

Dehydrogenation of Ammonia Borane with catalytic thermal decomposition

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ABSTRACT

The complex chemical hydride, Ammonia Borane (NH_3BH_3 , AB) is a hydrogen rich compound. It is a promising hydrogen source for applications using Proton Exchange Membrane Fuel Cells (PEMFCs) due to hydrogen content. It has reasonably lower operating temperatures compared with other solid state hydriding materials. At present AB is an expensive disposable source which in its pure form releases one mole of hydrogen at around 110°C . This temperature is much higher than the operating temperature of PEMFC ($\sim 80^\circ\text{C}$). At the operating temperatures of the fuel cell, the slow kinetics of pure AB is a deterrent which provides enough scope for experimentation. The paper is the result of experimental thermolysis effort by using nano-nickel as a catalyst with pure Ammonia Borane. The neat and catalyzed AB isothermal decomposition and kinetic behavior are illustrated through the experimental results obtained under various conditions. The focus of experimentation is to increase the rate and extent of release of hydrogen at lower temperatures.

Keywords: Ammonia Borane; Nano-Nickel; Dehydrogenation; Thermolysis; Kinetics; Decomposition

1. Introduction

The rapid rise in crude oil prices and likely depletion of petroleum resources in the future has directed the focus on economy based on hydrogen as fuel. Hydrogen is one of the interesting alternatives owing to its rich energy content and abundance.

Hydrogen with molecular weight of 2.016 g/mol and high chemical energy per mass equal to 142 MJ/kg which is approximately three times greater than gasoline has emerged as an alternative to hydrocarbon fuels.[1] Hydrogen can be stored for reasonably long periods of time without significant losses.[2]

Hydrogen is stored as compressed gas or cryogenic liquid and transported using high pressure trucks. Gaseous hydrogen has volumetric density of 40g/L at 700 bar pressure. This pressure is much higher than CNG which is stored at around 300 bars. Liquefied hydrogen has a better volumetric density of about 70 g/L at cryogenic temperatures of -253°C (20K) which is also its boiling point.[3]

Cooling and maintaining this cryogenic temperature is an energy intensive process. This is an extremely complex and critical challenge for general applications under ambient conditions. Due to restrictions, gaseous and liquid storage options are used to a limited extent. This is an important hurdle in hydrogen based applications.

A light duty vehicle has to carry about 4 to 10 kg of Hydrogen onboard, depending on the type of the

vehicle to allow a driving range of 300 miles between refueling, for widespread acceptance.[4]

The rate and time for refueling should also be comparable to the present refueling of petroleum based vehicles. The high pressure demands for huge volume insulated tank for storing required quantity of hydrogen onboard. This increases the size as well as weight of the vehicle. Low cost materials and components are necessary to ensure safety along with economic manufacturing methods for storage devices.

Solid-state storage, which is also the materials-based storage, is a safer method with extensive scope for research and development. Variety of materials viz. metals, chemical hydrides, MOF etc. offer immense promise for hydrogen storage. Experimentation of various types is expected to help and understand the mechanism of storage and release of hydrogen in these materials under practical operating conditions. It is also essential to overcome challenges related to capacity, kinetics, heat management, cost and life cycle.

1.1 Hydrogen Storage in Chemical Hydrides

Researchers have studied many materials over the last few decades for volumetric and gravimetric densities. The focus is the DOE targets for gravimetric density of 90 g H_2 /kg and volumetric density of 82 g H_2 /lit, by year 2015 with min/max delivery temperature of $-40^\circ\text{C}/85^\circ\text{C}$. The above targets are for the complete system which includes tank, material, valves,

regulators, piping, mounting brackets, insulation, added cooling capacity and other components.[7]

Ammonia borane (NH_3BH_3 , AB) is a promising hydrogen source material due to its high hydrogen content (19.6 wt %). AB is the colourless chemical solid with the simplest molecular boron-nitrogen-hydride compound. Ammonia borane was first synthesized and characterized by Sheldon Shore in the 1950s during his thesis research in Richard Parry's lab at the University of Michigan. They performed series of experiments to identify the 'mysterious' $\text{B}_2\text{N}_2\text{H}_6$ adduct, and study various by-products.[5]

Hydrogen can be released from AB by thermolysis, hydrolysis or hydrothermolysis.

