

CATALYTICALLY ENHANCED SYSTEMS FOR HYDROGEN STORAGE

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Abstract

The effects of two classes of dopants on the rates of the dehydriding of doped NaAlH_4 to Na_3AlH_6 and Al have been studied under the practical relevant conditions of 100°C and a constant pressure of 1 atm. Aluminum-transition metal alloys were found to have little or no effect while doping with transition metal-aluminum hydride complexes resulted in only modest kinetic enhancement. The dehydriding rates of hydride doped with 2 mol % $\text{Ti}(\text{O}^n\text{Bu})_4$ or $\beta\text{-TiCl}_3$ are adequate to meet the demands of a fuel cell operating under practical conditions. Mixtures of NaH and Al doped with 2 mol% $\text{Zr}(\text{O}^n\text{Pr})_4$ will undergo hydriding to NaAlH_4 in 15 minutes under 120 atm of hydrogen at 120°C . Methods have been developed whereby the different species that are present during the dehydriding of the doped hydrides can be directly observed and quantified by solid state ^{27}Al , and ^{23}Na NMR spectroscopy. Solid state ^1H NMR spectroscopy has allowed the unexpected observations that $\sim 25\%$ of the hydrogen in NaAlH_4 is highly mobile at even ambient temperature and that titanium doping results in a significant increase in the proportion of mobile hydrogen in the **bulk** material. ^{27}Al and ^{23}Na NMR studies indicate that the mobility of hydrogen results from the breaking of Na-H rather than Al-H bonds. The arsino pincer complex, $\text{IrH}_2\{\text{C}_6\text{H}_3\text{-}2,6\text{-(CH}_2\text{AsBu}^t\text{)}_2\}_2$ has been synthesized and found to catalyze the dehydrogenation of methylcyclohexane to toluene. The $>20\%$ conversion obtained using this catalyst is much greater than the 10% conversion obtained with $\text{IrH}_2\{\text{C}_6\text{H}_3\text{-}2,6\text{-(CH}_2\text{P}^t\text{Bu}^t\text{)}_2\}_2$ but far short of practically significant mark of $>90\%$.

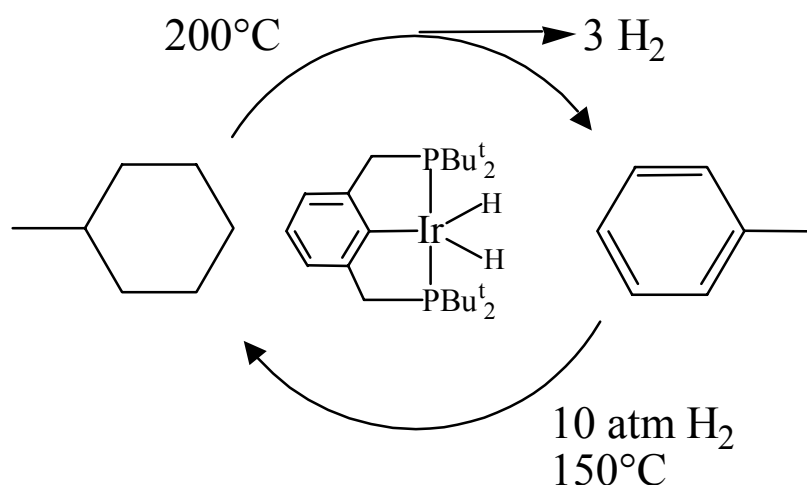
Introduction

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 that has the combination of a 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_4) would seem to be viable candidate for application as a practical onboard hydrogen storage material. It has a high weight percent available hydrogen content (5.6%), low cost (\$50/metric ton), and is readily available in bulk. However, thermal-activated evolution of hydrogen from NaAlH_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 recent studies that have shown that upon doping with selected transition metals, the dehydriding of anionic aluminum hydrides could be kinetically enhanced and rendered reversible under moderate conditions in the solid state (Bogdanovic and Schwickardi, 1997; Jensen et al., 1999; Zidan et al., 1999; Bogdanovic et al., 2000; Jensen and Gross, 2001). We have developed methods of doping NaAlH_4 with titanium, zirconium and other catalysts such that: 1) rapid dehydriding occurs at temperatures as low as 100°C ; 2) rehydriding can be accomplished in only 15 minutes; and 3) 5.0 weight percent hydrogen can be repeatedly cycled through dehydriding/rehydriding. It now appears that it is not unreasonable to think that catalytically enhanced complex aluminum hydrides could be developed as a means of practical storage of hydrogen for an onboard PEM fuel cell.

