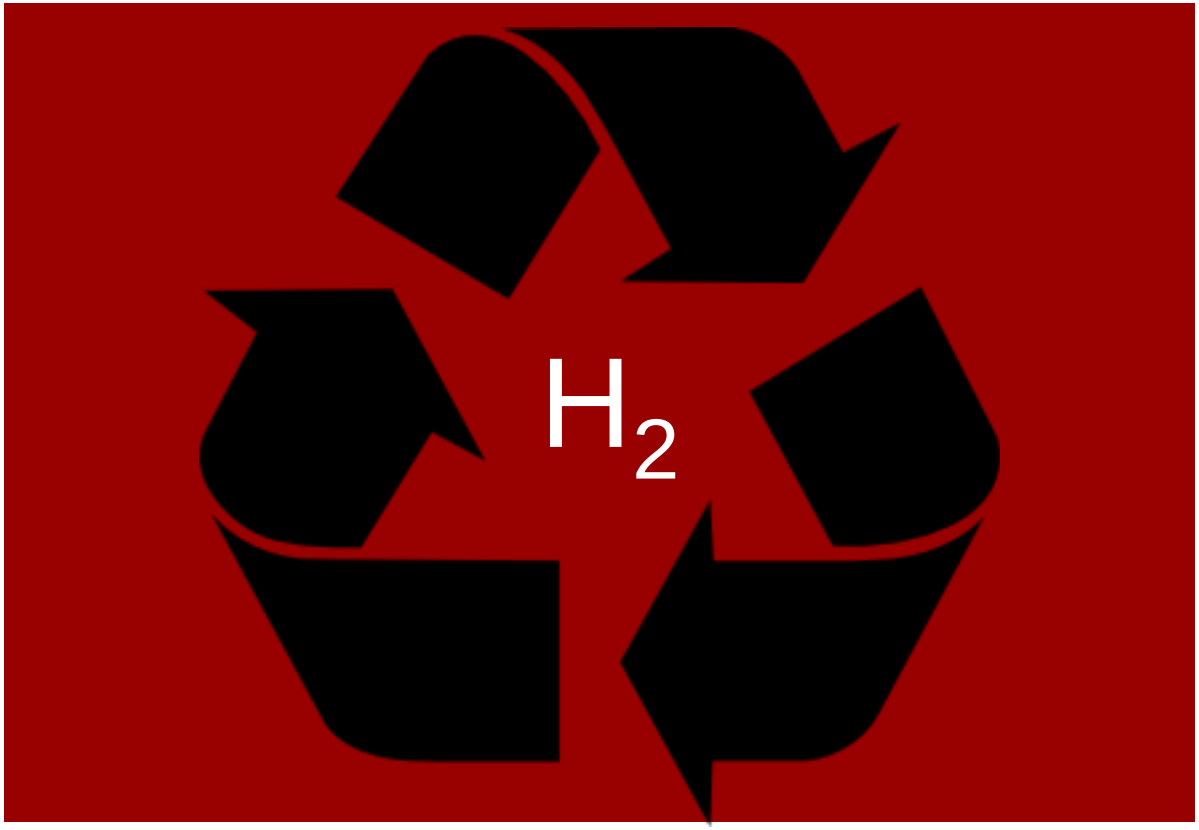
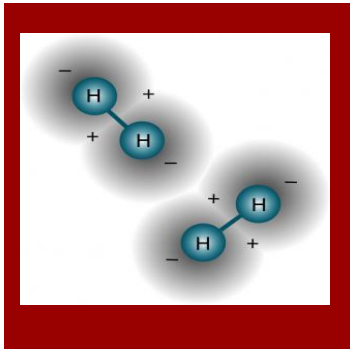
Recycling for a Hydrogen Future



A Look at the Future of Ammonia Borane and its potential as a fuel source and a recyclable material.

Tom Sublett
Marian University
Math and Science Dept.
Institute for Green and Sustainable Science
Indianapolis Indiana

Discussion of the paper:
Regeneration of Ammonia-Borane Complex for Hydrogen Storage
Nahid Mohajeri and Ali T-Raissi



what is hydrogen?

- Hydrogen is the lightest and most abundant element in the universe.
- Some fun facts:
  - We owe most of the energy on our planet to hydrogen. The Sun's nuclear fires convert hydrogen to helium releasing a large amount of energy in the process.
  - About 10 percent of the weight of living organisms is hydrogen - mainly in water, proteins and fats.
  - Hydrogen is the only atom for which the Schrödinger equation has an exact solution

http://www.chemicool.com/elements/hydrogen.html

Why hydrogen?