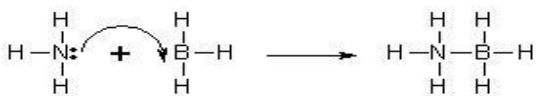


Fig.1 Structure of Ammonia Borane

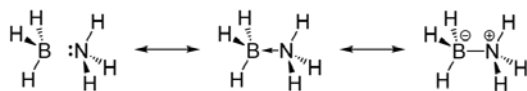


Fig.2 Crystal Structure of Ammonia Borane[6]

The primary elements that compose AB are nitrogen, hydrogen and boron. The elements nitrogen and hydrogen exist widely in the nature, eg. in air and water.[7]

Ammonia Borane is a non-volatile material with appreciable degree of stability in air and water under ambient conditions. It can prove out to be an energy carrier for low power applications using PEMFC at lower temperatures. Release of H_2 from Aminoboranes is a challenging process and efforts are made to study this phenomenon in the experimentation.

A simple molecular description of NH_3BH_3 shows that it is a donor-acceptor adduct formed as a result of the dative bond between a Lewis acid (BH_3) and a Lewis base (NH_3).[8] The compound is a solid at room temperature primarily due to di-hydrogen bonding and dipole-dipole interactions. Ammonia Borane and diammoniate of diborane (DADB) are chemically similar with different stability characteristics. DADB quickly reacts with water and solid DADB gradually transforms in to Ammonia Borane under ambient conditions. It may be inferred that AB is more readily applicable than DADB to hydrogen storage for automotive use.[9]

1.2 Hydrogen Release Studies

Recent work has shown that NH_3BH_3 can release more than 2 moles of H_2 with heating to modest temperature.

The reactions of hydrogen evolution can be summarized as shown in the table 1.1.

Decomposition reaction	Storage density*,wt. % H_2	Temperature#, °C	Product
$\text{NH}_4\text{BH}_4 \rightarrow \text{NH}_3\text{BH}_3 + \text{H}_2$	6.1	<25	Ammonia Borane
$\text{NH}_3\text{BH}_3 \rightarrow \text{NH}_2\text{BH}_2 + \text{H}_2$	6.5	<120	Polyaminoborane
$\text{NH}_2\text{BH}_2 \rightarrow \text{NHBH} + \text{H}_2$	6.9	>120	Polyiminoborane
$\text{NHBH} \rightarrow \text{BN} + \text{H}_2$	7.3	>500	Borane Nitride / Borazine

*Theoretical maximum, #Decomposition temperature

Table 1.1 – Decomposition reaction for a thermal chemical hydride[10]

The optimum thermal decomposition reaction of Ammonium Borohydride, $\text{NH}_4\text{BH}_4 \rightarrow \text{BN} + 4\text{H}_2$ occurs by a four-step process with very high H_2 yields (24 wt%). This exceeds the US DOE set ambitious goals. However the reactions are not reversible and off board regeneration is required. Even if the first two steps prove feasible, H_2 capacities of over 12wt% could be realized.[10][11]. In the first two steps, reaction of AB to form PAB, polyaminoborane, $(\text{NH}_2\text{BH}_2)_n$; and PAB to form PIB, polyiminoborane $(\text{NHBH})_n$ amount to 12 wt% hydrogen. The hydrogen release in these first two steps occurs at temperatures less than 160°C . Beyond this temperature, the cross-linking between molecules is responsible for the release of additional hydrogen. Cyclic borazine(NHBH) is formed as a product in the next reaction. Above 170°C , due to high vapour pressure, at elevated temperatures "Borazine" is formed as a side product. The stringent requirements of hydrogen purity for fuel cell applications demand minimization of side reactions.[11] The possibility of gaseous boranes in the evolved H_2 are toxic and likely to contaminate the fuel cell catalyst. Above 500°C , AB can be completely decomposed to form boron nitride (BN). For spent fuel regeneration BN is not preferred due to its high chemical and thermal stability.[12]

AB is a widely studied material for its decomposition by thermal route as well as by hydrolysis.[13] Thermolysis or direct heating is one of the methods of dehydrogenation. The main hurdle in hydrogen release is the slow kinetics, leading to long induction period.[14] Neat AB thermally decomposes initially at 70°C , it reaches a maximum at 112°C with the observed melting of AB to yield 1.1 ± 0.1 equiv. H_2 and mostly by-product polyaminoborane, $[\text{NH}_2\text{BH}_2]_n$. [7][15][16] The polyaminoborane obtained can decompose over a broad temperature range between 110°C and 200°C to lose 1 equiv. H_2 and form polyiminoborane $[\text{NHBH}]_n$ at the heating rate of 1°C min^{-1} . [7]

2. Experimental

Ammonia Borane complex (97% pure) purchased from Aldrich was used in 20mg quantity for the set of experiments. Neat AB sample FTIR analysis was done before dehydrogenation.

