

HYDROGEN STORAGE IN AMINE BORANE COMPLEXES

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ABSTRACT

Hydrogen has been projected for its potential to be an environmentally clean and efficient alternative energy carrier. Transition from carbon-based economy to hydrogen economy is crucial for hydrogen-based applications. Viable hydrogen storage system is a critical bottleneck in the development owing to volumetric and gravimetric issues for solid-state storage.

Ammonia Borane (AB), NH_3BH_3 , a solid state, complex chemical hydride is considered for study and experimentation due to its remarkably large hydrogen content (19.6 wt %). AB is being explored as a disposable hydrogen source for fuel cell based and other small power applications. Paper will present some of the experimental results including the factors influencing the hydrogen release in the reaction process.

Keywords: Solid State Storage, Ammonia Borane, Complex Chemical hydride, hydrogen release.

1.0 Introduction

Hydrogen Energy is one of the potential solutions to the projected global energy crisis for transport fuel. Most of the known current fossil resources are in their mid-depletion region, which are sourcing the present energy infrastructure. The growing demand for energy and the concern about rise in environmental pollution to alarming levels has resulted in the efforts for exploration of new, renewable and clean fuels. Abundant supply of such fuels can assist in maintaining the global growth phase and also help in controlling the pollution levels. Use of Hydrogen as an energy carrier can afford the availability of clean and adequate energy for sustainable development. This technology at present is in extensive research stage. Currently it is not commercially viable and available to limited extent in some of the developed countries. Emphasis on mitigating global climate change and the need for reduction in pollution strengthens the case of hydrogen. Commercial fuel cells and hydrogen would yield benefits to the society to a great extent. Hydrogen can be produced using either conventional fossil sources or by using renewable sources. This results in the fuel flexibility. Hydrogen will be matched with the renewable energy technologies like solar and wind power. Hydrogen based fuel cells generate electricity with no conventional pollutants. Even hybrid vehicles can help in reducing the use of conventional fuels of today. Transition from carbon-based economy to hydrogen economy is crucial for fuel cell vehicles (FCV). Viable hydrogen storage system is a crucial block in the development of FCV, owing to volumetric and gravimetric issues. Solid-state storage of hydrogen has been projected for its potential to be safe, environmentally clean and efficient alternative energy carrier.

Hydrogen storage is one of the critical technologies for commercialization and global acceptability of hydrogen for applications using fuel cells. Solid-state hydrogen storage i.e. Storage in the bound state uses variety of materials such as hydride forming metals, chemical hydrides, complex hydrides, carbon nanostructures, amide-imides composites and many other organic compounds. It is too premature to determine suitable storage materials as different materials are exhibiting advantages as well as limitations. Some of the research challenges are desorption temperatures, kinetics, recharge time and pressure, heat management, cost, cycle life, container's capability and optimization. One of the difficult challenges is volumetric and gravimetric capacities which none of the materials could achieve so far close to DOE targets. [1]

Storage Parameter	Units	2005	2010	2015
Specific Energy	kWh/kg	1.5	2.0	3.0
	H ₂ /kg System wt%	4.5	6.0	9.0
Energy Density	kWh/l	1.2	1.5	2.7
	gm H ₂ /l System*	36	45	81
Storage System Cost	\$/kWh	6	4	2
	\$/kg H ₂ capacity	200	133	67
Refueling Rate	kg H ₂ /min	0.5	1.5	2.0
Loss of usable H ₂	(g/hr)/kg stored	1	0.1	0.05
Cycle Life	Cycles (1/4 to full)	500	1000	1500

Table. 1 US DOE Hydrogen Storage Targets

Higher valency materials allow more hydrogen bonds per atom and we have considered ammonia borane for study due to its high hydrogen contents. It is a disposable source and is explored for low power applications. The present known sources of ammonia borane are limited and it is not likely to become a means of mass storage of hydrogen.[2] Solid Ammonia borane releases between ~2 to 2.5 mol equivalent of hydrogen corresponding to a material gravimetric capacity of 13 to 16 wt % of H₂. [3]

2.0 Materials and Methods

Ammonia Borane (AB) NH₃BH₃, a solid-state hydrogen storage material is considered for experimentation. Some of the properties of this non-volatile complex chemical hydride are its high degree of stability in water and air with an energy storage density of about 2.74kWh/l. It can prove out to be an energy carrier especially for low power applications using PEMFC at lower temperatures. Release of H₂ from Aminoboranes is a challenging process and efforts are made to study this phenomenon in the experimentation.