- Hydrogen, when it reacts, releases an incredible amount of energy.
  - $H_2(g) + 1/2\ O_2(g) \rightarrow H_2O(g)$
    - $\Delta H° = -241.8$ kJ ($= -\Delta H°_f(H_2O)$)
  - Highly exothermic reaction
- As can be seen from the above reaction, this reaction is highly exothermic.
- Also, water is found everywhere! (in case you didn't already know…)

how is hydrogen used?

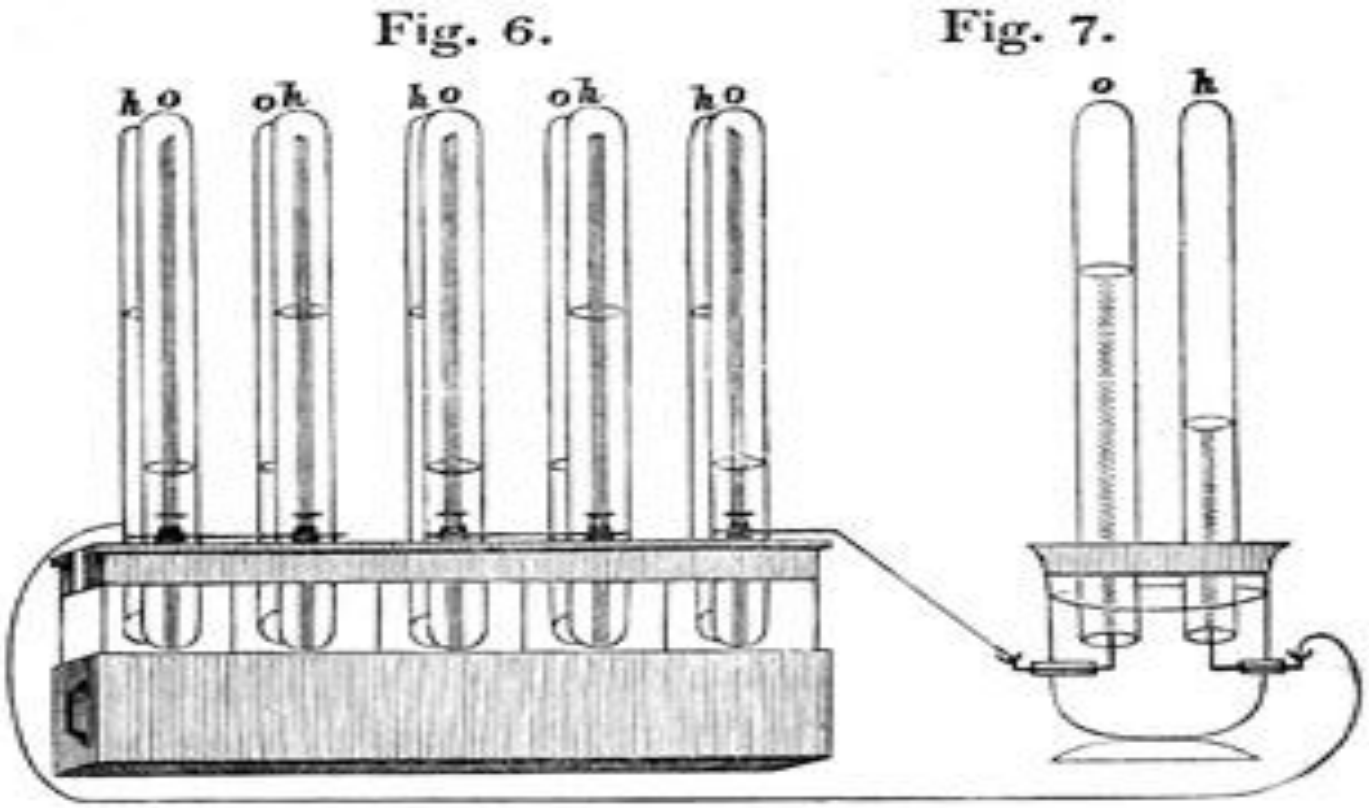
- Hindenburg Disaster

- 1. Combustion-
  - $H_2(g) + 1/2\ O_2(g) \rightarrow H_2O(g)$
  - This reaction is very exothermic, but this method is not the most "green" way of releasing energy from hydrogen.
  - It is also dangerous, due to the combustibility of hydrogen.
- 2. Fuel cells- specifically proton exchange membrane (PEM) fuel cells.

