Complex Hydrides for Hydrogen Storage

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Abstract

Complex hydrides, containing a minimum of 7.5 wt% hydrogen, are being investigated as hydrogen storage compounds for automotive use. As a new project, the work to date has largely involved refurbishment of equipment and acquisition of study materials. Initial experiments have confirmed that the instrumentation is functioning and that the data being obtained agree with that in the literature.

Introduction

Complex hydrides, sometimes referred to as classical chemical hydrides,[1] previously were considered for hydrogen storage only in the context of releasing the hydrogen via hydrolysis. While hydrolysis increases the amount of hydrogen liberated, it also requires that water be carried as a part of the system and the products of the reaction include an aqueous solution that is not readily reversible. To be considered as a viable hydrogen storage medium, a material must be capable of being regenerated with a minimal energy penalty. It also must release the hydrogen at a temperature of less than $100^{o}C$ in order to be compatible with fuel cells and must have an installed hydrogen density of 6.5 wt%.

Complex hydrides of aluminum are attractive as hydrogen storage compounds due to their large hydrogen content. Unfortunately, their application in this manner has been impractical as a result of the great difficulties in reversing the hydrogen release reaction. Since workers in several laboratories have reported the discovery of a number of catalysts that improve the reversing of the hydrogen release by $NaAlH_4$, Na_3AlH_6, and $LiAlH_4$, interest in the use of complex hydrides of aluminum as hydrogen storage media has been rekindled.

Bogdanović and coworkers have recently reported a study of the catalytic effects of transition metal compounds on both the hydrogen release and uptake by sodium aluminum hydrides[2]. In this report, it was revealed that the chlorides of many transition metals improved the hydrogen release and also provided reversibility to those reactions. This work also includes the study of combinations of these transition metal compounds for use as catalysts. It was found that titanium and iron function synergistically in their catalytic effect, particularly so with titanium in the form, $Ti(OBu)_4$.

Jensen, et al, found that the catalytic effect of titanium in the form $Ti(OBu)_4$ depends on the method of its combination with the sodium aluminum hydride.[3] These researchers reported that mechanical introduction of the titanium compound to the sodium aluminum hydride produced far superior results to those obtained by Bogdanović using solution methods. Not only were the reaction rates increased for hydrogen uptake and release, the reversible hydrogen content was

increased from the 3.2% reported by Bogdanović to 4.0%. This occurred by altering the first step of the dehydrogenation of $NaAlH_4$, in which

$$3\ NaAlH_4 \quad \rightarrow \quad Na_3AlH_6\ +\ 2\ Al\ +\ 3\ H_2$$

In a second paper by Jensen and coworkers,[4] it was reported that $Zr(OPr)_4$ also catalytically influenced the hydrogenation/dehydrogenation of sodium aluminum hydride. Mechanical incorporation of the catalyst into the hydride was again used, and it was found that this catalyst influenced the system differently than the titanium catalyst. While the titanium catalyst altered the first step of the decomposition of sodium aluminum hydride, the zirconium catalyst accelerated the second step,

$$2\ Na_3AlH_6 \quad \rightarrow \quad 6\ NaH\ +\ 2\ Al\ +\ 3\ H_2$$

It also was shown that titanium and zirconium can be incorporated simultaneously into a sample and function together to influence both steps in the dehydrogenation.

Zaluski and coworkers,[5] reported that lithium and sodium alanates could be prepared by ball milling. Three of the compounds produced in this work, Na_3AlH_6, $(Li-Na)_3AlH_6$, and $(Li-Na-B)_3AlH_6$, were found to reversibly release hydrogen. These compounds absorbed and released hydrogen much more rapidly than the previously reported catalyzed systems.

Studies involving complex hydrides of aluminum so far reported in the literature have been restricted to sodium and lithium aluminum hydrides. While these studies are very important from a fundamental and mechanistic point of view, they involve low reversible hydrogen capacities and thus are not practical for hydrogen storage applications.

