

HYDROGEN GENERATION FROM AMMONIA BORANE

YUDHISTER KUMAR

ABSTRACT. This is a research proposal for analyzing the hydrolysis of ammonia borane in the presence of novel catalysts, namely graphene and heavy metal nanoparticles, and constructing devices which pyrolyze the amineborane and capture the hydrogen in safe ways.

1. INTRODUCTION

Ammonia is one of the most widely produced chemicals on the planet, due to its integral nature in fertilizer production (as a result of the Fritz-Haber process) and as a nitrogen store. 175 million tons are produced yearly, at an average cost of \$150 per ton. Using ammonia as a hydrogen store would be economically beneficial, as it is cheap, has 30% higher hydrogen molar density than hydrogen itself, and the substance itself is incredibly common.

However, there are many downsides to using ammonia itself as a hydrogen store. For one, it is incredibly toxic, and handling it would be incredibly dangerous. Especially if stored in a vehicle, in close proximity to moving parts, most cars would become ticking time bombs. Also, liquid ammonia has to either be stored at sub-ambient pressure or temperature, as it is a gas at standard temperature and pressure.

Therefore, it makes sense that instead, ammonia complexes would be able to be hydrogen carriers in the same way that ammonia would be, but hopefully without the negative side effects. A promising class of these compounds is called amine-boranes, and they take the form A_xB_y , where the A group is the amine group and B is boron.

Of these, the simplest is ammonia borane (NH_3BH_3). It is stable at room temperature, hydrolyzes and pyrolyzes easily, and is nontoxic and nonexplosive. This makes it a perfect candidate for scalable, next-generation hydrogen storage.

2. HYDROGEN DECOMPOSITION PATHWAYS

We begin by analyzing the decomposition pathways of ammonia borane in more detail. There are generally two pathways to extract free hydrogen from an amine borane: *hydrolysis* and *pyrolysis*. Hydrolysis of a compound involves the breaking down of chemical bonds in the compound with the addition of water. It is commonly found in biological processes, where the formation and destruction of peptide or carbohydrate bonds is only possible through hydrolysis. Pyrolysis is a form of thermal decomposition where chemical bonds are broken with the addition of heat. A common example of this would be any combustion reaction. Ammonia borane can decompose via both of these pathways in a variety of different ways, each with differing strengths and weaknesses.

2.1. Pyrolysis of NH_3BH_3 . There are three thermal decomposition steps that have been observed in the pyrolysis of ammonia borane. At 110°C and 130°C , roughly 1 mol of H_2 is released per mol of ammonia borane. This transforms the structure into first a polyaminoborane with monomer structure NH_2BH_2 , and then a different polyaminoborane with monomer structures approximating NHBH . The second decomposition is less stable than the first, and also results in some release of borazine gas ($\text{N}_3\text{B}_3\text{H}_6$). See 3 for more details.

It is also worth stating that this decomposition is exothermic and thermodynamically favorable, a major reason why this pathway is promising for hydrogen storage