How is hydrogen used cont.

- PEMs utilize a catalyst and a semipermiable membrane to separate the proton and electron from the hydrogen atom.
  - "Hydrogen separates into hydrogen ions and electrons. The 25 cations (protons) migrate through the electrolyte membrane to the cathode. The electrons migrate via an external circuit in the form of electricity. An oxidant, in the form of oxygen or oxygen containing air, is supplied to the cathode where it reacts with the 30 hydrogen ions that have crossed the membrane and the electrons from the external circuit to form liquid water as the reaction product. The reaction is also usually catalyzed by platinum and occurs as follows:35Cathode reaction: $1/20_2+2H^+$+2e_^H20. Thus the fuel cell generates electricity and water through the electrochemical reaction."

Lehman, Peter A., Charles A. Chamberlin, Ronald M. Reid, and Thomas G. Herron. Proton Exchange Membrane Fuel Cell. Humboldt State University Foundation, assignee. Patent 5,879,826. 19 Mar. 1999. Print.



a brief history of fuel cells

Fuel cells have been around for a long time compared to their current use.

Early 1800s: William Nicholson and Anthony Carlisle invent a process to convert water into hydrogen and oxygen.

William Robert Grove makes first working fuel cell, generating water and electricity.

http://www.princeton.edu/~chm333/2002/spring/FuelCells/fuel_cells-history.shtm

why is hydrogen not being used in fuel cells?

- From previous examples, hydrogen is very volatile when exposed to oxygen.
- The process of electrolysis is energy dependent.
- The infrastructure of the US is based on a fossil fuel economy, not hydrogen.
- Storage is difficult with hydrogen, due to its nature as a gas.
- Fuel cells use platinum catalysts, an expensive material that drives costs up.


THAT FUEL CELL DOESN'T REALLY SOLVE THE PARKING-PROBLEM...
H_2
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hydrogen storage solutions

- Metal Organic Frameworks-
  - Metal-organic frameworks are a recently-identified class of porous polymeric material, consisting of metal ions linked together by organic bridging ligands, and are a new development on the interface between molecular coordination chemistry and materials science.
- Storage Tanks- Large and potentially dangerous due to high pressure and risk of explosion.
- Amine-Borane Compounds

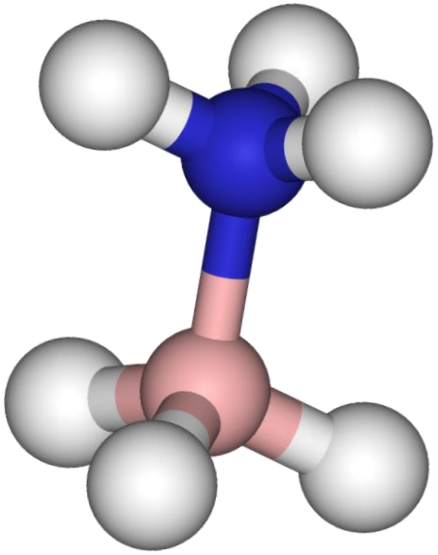
James, Stuart L. "Metal-organic Frameworks." Chemical Society Reviews 32.5 (2003): 276-88. Print.

what are amine-boranes?

- They are compounds that contain ammonia (NH_3) a hydrogen carrier.
  - " It builds on the decades-old idea of storing hydrogen in the form of ammonia, NH3. Unlike hydrogen gas, which requires cryogenic temperatures to liquefy, ammonia becomes a liquid at -34 degrees Celsius. It also does so at room temperature and 9 atmospheres pressure (it is similar to propane in this regard), making it much more convenient to use as a transportation fuel. Ammonia is comparatively inexpensive to produce, and the hydrogen can be separated out using catalysts without undue losses."

Schneider, David. "Filling Up with Hydrogen." American Scientist Sept. 2005: 410-11. American Scientist. American Scientist. Web. <www.americanscientist.org>.