It has been reported that there are about 70 known complex hydrides.[6] Some of those, such as $BaReH_9$ with 2.7 wt% hydrogen,[7] have been reported to dehydride at less than 100^oC but the low hydrogen content renders them ineffective as storage materials. The one family of complex hydrides that contains as much hydrogen as the aluminum hydrides is the borohydrides. The borohydrides vary widely in hydrogen content, up to a maximum of 20.8 wt% for $Be(BH_4)_2$. This compound is usually not considered because of the toxicity of beryllium,[8] however, there are numerous other known borohydrides. A major reason that these compounds have not previously been considered for hydrogen storage is their reported lack of reversibility. The recent reports of the catalysts being identified that assist in the hydrogenation/dehydrogenation of the complex hydrides of aluminum suggest the examination of other complex hydrides, especially borohydrides.

Bogdanović[2] utilized SEM, EDS, and Mossbauer spectroscopy to determine the fate of the transition metals added as catalysts. In samples of $NaAlH_4$ doped with both $Ti(OBu)_4$ and $Fe(OEt)_3$, the iron was found to be in the form of nanoscale particles of elemental iron. After 11 cycles of dehydriding and hydriding, the spectra changed indicating that the iron was probably in an alloy with aluminum. While the data were not definitive here, they did support the formation of an Fe/Al alloy. Only indirect evidence as to the fate of the Ti in these samples was provided and this evidence supported the presence of a Ti/Al alloy.

In Jensen's study,[3] the initial combination of $NaAlH_4$ with $Ti(OBu)_4$ resulted in the formation of a red-violet substance, which suggested the reduction of the titanium from Ti^{4+} to Ti^{3+}. Elemental

analysis showing virtually no carbon in the samples along with x-ray data indicating the presence of non-metallic Ti on the surface, suggested the loss of the organic groups as butanal leaving behind a titanium-hydride species on the surface. No data were included in the paper.

Because of the implication of alloying of the catalytic transition metals with aluminum, plans were made to study a series of metals that alloy with aluminum for catalytic effects. A number of alloys of aluminum have been shown to have hydrogen uptake capabilities. These metals are being targeted first. Additionally, it has been reported that hydrogen molecules will not bind to an aluminum surface because of excessive surface electron density on the aluminum.[9] This electron density results in an activation barrier of about 1 eV, which must be overcome before hydrogen can be adsorbed.[10] Thus, a number of metals and non-metals that will react with aluminum to reduce the electron density of aluminum are being included for study. These metals and nonmetals will be incorporated in a number of ways and will be studied when added to the hydrides as well as to the starting materials.

Industry has long made use of $Al(Et)_3/TiCl_4$, as an efficient hydrogenation catalyst.[11] This catalyst, known as a Ziegler-Natta catalyst, can have varying formulations. The Ziegler-Natta catalyst is typically a combination of alkylaluminum and $TiCl_4$. While this catalyst is commonly used for alkyl insertion reactions, it has been shown to act as a catalyst for hydrogenation of aromatic hydrocarbons. It is possible that the mechanism by which Ti is affording reversibility to $NaAlH_4$ has features in common with the ZN catalyst (empty coordination sites on Ti) and can be used as a guide in investigation of other catalysts.

As discussed above, Ziegler-Natta catalysts have been used as effective hydrogenation catalysts. These catalysts are very important in the polymerization of ethylene and conventionally are supported on $MgCl_2$ or SiO_2 for use. However, Cao and Feng[12] have demonstrated that the rate determining step in the polymerization is different when the catalyst is supported on carbon black. Carbon is very commonly used as a catalyst support in a variety of reactions. Hills, et al[13] have investigated the use of carbon-supported Pt-Ru catalysts for methanol electrooxidation and have determined that they exhibit an improved resistance to poisoning when compared to unalloyed Pt. Gil, et al[14] reported that use of activated carbon, as a support, improved catalytic activities in such reactions as hydrodesulphurization and hydrodenitrogenation. Other researchers, including Carrasco-Marin, et al,[15] have investigated the use of activated carbons as catalysts for such things as dehydration and dehydrogenation reactions of ethanol. In fact, the use of carbon as a catalyst is a rapidly growing area of research.[16] Carbon is also well known for use as a hydrogen storage material[17] and has been investigated as a component in composite materials for hydrogen storage.[18] Zaluska, et al[19] reported that ball milling sodium alanates with carbon lowered the dehydrogenation temperature to $80^{\circ}C$ and provided for rehydrogenation at 75-90 atm.