The thermal decomposition of neat AB and nano-nickel catalyzed AB sample were studied in a locally developed Sievert's type apparatus by volumetric process. In this apparatus the samples are subjected to isothermal decomposition and the volume of the evolved gas w.r.t. time and pressure are recorded.

Among the catalyst systems, platinum has highest activity in reactions. However the concerns over the practical usage of platinum have motivated the search for low cost catalyst.[17]

Nickel is the catalyst considered for its abundant availability and lower cost over other catalysts. The catalyst is used in 10% quantity (2mg for 20mg of pure AB). The process Mechanical Alloying (MA) is a solid state powder processing technique which was originally used to produce dispersion. The process results in synthesized non-equilibrium phases such as meta-stable crystalline & quasi crystalline phases, nanostructures as well as amorphous alloys.[18] The Neat AB is milled with nano-nickel for a period of 30 min. This reaction proceeds via oxidative addition of nano-nickel into a B-H bond of NH_3BH_3 followed by β -hydride elimination and hydrogen production.[19]

The alloy mixture turned into gray colour in the MA process. The finely alloyed mix is used to perform isothermal decomposition test at different temperatures starting from 80°C. Each sample was then loaded in a crucible of cylindrical shape within the reactor. By using different valves, sample holder is connected at separate instants to vacuum pump, hydrogen gas cylinder and the apparatus. In each set of experiment and monitoring, the sample holder was evacuated and filled with hydrogen gas before finally connecting to the measuring setup of apparatus. A thermocouple is placed very close to the sample holder to measure the temperature to which the sample is subjected. The temperature and pressure are recorded digitally at intervals of one minute using a data logger.

The experiments of isothermal decomposition were conducted at 80°C, 100°C, 120°C, 140°C and 160°C, with different samples of AB and ABNi. In each set, the volume and change in the pressure are recorded. The change in pressure of the apparatus was used to calculate the amount of hydrogen released in wt%.

2.1 Kinetic Analysis

The Arrhenius equation $k = A.e^{-E_a/RT}$ gives qualitative basis of the relationship between the activation energy and the reaction rate progress. In

this equation A is the frequency factor for the reaction, R is the universal gas constant, T is the temperature in Kelvin, k is the reaction rate coefficient. At 80°C the activation energy of neat AB is calculated to be 130 kJ/mol. With the catalysis the activation energy required for the reaction is reduced to 120 kJ/mol.

Nano-nickel is the catalyst which modified transition state to lower the activation energy. It can be noted that the catalyst inversed the rate of reaction without being consumed. It is significant to note that the catalyst reduced the activation energy without changing the energies of reactants and the products.

3. Results and Discussion

3.1 Isothermal decomposition

Thermolysis is a method which requires heating with temperature control. The Sievert's type apparatus is a set up which permits this type of test on small quantities of material. Additional measures are necessary to deal with challenges associated with solid state reactions at elevated temperatures for the dehydrogenation in various stages from the material.

The isothermal decomposition of neat AB at 80°C is an extremely slow process with the induction period in excess of 125 minutes. The max release of around 3 wt% was achieved beyond 250 minutes which remains steady thereafter. Considerable reduction in the Induction period is observed when isothermal decomposition was performed at 100°C and 120°C. Beyond induction period 6 to 7 wt% gas is released. The literature provides the detail of melting point of AB is 112-114°C and at this temperature one mole equivalent of gas is liberated.

During 120°C isothermal cycle the Hydrogen released is over 9 wt% which remains steady after 100 min with nominal induction period. The observations indicate that the increase in temperature decreases the induction period as well as expedite dehydrogenation kinetics.

3.2 Catalytic Dehydrogenation

The results of ABNi milling and subsequent characterization are indicated graphically. The amount of catalyst used is around 10% of the mass of neat AB. Milling ensures proper mixing and dispersion of the catalyst with the base material to have increased surface area. The isothermal volumetric hydrogen release measurements presented the features that the neat AB sample released first mole of hydrogen at 110°C and the second mole at 160°C.

It can be observed that the Ni doped AB started dehydrogenation at 80°C with reduced induction period of 8 min. It was also noted that doped samples did not foam during dehydrogenation. The strong chemical bonding in neat AB is one of the factors

responsible for slow kinetics and dehydrogenation. The overall hydrogen decomposition process is represented in the characteristics.