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 .

The PCP pincer complex, $\text{IrH}_2\{\text{C}_6\text{H}_3\text{-}2,6\text{-(CH}_2\text{P}^t\text{Bu)}_2\}$ (**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_2 (Gupta, Hagen 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 methylcyclohexane/toluene system seen in Scheme 1.

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. 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 product from the catalyst is apparently reversible and, at high concentrations, arenes effectively compete with alkanes for coordination to complex. In an attempt to eliminate this problem, we have synthesized a novel iridium complex containing a pincer ligand in which the phosphorous donor atoms are substituted by arsenic atoms. It is our premise that this adjustment will alter the electronic environment at the metal center and improve the alkane/arene binding selectivity. We have found that significantly improved levels of conversion of methylcyclohexane to toluene can be achieved with the arsino complex.

Results

Task 1. Testing of Aluminum-Transition Metal Catalysts for the Reversible Dehydrogenation of NaAlH₄. The aluminum-transition metal alloys (TiAl, Ti₃Al, Zr₃Al, and Ni₃Al) and the transition metal-aluminum hydrido complexes: $[(C_5H_5)_2ZrH(\mu-H)_2AlH_2(NMe_3)]$ and $[(C_5H_5)_2Ti(\mu-H)_2AlH_2(THF)]$ were studied as catalysts for the reversible dehydrogenation of NaAlH₄. The complexes were synthesized through methods that have been reported in the literature (Khan et al., 1997; Fryzuk et al., 1997) while the alloys were purchased from Alfa Aesar. Small amounts (~2 mole%) of the alloys and complexes were introduced into the bulk NaAlH₄ through ball milling techniques under an inert atmosphere. The dehydrogenation behavior of the doped hydrides were screened by thermal programmed desorption and isothermal

desorption studies using a modified Sievert's type apparatus. Little or no kinetic enhancement was observed in all of the samples doped with aluminum alloys. Hydrogen desorption was accelerated in the samples doped with the transition metal-aluminum hydride complexes. However, the desorption rates were much lower than those observed for samples doped with $\text{Ti}(\text{O}^n\text{Bu})_4$ or $\text{Zr}(\text{O}^n\text{Pr})_4$.

In order to obtain a meaningful comparison of the relative catalytic enhancement produced by the various dopants, we conducted isothermal desorption studies of samples of the hydrides under the practical relevant conditions of 100°C while maintaining a constant pressure of 1 atm. During the initial dehydriding reaction



we observed the hydrogen flow rates seen in Table 1.

Table 1. Rates of dehydriding of NaAlH_4 containing 2 mole % dopant at 100°C , against a constant pressure of 1 atm.

| Catalyst Precursor | Rate of desorption (wt %/hr) |
|--|------------------------------|
| $\text{Ti}(\text{O}^n\text{Bu})_4$ | 1.8 |
| $\beta\text{-TiCl}_3$ | 1.8 |
| TiCl_4 | 1.8 |
| $\text{Zr}(\text{O}^n\text{Pr})_4$ | 0.6 |
| $\{(\text{C}_5\text{H}_5)_2\text{ZrH}(\mu\text{-H})_2\text{AlH}_2(\text{NMe}_3)\}$ | 0.2 |
| $\{(\text{C}_5\text{H}_5)_2\text{Ti}(\mu\text{-H})_2\text{AlH}_2(\text{THF})\}$ | 0.2 |

We were surprised to find that the rates observed for hydride doped with either $\text{Ti}(\text{O}^n\text{Bu})_4$ or $\beta\text{-TiCl}_3$ are 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 $\text{Zr}(\text{O}^n\text{Pr})_4$ will undergo the reverse of the dehydriding reactions seen in equations 1 and 2 (below) more rapidly and under milder conditions than had been previously appreciated.