Currently, the only systems that allow the storage of the DOE targeted 6.5 wt% hydrogen, with the fuel being available at less than $100^{\circ}C$ are composite cylinders containing gaseous hydrogen and heavily insulated tanks containing liquid hydrogen. Neither of these are considered acceptable for passenger vehicles.

While the recent advances in hydride storage by the research groups of Bogdanović,[2] Jensen,[3] Zaluski,[5] and Gross[20] have illustrated the reversibility of select complex hydrides, none have been shown to contain the required amount of hydrogen. Successful completion of the objectives of this research will result in a hydrogen storage material that contains a minimum of

7.5 wt% hydrogen and that is compatible with the requirements of a fuel cell powered vehicle. Following is a summary of the work performed toward that goal as of April 30, 2002.

Experimental

General

The sodium borohydride, powder 98%, was purchased from Aldrich; the lithium aluminum hydride, powder 97%, from Lancaster; the lithium borohydride, powder 95%, from Acros and the sodium aluminum hydride, powder 86.3% from Albemarle. Each was used as received with no additional purification.

Differential Scanning Calorimetry

The uncatalyzed, commercially available compounds were characterized at UCF using a SETARAM DSC111, equipped with high pressure cells. The high pressure cells are made of Hastelloy C22 and are equipped with quick disconnects and pressure transducers. This instrumentation allows simultaneous pressure, temperature, and heat flow measurement in hydrogen atmospheres up to 5,000 psi at 500°C. This instrument allows acquisition of data that are comparable to those obtained from a TVA. Additionally, the DSC provides direct information on the enthalpy change of a process. Most importantly, the DSC allows the use of small samples, around 100 mg. This is significant when characterizing compounds, such as the borohydrides, that could potentially decompose to very unstable substances.

Flowing atmospheres can also be used, and in this mode, the DSC can be interfaced to a gas chromatograph to allow identification of evolved gases. Characterization trials were run in triplicate. Hydrogen release was studied in an argon atmosphere, initially at ambient pressure. Hydrogen uptake was studied in an atmosphere of hydrogen at 120 psi. In all analyses, the furnace temperature was changed at a rate of either 3°C/min or 5°C/min from ambient to 450°C.

Thermovolumetric Analysis

Thermovolumetric analysis was obtained using one gram samples of each hydride. The TVA is a modified Sievert's apparatus and the high pressure vessel is constructed of Monel. The sample was loaded in the TVA, under a nitrogen atmosphere. The temperature of the reactor was ramped from ambient to 300 °C, at 2°C/minute. Data for temperature and pressure were acquired using National Instruments hardware and LabView software. Data were plotted with weight percent hydrogen released as a function of time.

Results and Discussion

The goal of this project is to investigate a series of complex hydrides of aluminum and/or boron, with large hydrogen contents, as hydrogen storage media. These compounds are listed in Table I. Each compound contains a minimum of 7.5% hydrogen by mass. While some of these hydrides have been reported to decompose to compounds that still contain one or more hydrogens, the numbers shown reflect total hydrogen content. An additional goal is to identify a catalyst for each hydride that allows decomposition to the elements. The catalyst candidates are listed in Table II.