The molecular description of NH₃BH₃ shows that it is a donor-acceptor adduct formed as a result of dative bond between acid BH₃ and base NH₃. The compound is a solid at room temperature primarily due to dihydrogen bonding and dipole-dipole interaction. Recent works have indicated that AB can release over 2 moles of H₂ with heating upto modest temperatures due to various reactions leading to hydrogen evolution.[4] The stepwise release of H₂ through thermolysis, it can yield about 6% of total thermolysis. One of the challenges is the lowering of H₂ release decomposition temperatures and increasing the release kinetics. The material sample is studied for isothermal decomposition and non-isothermal decomposition.

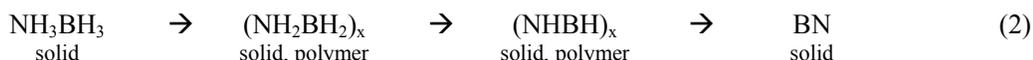
Generalized thermolysis of Ammonia Borane:

Thermal decomposition of AB in the solid state is studied by many researchers in different stepwise processes. The exact temperature at which decomposition occurs and even the shapes of Thermo Gravimetric Analysis (TGA) and Differential Scanning Calorimetric (DSC) curves are dependent on the heating rate. The thermally unstable molecule of ammonia borane has been found to decompose in three distinct steps. These steps are studied by TGA, DTA and Thermo Gravimetry. The Thermal Gravimetric Analysis is a type of testing performed on the sample to determine changes in weight in relation to determine changes in temperature. This analysis relies on a high degree of precision in measurements i.e. weight, temperature and temperature change. Simultaneous TGA-DTA/DSC measures both heat flow and weight changes in a material as a function of temperature or time in a controlled atmosphere.

The Differential Thermal Analysis (DTA) is a thermo analytic technique. In this method, the material under study and an inert reference are made to under go identical thermal cycles, while recording any temperature difference between the sample and the reference. The differential temperature is then plotted against time or temperature (DTA curve/ thermogram) changes in the sample. The reaction

can be exothermic or endothermic relative to the inert reference. DTA curve provides the data transformations that have occurred. The Thermo Gravimetric Analysis (TGA) provides both mass loss and thermal information.

Thermolysis is a method of choice to generate hydrogen from Ammonia Borane. It is a method in which several competing reactions take place, which results in the formation of various byproducts. Some of these are monomeric aminoboranes, diboranes and borazine (AB). The release of H₂ in pure ammonia borane starts at around 140°C and substantial amount of hydrogen is released at temperatures above 500°C. The overall reaction is exothermic and hence needs heat addition to release hydrogen and for activating the AB complex. The important reactions [5] are



It may be seen that the high gravimetric storage density upto 19.6 wt% and non-flammability and non-explosiveness under standard conditions makes AB a good candidate for hydrogen storage. However when all 3 equivalents of hydrogen were to be released, the reaction would yield borone nitride (BN). This is a chemically very stable compound and very difficult to be used for regeneration.[6]

3.0 Results and Discussion

Isothermal Decomposition of Neat AB

The material sample taken for experiment was first characterized and then used for the study. The isothermal decomposition study of Neat AB performed in the lab in a Sievert's Type apparatus at a temp of 90°C is represented in the plot. The apparatus is based on the volumetric measurements and the products of decomposition remain in the apparatus. The curves indicate the amount of gas released against time. The study was performed for period of 400 minutes. The decomposition showed steep rise after warm up period of 150 minutes which is the time taken for the start of decomposition process. The release rate reached over 4 wt% at around 200 minutes and then again remained almost steady thereafter. The three regions in the Isothermal decomposition can be identified as the induction part, the acceleratory part and the deceleratory part. In the induction part the reaction process begins and then results in rapid acceleration and finally decelerates making the curve almost flat.