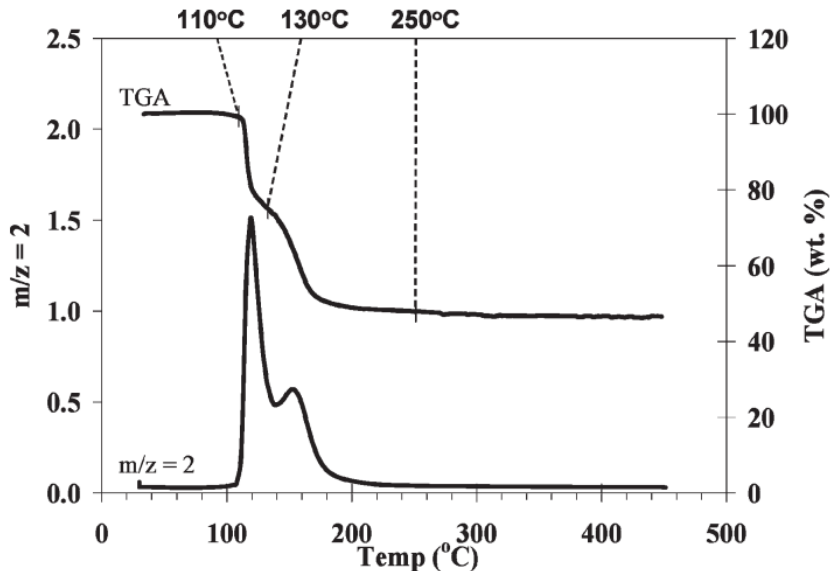


Figure 1. From [FKM⁺11], shows weight decrease as temperature increases for ammonia borane, with peaks at 110 and 130 °C.

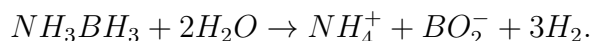
The third decomposition occurs at approximately 1170°C , from which the polyaminoborane $[\text{NHBH}]_n$ further decomposes into a hexagonal boron nitride $h\text{BN}$. This decomposition step requires much more energy than previous ones (due to the order of magnitude difference in temperature) and is not efficient - less than 1 mol H_2 is released per mol of the polyaminoborane complex (see 2).

According to [FKM⁺11], rapid heating of ammonia borane to 240°C causes 10.5% wt of H_2 to be released, with 95% released in under a minute and all within 5 minutes. This showcases the potential of pyrolysis as a quick and efficient way to dehydrogenate ammonia borane.

2.2. Hydrolysis of NH_3BH_3 . As opposed to adding large amounts of energy to ammonia borane and extracting hydrogen that way, would it be possible to extract hydrogen in a more energy efficient manner?

It turns out that under certain conditions, metal-catalyzed hydrolysis of ammonia borane can release up to 7-8% H_2 by weight, which is only about 20% worse than pyrolysis at sane temperatures.

The fundamental hydrolysis is pathway is as follows:



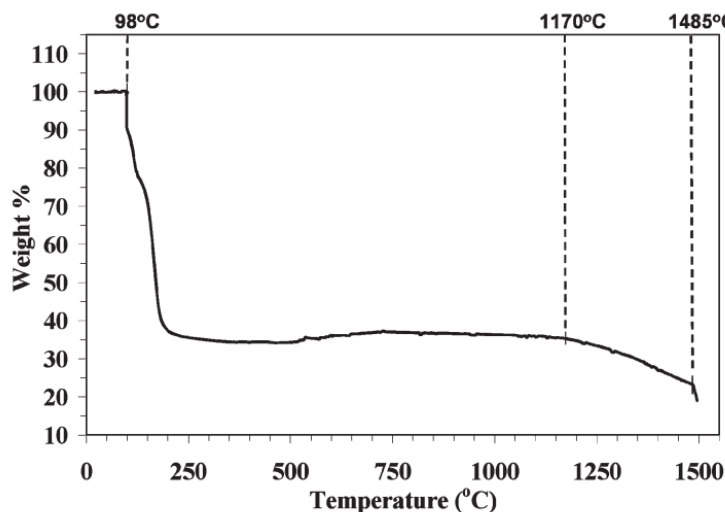
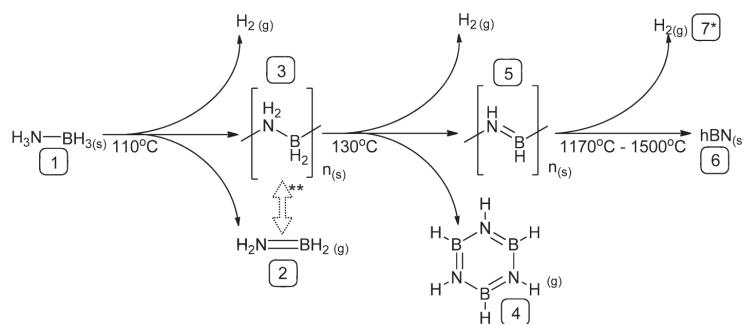


Figure 2. From [FKM⁺11], shows the existence of the third thermal decomposition with weight decrease.