Table I. Selected Complex Hydrides

Hydride	Wt %	Availability or Syn. Reference
$LiAlH_4$	10.5	Commercially Available
$LiBH_4$	18.2	Commercially Available
$Al(BH_4)_3$	20.0	J. Am. Chem Soc.,75, 209 (1953)
$LiAlH_2(BH_4)_2$	15.2	British Patents 840,572 and 863,491
$Mg(AlH_4)_2$	9.3	Inorg. Chem., 9, 325 (1970)
$Mg(BH_4)_2$	14.8	Inorg. Chem., 11, 929 (1972)
$Ca(AlH_4)_2$	7.7	J. Inorg. Nucl. Chem., 1, 317 (1955)
$Ca(BH_4)_2$	11.4	Synthetic procedure to be developed
$NaAlH_4$	7.5	Commercially Available
$NaBH_4$	10.5	Commercially Available
$Ti(BH_4)_3$	12.9	J. Am. Chem Soc., 71, 2488 (1949)
$Ti(AlH_4)_4$	9.3	Synthetic procedure to be developed
$Zr(BH_4)_3$	8.8	J. Am. Chem Soc., 71, 2488 (1949)
$Fe(BH_4)_3$	11.9	Synthetic procedure to be developed

Table II. Catalysts

Catalyst	Form
Ti	$TiCl_4$
	$TiCl_3$
	$Ti(OBu)_4$
Fe	$FeCl_3$
Zr	$Zr(OPr)_4$
C	graphite
	Activated

Of the hydrides that were proposed for study, four of them were found to be commercially available, seven had methods of preparation available in the literature and the remaining ones needed to have methods developed. Those commercially available were obtained and baseline measurements begun.

While the initial measurements were being made using the differential scanning calorimeter, the Parr high pressure reactor that was used in earlier DOE funded hydride work was returned to Parr for refurbishment and pressure testing to insure that safety standards were still being met. The data acquisition system formerly used with the Parr system was outdated and in need of replacement. Currently available systems were assessed and compared and the decision to obtain National Instruments hardware driven by the LabView program was made. Unfortunately, delivery time for the new system was two months and the new equipment was not received until late January. Additional problems followed, including several NI modules that were defective and had to be replaced and a thermocouple pair received from Omega that was fabricated with one J-type and one K-type thermocouple. The system, a thermovolumetric analyzer, was finally tested and ready for use in late March.

The differential scanning calorimeter in the chemistry department also required updating and refurbishing. The update of the computer and software should occur within the next couple of weeks. The updated software and interface module have been obtained from the instrument manufacturer (SETARAM) and the new computer has arrived. Because one of the P.I.s labs (MDH) is located under the NMR room, there is a prominent magnetic field. This was not a problem with old computers and equipment, however, new computers and monitors do not function well in the presence of this magnetic field. As a result, new space away from the magnetic field had to be found and allotted. This was done and the DSC has been moved into the new space. The new lab space has been equipped with the proper power outlets to receive the DSC.

After consultation with a UCF colleague, C. Suryanayayana, who is an expert in ball milling, it was decided to purchase a Spex 800M mixer/mill with a stainless steel container and media. This is a high energy ball mill that should be useful for incorporation of brittle catalyst materials into brittle alanates and borohydrides. The mill has been received and is in use.

The purchased hydrides were all subjected to characterization in their as-received state, using both differential scanning caloimetry (DSC) and thermovolumetric analysis (TVA). Because plans call for these hydrides to be modified by the addition of catalysts, it is necessary to know their initial hydriding/dehydriding characteristics in order to determine the effect of the catalyst addition. Also, these baseline data will be useful for comparision to those obtained for any new compounds that are synthesized.

The baseline data from the two methods of characterization were found to corroborate the data in the literature. The dehydriding proceeds via a two-step mechanism and, without a catalyst, is not reversible. The TVA data, in addition to illustrating the kinetics of the hydride, allowed the calculation of the weight percent of hydrogen released from the material, Table III. The TVA data for the sodium aluminum hydride and the lithium aluminum hydride showed obvious release temperatures, while the corresponding borohydrides did not. Additional trials are needed to confirm the data. Problems were also encountered with the temperature controller that was used. Plots of the data clearly indicated that the ramp rate was not a constant

2°C/minute. A new temperature controller is expected to solve the problem. Rehydriding of the samples has not yet been attempted.