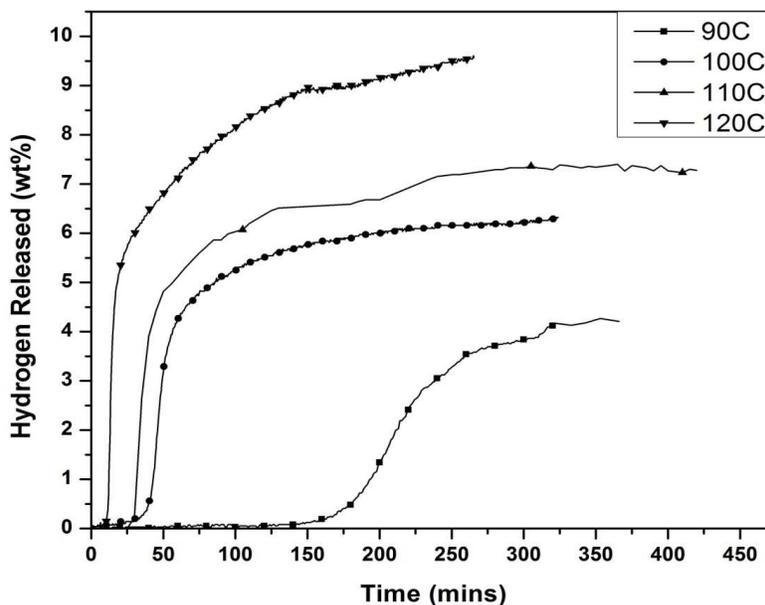


Fig. 1 The curve indicating the hydrogen release through Isothermal Decomposition of Neat AB at 90°C

It may be noted that the boiling point of pure AB is about 110°C and the decomposition reaction improves if the experiments are conducted at elevated temperatures. It results in larger amount of Hydrogen release when isothermal decomposition is performed above 110°C. Even though 4.5 wt% is the hydrogen release at 90°C, it will increase substantially if the temperature is raised above 120°C.

The increase in temperature will decrease the decomposition time as well as increase the hydrogen release kinetics and wt%. Every 10°C rise in temperature increases the hydrogen release rate to a considerable extent. However methods are to be looked at maintaining lower operating temperature and increase in hydrogen release quantity. Isothermal decomposition is one of the safe methods of dehydrogenation.

Non-isothermal decomposition of Neat AB

The non-isothermal decomposition of neat AB was studied with small quantities (3 to 4 mg) of above sample using perkin elmer TGDTA System at SAIF Lab. The TGA and DTA curves are obtained at heating rates of 3, 4, 5 °C/min with nitrogen flow of 50 ml/min. The figures 2 and 3 indicate TG and DTA curves of the sample under test. The total weight loss in two steps was found to be 40%, 40.6%, 42.4% for 3°C, 4°C, 5°C steps respectively. The higher heating steps gradually shifted the weight losses resulting in reduction in the amount of gas released.