Scheme 1. Experimentally Observed Chemical Pathways in the Pyrolytic Decomposition of Ammonia Borane to Boron Nitride



Species found to be involved in ammonia borane pyrolysis: [1] Ammonia Borane; [2] Molecular Aminoborane; [3] Polyaminoborane (PAB); [4] Borazine; [5] Polyiminoborane (PIB); [6] Semi-Crystalline *P63/mmc* (hexagonal) boron nitride; [7*] Hydrogen abstraction by the evolution of molecular hydrogen at high temperature, is assumed, but other possible pathways exist. **Reversibility between molecular aminoborane, [2], and PAB, [3] is inferred and likely to depend on temperature, chain length, and the extent of branching in the PAB polymer. At low temperatures, PAB is preferred and at higher temperatures PAB decomposes into molecular aminoborane [2] hydrogen, borazine [4], and polyiminoborane [5].

Figure 3. From [FKM⁺11], shows the structure of the experimentally observed decomposition residues.

Essentially, ammonia borane in the presence of water decomposes into ammonium, boric acid, and hydrogen gas. However, this is not a spontaneous reaction, so it must be catalyzed. According to [WTW⁺17], catalysts allow for the reactants in this reaction to attach to some binding surface, weakening the intramolecular forces and reducing the necessary energy to break bonds. A series of intermediates are created this way: BH_3OH , $BH_2(OH)_2$, $BH(OH)_3$.

As such, the hydrolysis process can be broken down into "reactant adsorption, activation of bonds within the reactants, surface diffusion of active molecules, intermolecular diffusion, and the formation and desorption of hydrogen." We now analyze the benefits and costs of various catalysts.

2.2.1. *Catalysts*. The metric by which we measure catalytic performance is as follows:

$$r = \frac{\Delta V_{H_2}}{\Delta t \cdot \omega_M}.$$

In other words, the more hydrogen gas produced in shorter amounts of time, the better the catalyst is (higher r). However, over non-instantaneous time periods, durability also becomes a factor.

- **Zero Valent Metal Nanoparticles.** These are nanoparticles made of metals with overall net zero electric charge. The most promising such catalysts are rhodium-palladium complexes, as they had the highest turnover frequency of the ones tested in [WTW⁺17]. Platinum-nickel nanoparticles also scored highly.
- **Supported Metal Catalysts.** These are catalysts with some molecular structure. Three-dimensional nanoarrays are an example of SMCs, and cobalt-copper compounds seem to be the most promising in this area.
- **Carbon Loaded Metal Catalysts.** Essentially metal, but with more carbon (like carbon steel). Their biggest benefit is their inexpensiveness. Carbon-doped nickel nanoparticles have the best results here, but not as good as the other two.

3. PRACTICAL APPLICATIONS AND FURTHER RESEARCH AREAS

Ammonia borane has two energy efficient dehydrogenation pathways: pyrolysis, which requires large amounts of energy input, and hydrolysis, which requires the presence of metal catalysts. Pyrolysis has a higher mol efficiency, but only about 20% better than hydrolysis.

I would be interested in developing a proof of concept fuel cell that is powered by a pyrolytic or hydrolytic ammonia borane decomposition. Pyrolysis may be slightly more dangerous, as it requires high temperatures and hydrogen gas is flammable, but it is also likely cheaper than engaging in a hydrolytic system. However, with the inexpensiveness of carbon-doped nickel nanoparticles, making a proof of concept with that technology is not out of the question.

Additionally, I would like to explore better *synthesis* pathways of ammonia borane. As a compound, it is quite expensive right now (at around \$150 per gram), and lowering the cost is essential for it to be accepted as a hydrogen storage mechanism, and for fusion to become the energy source of the future.

REFERENCES

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Email address: cyclicalreasoning2021@gmail.com