Table III. TVA Data

Hydride	Release Temp. (°C)	wt % Hydrogen
LiAlH$_4$	157	6.4
NaAlH$_4$	190, 269	4.3
LiBH$_4$	36	0.46
NaBH$_4$	33	0.69

The baseline data obtained from the DSC are summarized in Table IV. To date, two trials of each analysis have been done. Due to the variability in the data, additional trials will be run to assure reproducibility and reliability of the data. The source of the variability in the data at this point relates to sample handling. The moisture sensitive nature of these compounds dictates that they be handled in a carefully controlled atmosphere. The glove bag used in these experiments was obviously inadequate. This problem is being addressed and will soon be solved.

Synthesis of compounds with literature preps has begun and development of procedures to synthesize those without literature preps is in progress. The synthesis of titanium borohydride was attempted by preparation of TiB$_2$ and then the hydriding of this compound. Low energy ball milling was utilized to prepare TiB$_2$ from Ti and B powders using stainless steel balls and a ceramic canister with an Ar atmosphere for 100 hours. Two samples of the resulting mixture were analyzed for hydrogen uptake and release. The first sample exhibited an exothermic event at 223°C that was accompanied by a slight pressure decrease. The second sample had an exothermic event occur at 254°C that had associated with it a small pressure decrease. This indicates that the samples did take up a small amount of hydrogen. Both samples showed a pressure increase, indicating hydrogen release, without an associated event. The first sample released gas at 280°C and the second at 150°C. This synthesis is being attempted again using the high energy ball mill.

An attempt was also made to prepare titanium aluminum hydride from commercial TiAl$_3$. This was tried without a catalyst present. It was found that this alloy did not absorb hydrogen, even after ball milling. The effect of a catalyst on the hydrogen uptake by this alloy will be investigated in the near future.

Conclusion

The refurbishment of the equipment took longer than anticipated but was virtually complete as of the end of April. The TVA had been returned from Parr Instruments and was installed and functioning. The DSC update software and interface module were received and the integration of this interface was begun. The high energy ball mill was also received and put into service. The data obtained for each of the commercially available compounds illustrated the kinetics of hydrogen release and allowed calculation of weight percent hydrogen content. A new temperature controller had been ordered because the one being used was incapable of

accurately controlling the ramp rate. The new ball mill has arrived and is being set up. The update for the DSC should arrive within days.

Table IV. DSC Analysis of Commercial Compounds

Compound	Dehydriding, Trial 1			Dehydriding, Trial 2			Rehydriding	
	Exo	Endo	Pressure	Exo	Endo	Pressure	Thermo	Pressure
$NaBH_4$	------	397 °C	↑ 350 °C	------	------	↑ 240°C	------	------
$LiBH_4$	75°C	100°C, 275°C	↑ 75°C, 330°C	75°C	115°C, 287°C	↑ 75°C, 330°C	endo 75°C, 230°C	------
$NaAlH_4$		182°C, 251°C	↑ 182°C, 220°C	182°C 251°C	182°C 220°C	↑ 75°C, 330°C		
$LiAlH_4$	100°C, 152°C	150°C	↑100°C, 150°C	163°C	------	↑ 95°C, 160°C	------	------

While the TVA refurbishment was ongoing, initial data were collected via the DSC, which was functional but in need of updating. The data obtained with the DSC have shown the number of thermal events for each cycle, the enthalpy associated with and the temperature for each event. Additionally, data were obtained to show any pressure increases or decreases.

Progress is slightly behind schedule because of the difficulties encountered during refurbishment. However, it is anticipated that work will be virtually on schedule again by the end of May because we have moved compound synthesis up in the schedule.

Future Work

Several compounds must still be synthesized, using literature preps or by procedures yet to be developed. These pure compounds will be subjected to characterization to obtain baseline data. Upon completion of the baseline characterization of pure compounds, work will focus on the incorporation of catalysts. After incorporating a catalyst via solution chemistry or ball milling, each catalyzed compound will be characterized to determine the effect, if any, of the catalyst. Those showing a positive effect will then be investigated to determine the catalyst fate. This will be of value in determining other possible catalysts for improving kinetics and reducing release temperature. After determination of the best complex hydride-catalyst system, extended cycling tests will be begun.

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