations undergo relative fast dehydrogenation but [AlH₆]₃⁻ anions that are proximal to zirconium cations undergo relative slow dehydrogenation. The opposite dichotomy is established for complex anions that are proximal to zirconium cations.

II. Characterization of “mobile hydrogen” and identification of the “active catalyst” by NaAlH₄ by Solid State NMR Spectroscopy. The wide-line solid state $^1$H NMR spectrum of a balled milled sample of undoped NaAlH₄ is seen to contain both a broad and narrow component. The narrow feature has a chemical shift of ca. 2 ppm and an unusually narrow linewidth of ca. 1-2 kHz while broad feature has a more typical linewidth of ca. 40 kHz. Using inversion-recovery experiments, the $T_1$ of the narrow and broad features were determined to be 2 msec and 25 seconds, respectively. The former is particularly striking, because this short $T_1$ is atypical for protons in the solid-state. The relative intensity of the narrow component was unchanged upon heating a ball milled sample under dynamic vacuum at 100 °C for 24 h. Thus it would seem unlikely that the narrow feature is associated with residual organic solvent as this treatment would remove the majority of this type of impurity. Additionally, the infra red spectrum of this material was devoid of any absorptions in the C-H stretching region. Furthermore, the relative intensity of the narrow component increases as the hydride is subjected to ball milling for longer periods of time. Obviously, this should not increase the level organic solvent in the material. The remarkably short $T_1$ of the narrow feature suggests that the second population hydrogen is metal bound hydrogen which is not in a discrete, rigid [AlH₄]⁻ environment and may participate in direct H-H bonding
We have obtained the spectrum of samples of the hydride that were doped with 1, 1.5, 2, and 4 mol % titanium by our mechanical doping method. As is the case with the undoped sample, the spectra contain both the relatively narrow and broad features. The chemical shifts and linewidths of both components appear nearly identical to those observed for the undoped sample. However, upon comparing the spectra it is apparent that the relative intensity of the narrow component increases with increasing doping until the 4 mol % level. Further increase in the dopant level does not result in a greater mobile hydrogen population. This dependency is illustrated in Figure 2. Interestingly, these intensity changes closely mirrors the trends in lattice parameters as determined by X-ray crystallography whereby the lattice contracts with increasing doping to the 2 mol % level and then expands as dopant level increases beyond 2 mol % [Sun et al., 2002]. This data supports our hypothesis that doping results in the perturbation of Al-H bonding throughout the bulk of the hydride. Furthermore, it is clear that the population of the apparently mobile, or mobilized, hydrogen is directly related to the hydrogen cycling kinetics of the hydride.

**Task 3. Testing of the Arsino Pincer Complex as a Catalyst for Reversible Alkane Dehydrogenation.** The arsino pincer complex, IrH$_2$(C$_6$H$_3$-2,6-(CH$_2$AsBu$_2$)$_2$ was found to be an active catalyst for the dehydrogenation of decalin to hydronaphalenes as well as dicyclohexyl to biphenyl. Solutions containing the cycloalkanes and 0.1 mol % of the complex were heated to 200 °C for periods as long as one week. Analysis of the reaction mixtures by gas chromatography showed that the maximum conversion unsaturated was ~20%. Thus there

![Figure 2](image.png)

**Figure 2.** Variation in relative population of mobile hydrogen in NaAlH$_4$ observed by solid state $^1$H NMR spectroscopy as a function of level of Ti doping.

is no significant improvement in the level of conversion that can be achieved with methylcyclohexane.
Conclusions