Absorption of 4.4 weight percent hydrogen was seen to occur within 15 minutes at 120°C under a pressure of 125 atm of hydrogen. Thus our benchmarking of the previously reported catalysts revealed that the only remaining kinetic barrier to the practical utilization of NaAlH_4 is the development of an improved catalyst for the "second" dehydriding reaction seen in equation 2.

Task 2. Solid State Nuclear Magnetic Resonance Spectroscopic Studies of the Reversible Dehydriding of NaAlH_4 and Active Catalyst. In collaboration with Prof. K. Kumashiro and Dr. W. Niemczura of the UH Department of Chemistry, we developed methods whereby we have directly observe and quantify the different species that are present during the dehydriding of the doped hydrides by solid state ^{27}Al , and ^{23}Na NMR spectroscopy. Additionally, as seen in Figure 1, wideline ^1H NMR spectra show that, contrary to the accepted model of the bonding in

Group 13 complex hydrides, ~25% of hydrogen in NaAlH₄ is highly mobile at even ambient temperature.

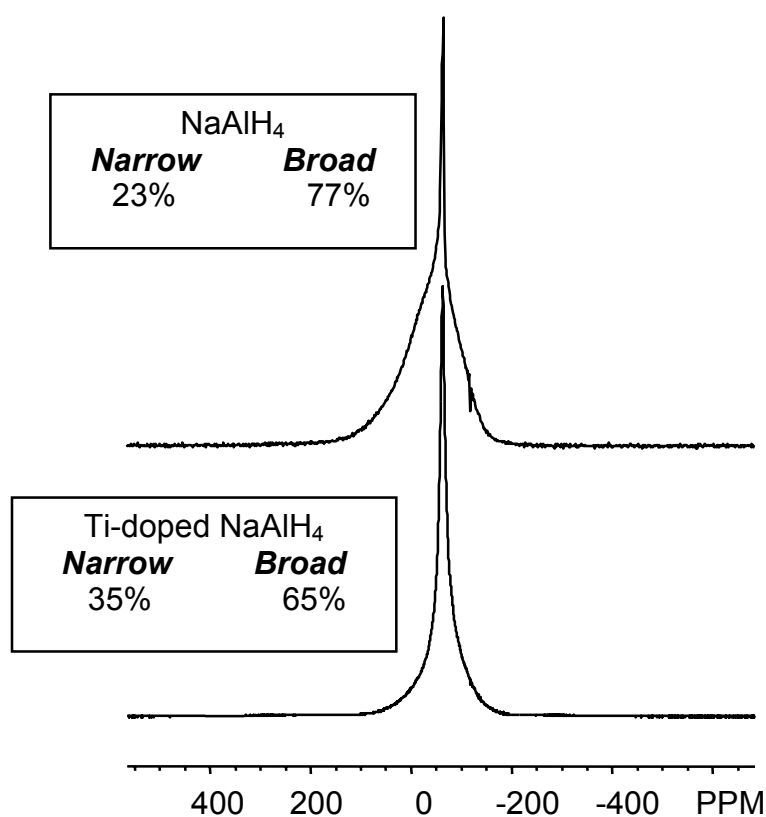


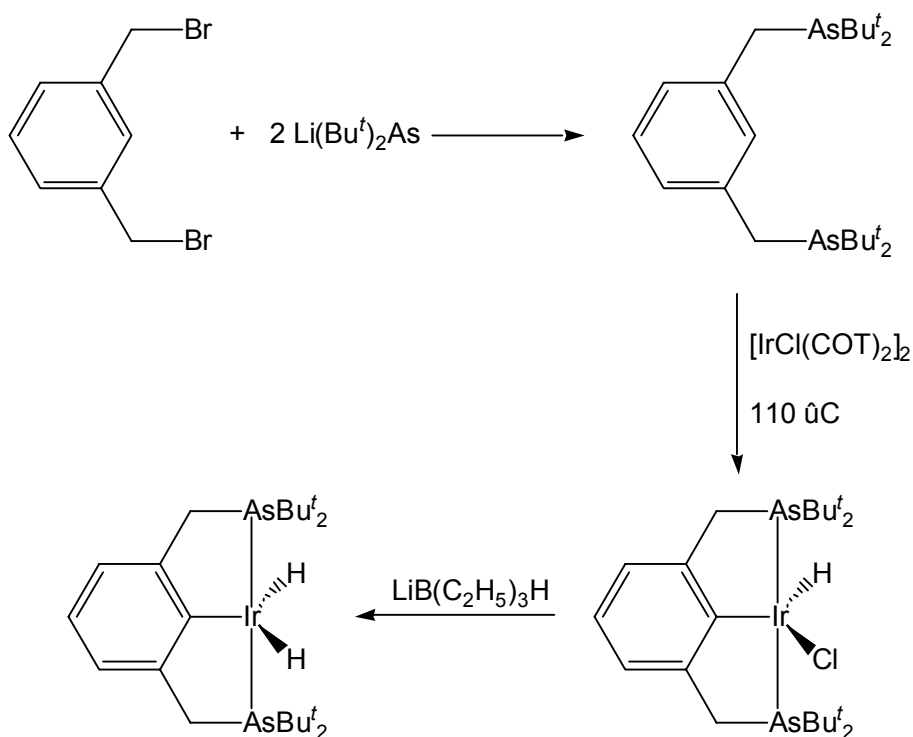
Figure 1. Solid state ¹H NMR spectra of NaAlH₄ with and without doping with 2 mol% Ti(OⁿBu)₄.

Surprisingly, the ²⁷Al, and ²³Na NMR studies indicate that the mobility of hydrogen results from the breaking of Na-H rather than Al-H bonds. We have observed (Figure 1) that samples of the hydride that are doped with titanium have a significant increase in the proportion of mobile hydrogen in the **bulk** material. Therefore, we can directly observe the lowering of the energetic barrier to the activation of hydrogen in the hydride and thus quantify the fundamental catalytic effect of the dopant. We are now beginning studies in which the populations of mobile hydrogen in undoped, titanium-doped, and zirconium-doped hydrides are quantified at temperatures ranging from 20-150°C. The activation parameters for the fundamental hydrogen activation process will be calculated from the variable temperature data.

Task 3. Synthesis and Testing of an Arsino Pincer Catalyst for Reversible Alkane Dehydrogenation. We successfully synthesized the arsino pincer complex, IrH₂{C₆H₃-2,6-(CH₂AsBu^t₂)₂} as seen in Scheme 2. Reaction of α,α'-dibromoxylene with two equivalents of lithium di-*t*-butylarsinide gave α,α'-bis(arsino)xylene in >90% yield. The hydrido chloride iridium complex, IrHCl{C₆H₃-2,6-(CH₂AsBu^t₂)₂} was then synthesized by refluxing the α,α'-bis(arsino)xylene with [Ir(COE)(μ-Cl)]₂ in toluene for 24 h. Subsequent reaction of the hydrido chloride complex with LiBEt₃H under an atmosphere of H₂ gave the target dihydride complex