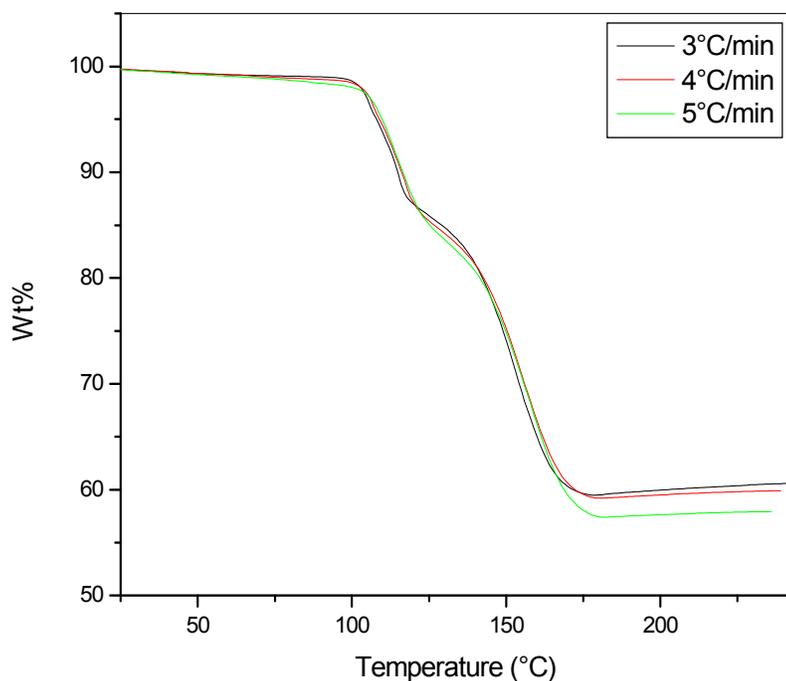


Fig. 2 TGA Curves of Ammonia Borane Sample studied using perkin-elmer setup

The DTA curves in the figure indicate the peaks of mass loss. Even the endothermic peak is shifting with increasing heat rate. At 3°C heating rate, melting peak was seen at 105.98°C with the onset at 102.65°C. The peak shifts to 115.3°C with the onset at 108.65°C. The first major weight loss step keeps shifting with the increasing shift rate and the peaks are gradually getting broadened with exothermic decomposition reaction.

The TGDTA studies conducted on the same sample indicated the first lump at 110.5°C at 3°C step, 112.51°C at 4°C step and 113.51°C at 5°C. With the step change, we have observed a nominal shift in the peaks, which indicate major weight losses. The further weight loss was observed at 152.45°C, 155.60°C and 156.63°C respectively for the above steps.

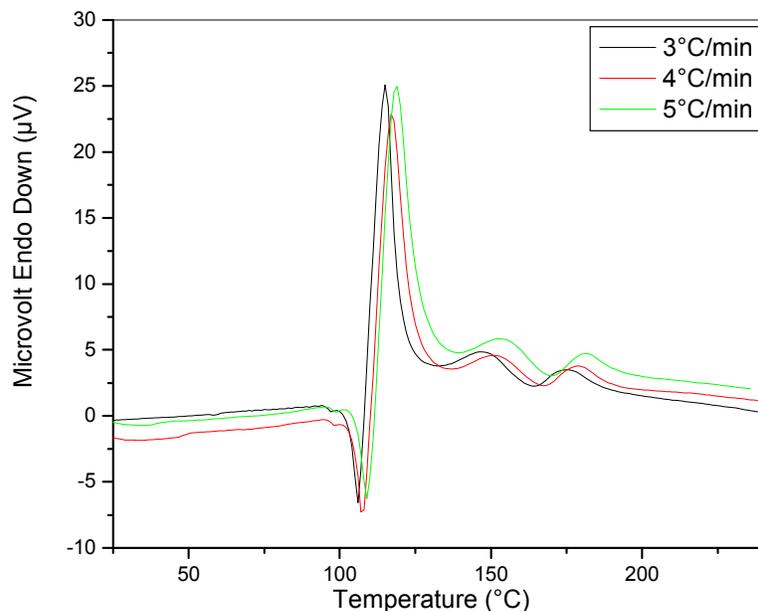


Fig. 3 DTA Curves of Ammonia Borane Sample test performed using perkin-elmer setup indicating different peaks of weight losses in each step

4.0 Conclusion

The thermolysis method used involves several reactions leading to formation of different byproducts at different stages. The hydrogen release process can be accelerated through inducing kinetic behaviour as well as using catalysts. The isothermal decomposition study of neat AB conducted at 90°C indicates considerable slow start of kinetics. Even this temperature is much above the DOE set target of 60°C. The TGDTA analysis indicates substantial release of H₂ above melting point of AB (112°C to 117°C). It is observed that the hydrogen release involves extended induction period w.r.t. reaction onset temperature. With around 2 mol equivalent of hydrogen release and gravimetric capacity of maximum 19.6 wt%, the material seems to be a good medium of hydrogen storage even though many technical issues are yet to be resolved. Some of the issues include economical methods of synthesis, increase in hydrogen release rate at lower temperatures and recharging of spent ammonia borane. It is also essential to identify economical and abundant sources of Ammonia borane to make it available for the possible future applications.

Acknowledgment

Authors gratefully acknowledge the support of ESE and SAIF departments of IIT Bombay for allowing the researcher to use their facilities of Hydrogen storage laboratory and TGDTA studies.

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