During the past year, our studies of doped NaAlH\textsubscript{4} have given important insights into the highly promising but enigmatic hydrogen storage properties of this material. The values determined for $\Delta H^{\ddagger}_{\text{dehy}}$ from our kinetic studies of both titanium and zirconium doped hydride are nearly equal to sum of the values we determined for $\Delta H^{\ddagger}_{\text{rehy}}$ and the known values $\Delta H$. This strongly suggests that the kinetics of dehydrogenation and hydrogenation reactions are limited by the micro-reverse, of the fundamental, Al-H bond breaking process. Our X-ray diffraction and solid state NMR studies have shown that doping results in bulk changes the crystal lattice of the hydride rather than the generation of surface isolated catalytic sites. This structural augmentation of the hydride effects bulk perturbation and mobilization of hydrogen. However, the relative amount of mobile hydrogen increases linearly with increased doping only to the 2 mol \% level. These observations that bulk structural occur upon doping the hydride have led us to develop a new model of the doped hydrides. We have hypothesized that the structural changes are the result of substitution of Na\textsuperscript{+} ions by M\textsuperscript{3+} at low (≤2 mol \%) doping levels and M\textsuperscript{2+} at higher doping levels and the generation of the requisite number of Na\textsuperscript{+} vacancies in the hydride lattice to maintain charge neutrality. In support of this “Na\textsuperscript{+} substitution” model, the presence of Ti\textsuperscript{3+} in samples NaAlH\textsubscript{4} that were dope with a variety of titanium precursor has been confirmed through electron spin resonance (ESR) studies. The model predicts that the dopants should effect dehydrogenation and hydrogenation kinetics only in the local domain of a substitution site and thus accounts for the ineffectiveness of “duel dopant” strategies for the improvement of the overall enhancement of the hydrogen cycling kinetics of the hydride.

We have attempted to develop a hydrogen storage system based on the reversible dehydrogenation of cycloalkanes to arenes utilizing iridium “pincer” complexes, IrH\textsubscript{2}{C\textsubscript{6}H\textsubscript{3}-2,6-(CH\textsubscript{2}AsBu\textsubscript{t\textsuperscript{2}})}\textsubscript{2} and IrH\textsubscript{2}{C\textsubscript{6}H\textsubscript{3}-2,6-(CH\textsubscript{2}PBu\textsubscript{t\textsuperscript{2}})}\textsubscript{2}. These complexes appreciable catalytic activity at low concentrations at temperatures as low as 100 \textdegree C. The complexes also showed appreciable catalytic for hydrogenation of arenes to cycloalkanes under moderate (10 atm) pressures of hydrogen. Despite this two-way hydrogenation/dehydrogenation activity, their practical application in a hydrogen storage system seems unlikely as the dehydrogenation activity of the pincer catalysts were found to be pronounced inhibited by all the arene products of all of the substrates tested after about 10-20 \% conversion.

Future Work

A key question remaining in our newly emerged model of doped NaAlH\textsubscript{4} is whether the enhanced hydrogen cycling kinetic are the result substitution of Na\textsuperscript{+} by M\textsuperscript{3+} and M\textsuperscript{2+} or both. Thus we plan to continue ESR studies to determine whether Ti\textsuperscript{3+} and Zr\textsuperscript{3+} are present in doped material over a broad range of doping levels and whether there is a direct relationship between the amount of Ti\textsuperscript{3+} and Zr\textsuperscript{3+} and the kinetic performance of the hydride. These studies should also establish whether M\textsuperscript{2+}, and/or M\textsuperscript{0} are present in 1-6 mol \% Ti and Zr doped hydride. If in fact the transition metal cations have difference valance states at high and low doping levels, we plan to carry out studies of the full cycling kinetics of NaAlH\textsubscript{4} doped solely with Ti\textsuperscript{3+}, Ti\textsuperscript{4+}, Zr\textsuperscript{3+}, Zr\textsuperscript{4+} or other transition metal cations. Also plan to continue our efforts to characterize the mobile hydrogen in NaAlH\textsubscript{4} through solid state NMR spectroscopy. It should be possible to elucidate the of nature of motion (i.e. rotation or long range mobility) through variable temperature and T\textsubscript{2} studies. We are also scheduled to supplement these studies of the dynamics of the mobile hydrogen with inelastic neutron scattering studies that are scheduled to be conducted in collaboration with Dr. Juergen Eckert at Los Alamos National Laboratory. Our discovery of the mobile hydrogen in NaAlH\textsubscript{4} has raised many questions as to the nature of the bonding interactions of this hydrogen population. In order to probe these questions we have
scheduled collaborative neutron diffraction studies with Sandia National Laboratory and other participants in the International Energy Agency.

Our newly emerged model of the structure of the doped hydride and discovery of mobile hydrogen in these material points to several fresh approaches to improving the hydrogen storage properties of alanates and other saline hydrides. Several new types of materials will be prepared and evaluated in the near future.

References