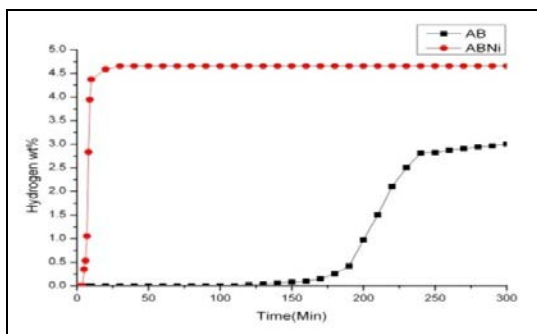


Fig. 1 The curve indicating the hydrogen release through Isothermal Decomposition of Neat AB and catalyzed AB at 80°C

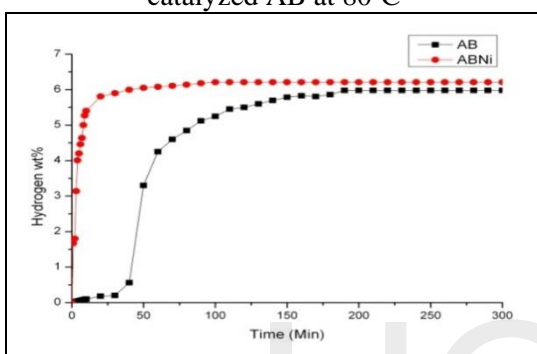


Fig. 2 The curve indicating the hydrogen release through Isothermal Decomposition of Neat AB and catalyzed AB at 100°C

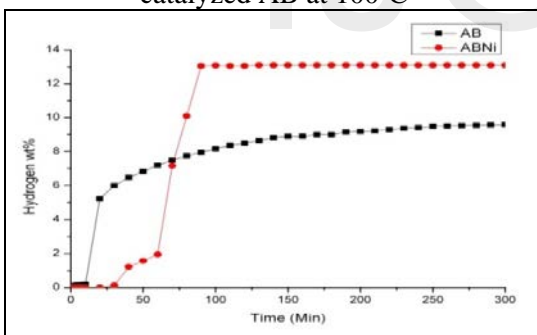


Fig. 3 The curve indicating the hydrogen release through Isothermal Decomposition of Neat AB and catalyzed AB at 120°C

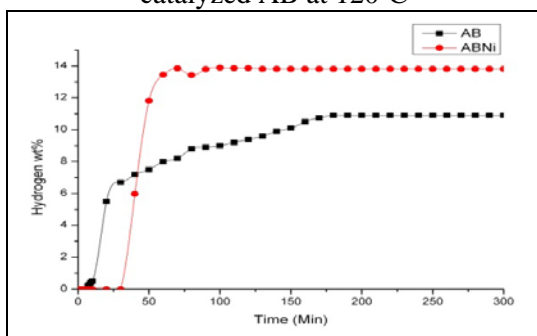


Fig. 4 The curve indicating the hydrogen release through Isothermal Decomposition of Neat AB and catalyzed AB at 140°C

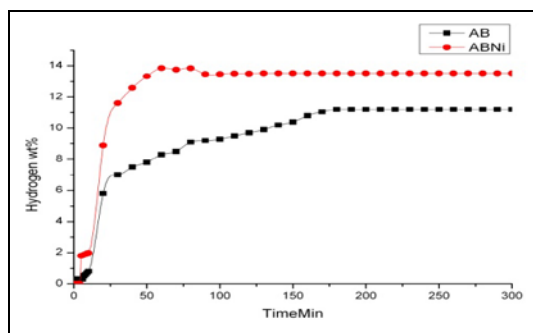


Fig. 5 The curve indicating the hydrogen release through Isothermal Decomposition of Neat AB and catalyzed AB at 160°C

3.3 Transmittance spectrum of neat AB and Ni catalyzed AB

The FTIR analysis of neat AB and Ni catalyzed AB was conducted before and after decomposition.