that was characterized by ^1H , ^{13}C , and ^{31}P NMR spectroscopy. The catalytic activity of the arsino pincer complex for the dehydrogenation of toluene to methylcyclohexane at 200°C was quantified by gas chromatography. We have observed that the catalytic dehydrogenation of methylcyclohexane to toluene proceeds to $>20\%$ compared to the only 10% conversion that was obtained with the phosphino catalyst. This result verifies 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 the practically significant mark of $>90\%$ and it seems unlikely that we will be able to adjust the catalytic system such that we can attain such high levels of conversion.

Scheme 2. Synthesis of $\text{IrH}_2\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{AsBu}^t\text{)}_2\}$.



Conclusions

We have examined the effects of two classes of dopants on the rates of the dehydriding of doped NaAlH_4 to Na_3AlH_6 and Al under the practical relevant conditions of 100°C and a constant pressure of 1 atm. Aluminum-transition metal alloys were found to have little or no effect while doping with transition metal-aluminum hydride complexes resulted in only modest kinetic enhancement. However, benchmarking the dehydriding rates of hydride doped with $\text{Ti}(\text{O}^i\text{Bu})_4$ and $\beta\text{-TiCl}_3$ has revealed that these materials undergo dehydriding at rates 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 $\text{Zr}(\text{O}^n\text{Pr})_4$ will undergo hydriding to NaAlH_4 more rapidly and under milder conditions that had been previously appreciated. Thus, three key practical kinetic parameters have now been established for NaAlH_4 at acceptable doping levels: 1) dehydriding of NaAlH_4 to Na_3AlH_6 and Al at the rate of 1.8 wt% per hour at 100°C under 1 atm; 2) rehydriding of 4.4 wt% can be accomplished in only 15 minutes; and 3) 5.0 wt% hydrogen can be repeatedly cycled through dehydriding/rehydriding. Thus these materials hold great promise as hydrogen carriers for onboard fuel cells. However, further catalyst development is required in order for these materials to achieve commercial viability.

We have developed methods whereby the different species that are present during the dehydriding of the doped hydrides can be directly observed and quantified by solid state ^{27}Al , and ^{23}Na NMR spectroscopy. Additionally, solid state ^1H NMR spectra has allowed the unexpected observations that ~25% of the hydrogen in NaAlH_4 is highly mobile at even ambient temperature and that titanium doping results in a significant increase in the proportion of mobile hydrogen in the **bulk** material. Furthermore, ^{27}Al , and ^{23}Na NMR studies indicate that the mobility of hydrogen results from the breaking of Na-H rather than Al-H bonds. Thus we can directly observe the lowering of the energetic barrier to the activation of hydrogen in the hydride and therefore quantify the fundamental catalytic effect of the dopant. Extensions of these studies should elucidate the mechanism of the catalyzed dehydriding reactions and lead to the characterization the enigmatic active catalyst in the doped hydrides.

We have successfully synthesized the arsino pincer complex, $\text{IrH}_2\{\text{C}_6\text{H}_3\text{-}2,6\text{-(CH}_2\text{AsBu}^t_2)_2\}$ and to found it to catalyze the dehydrogenation of methylcyclohexane to toluene. The >20% conversion obtained using this catalyst is much greater than the 10% conversion that was obtained with the phosphino catalyst. This result verifies 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 the practically significant mark of >90% and it seems unlikely that we will be able to adjust the catalytic system such that we can attain such high levels of conversion.

Future Work

Despite progress in maximizing the catalytic enhancement of both the dehydriding and rehydriding process, it has not yet been demonstrated that >5 wt% hydrogen can be reversibly released from these materials under conditions that are required for the practical operation of an onboard fuel cell. Our studies also indicate that the titanium and zirconium catalysts can act in concert to yield a material with adequately enhanced kinetic performance over the course of the complete dehydriding reaction sequence and its reverse (Zidan et al., 1999). However, the requirement of dual catalysts significantly affects the cyclable hydrogen weight percentage of the hydride. Therefore, the contribution of the transition metal dopant to the weight of the material must be minimized. During the next year of this project, we plan to determine the minimum levels of titanium and zirconium loadings that are required to adequately enhance the kinetics of NaAlH_4 under the practically relevant conditions. Dehydriding studies will be carried out under

positive pressures (1-2 atm) of hydrogen and rehydriding will be carried out at pressure of less than 100 atm and temperatures of less than 100°C.

As discussed above, we have found that solid state ^1H NMR spectroscopy allows us to directly observe the lowering of the energetic barrier to the activation of hydrogen in the hydride. Therefore we plan to quantify the fundamental catalytic effect of the titanium and zirconium dopants. We are now beginning studies in which the populations of mobile hydrogen in undoped and doped hydrides are quantified at temperatures ranging from 20-150°C. The activation parameters for the fundamental hydrogen activation process will be calculated from the variable temperature data. We also plan to prepare bulk quantities of the catalytically active species through the stoichiometric reaction of NaAlH_4 with catalyst precursors. We will then characterize the materials that are produced through solid state ^1H , ^{27}Al , and/or ^{23}Na NMR spectroscopy. We hope to then determine the identity of the active catalyst through comparison of these spectra to those of samples of titanium and aluminum compounds that are considered to be likely catalyst candidates.

Finally, before abandoning our efforts with the arsino pincer catalyst, we plan to conduct wrap-up studies in which we will examine the dehydrogenation of other cycloalkanes including decalin and dicyclohexyl. It is conceivable that the increased steric bulk of the corresponding products, naphthalene and biphenyl will result in reduction of the bond strengths to the iridium center and therefore allow higher conversion levels to be attained.

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