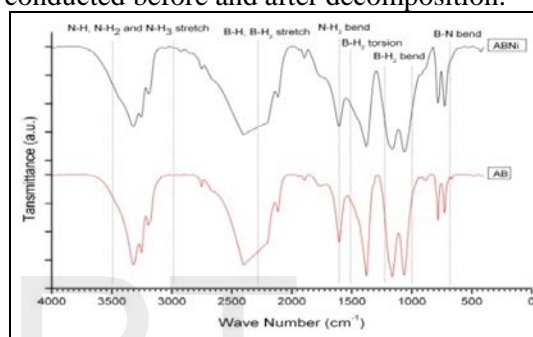


Fig. 6 FTIR curves for Neat AB and Catalyzed AB before decomposition

The FTIR of neat AB and Catalyzed AB before decomposition is shown in Fig.6. It is observed that various bonds are resembling in both the samples indicating the B-N bend at 700 cm^{-1} , BH_2 torsion at 1500 cm^{-1} , BH_2 bend at 1300 cm^{-1} , BH, BH_2 stretch at 2300 cm^{-1} and NH, NH_2 , NH_3 stretch above 3000 cm^{-1} . This justifies the use of the Catalyst and that the Catalyzed sample has not resulted in unwanted reaction and by-products.

3.3 Transmittance spectrum of dehydrogenated catalyzed AB

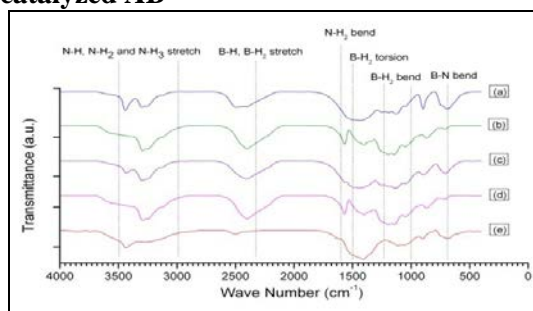


Fig. 7 FTIR curves for dehydrogenated sample a)80°C b)100°C c)120°C d)140°C e)160°C

Isothermal decomposition of neat AB and catalyzed AB was studied separately in the Sievert's type apparatus.

The FTIR analysis of catalyzed dehydrogenated sample solid residue after each experiment with 80°C, 100°C, 120°C, 140°C and 160°C was performed to understand the effect of catalyst on chemical bond structures. The transmittance spectrum in each case is indicated in Fig.7. The spectrum in (a) to (e) is almost identical with the broadening of peaks in the N-H stretch or B-H stretch which indicates the material decomposition and hydrogen release. The release of Hydrogen in terms of wt% has showed improvement in comparison with neat AB with considerable reduction in the induction period.

The second mole release in the experiment at 160°C is visible in the transmittance curve with the almost broadening of N-H and B-H stretch. Broadening of peaks indicates the disruption of bonds resulting in the release of hydrogen. It is seen that the B-N bend is intact and hasn't got affected either due to catalysis or due to elevated temperatures. The non formation of borazine is an indication that there are no unwanted reactions and by-products.

The FTIR study has indicated that there is gradual release of the hydrogen gas as the bonds are getting affected and the reactions are taking place at lower temperatures. With the rise in temperature, significant improvement in hydrogen release is observed at every stage with fast reaction kinetics.

Conclusion

The neat and catalytic AB dehydrogenation with nickel as catalyst is studied under isothermal conditions in a Sievert's Type Apparatus of standard volume.

At 80°C, the neat AB decomposes with the induction period of around 125 mins. In the catalytic dehydrogenation, the induction period has reduced to 8 mins which is a significant improvement in the release kinetics at this temperature. The hydrogen gas release in the catalyzed AB sample is 4.5wt% as against 2.5wt% of neat AB. At 100°C, there is a marginal improvement in the hydrogen release with significant improvement in the induction period. Max. wt% release and drastic reduction in induction time was observed at 80°C which is one of the important stages of experimentation. Lowering the temperature for the release is an important stage in making it suitable for fuel cell based applications and 4.5wt% H₂ release was observed within 8 minutes of induction period.

The Arrhenius calculation indicated significant reduction in the activation energy and improvement in the rate of reaction for the catalyzed sample, which is visible in the isothermal decomposition characteristics.

The ABNi decomposition at 140°C and 160°C has a nominal induction period with substantial increase in the hydrogen gas release. The neat AB hydrogen

release at this temperature was in the range of 12wt% whereas catalyzed decomposition resulted in release of 13.5wt%.

The FTIR of neat and catalyzed AB are indicating no much difference in the transmittance characteristics. This helps in concluding that the presence of nickel as a catalyst is just facilitating the dehydrogenation process.

The FTIR of dehydrogenated sample indicates the release of hydrogen from various B-H and N-H bonds. The alloyed mixing of Ni with neat AB has resulted in considerable reduction in the induction time and improvement in hydrogen release rate.

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