Enter Ammonia Borane



- Ammonia Borane (NH_3BH_3) is a species in the amine borane family.
- It stores almost 20% hydrogen by weight, making it look very promising as a storage material for hydrogen. (It already meets the DOE standard for hydrogen storage materials.)
- It is solid at room temperature.
- Hydrogen evolution is relatively easy with a thermolysis or hydrolysis reaction.
- Relatively stable at room temperature.

http://www.energy.gov/index.htm

Problems with ammonia borane

- Not a viable "drop in" technology yet.
- Expensive to purchase.
  - 1 g of ammonia borane retails for $138.50.
- Difficult to recycle.
  - figuring out exactly how to re- generate ammonia borane from the residuum left after hydrogen has been extracted remains a stumbling block.

Schneider, David. "Filling Up with Hydrogen." American Scientist Sept. 2005: 410-11. American Scientist. American Scientist. Web. <www.americanscientist.org>.

recycling ammonia borane

- One group in particular is studying the process of recycling ammonia borane, namely the Florida Solar Energy Center.
- In their work, Nahid Mohajeri and Ali T-Raissi worked to utilize the byproducts generated by ammonia borane thermolysis.
  - "We are studying two ammoniaborane (NH3BH3)-based systems with high hydrogen storage capacity. The first system employs a borazine-cyclotriborazane cycle. Borazine is a product of NH3BH3 thermolysis. Cyclotriborazane is the inorganic analog of cyclohexane. The second system employs polymeric AB complexes such as poly-(aminoborane) and polyborazylene. Poly-(aminoborane), an inorganic analog of polyethylene, is also a product of amoniaborane thermolysis whilepolyborazylene is the product of borazine thermolysis.For the two systems above, we are developing regeneration (*i.e. reduction of borazine, poly-(aminoborane) and polyborazylene) schemes based on: 1) catalytic hydrogenation and 2) indirect (multi-step) synthesis techniques.*"

Mohajeri, Nahid, and Ali T-Raissi. "Regeneration of Ammonia-Borane Complex for Hydrogen Storage." Materials Research Society Symposium Proc. 884 E (2005): GG1.4.1.-G1.4.7. Print.

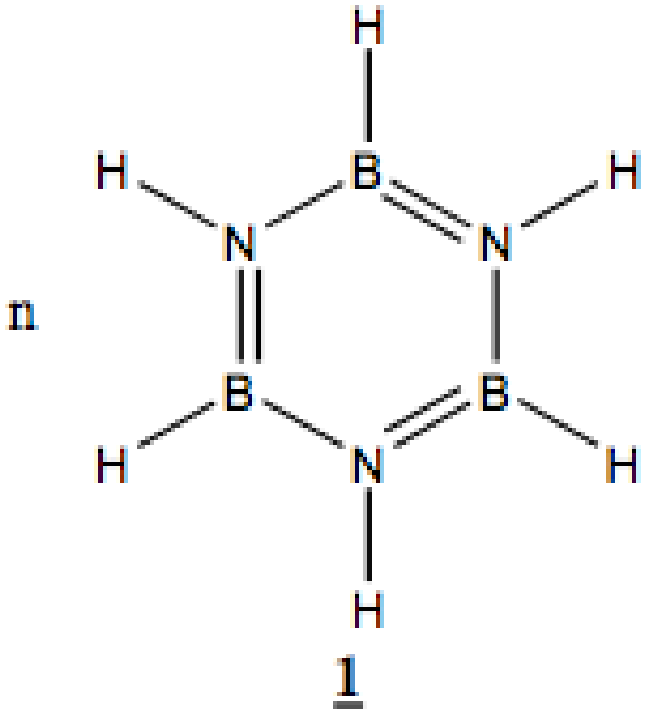
Recycling ammonia borane cont.

- "The release of hydrogen gas from ammoniaborane is accomplished via thermolysis. This process begins at temperatures below 140 °C but a temperature of about 1200 °C is needed to liberate the last mole of H2 and to form boron nitride (BN). The overall process is exothermic but heat must be supplied to activate the material [2a-f]. Since high temperatures are required for complete dehydrogenation of BH3NH3 and the chemical inertness of BN, it is preferable to end the dehydrogenation reaction at an intermediate stage. In that case, poly-(aminoborane), borazine (B3N3H6), and hydrogen are the main intermediate decomposition products."

Mohajeri, Nahid, and Ali T-Raissi. "Regeneration of Ammonia-Borane Complex for Hydrogen Storage." Materials Research Society Symposium Proc. 884 E (2005): GG1.4.1.-G1.4.7. Print.

what is borazine?

- Borazine is a cyclic molecule that forms as a byproduct of the thermolysis reaction in ammoniaborane. It is a gas at STP and was utilized in this paper as a method for hydrogenation.



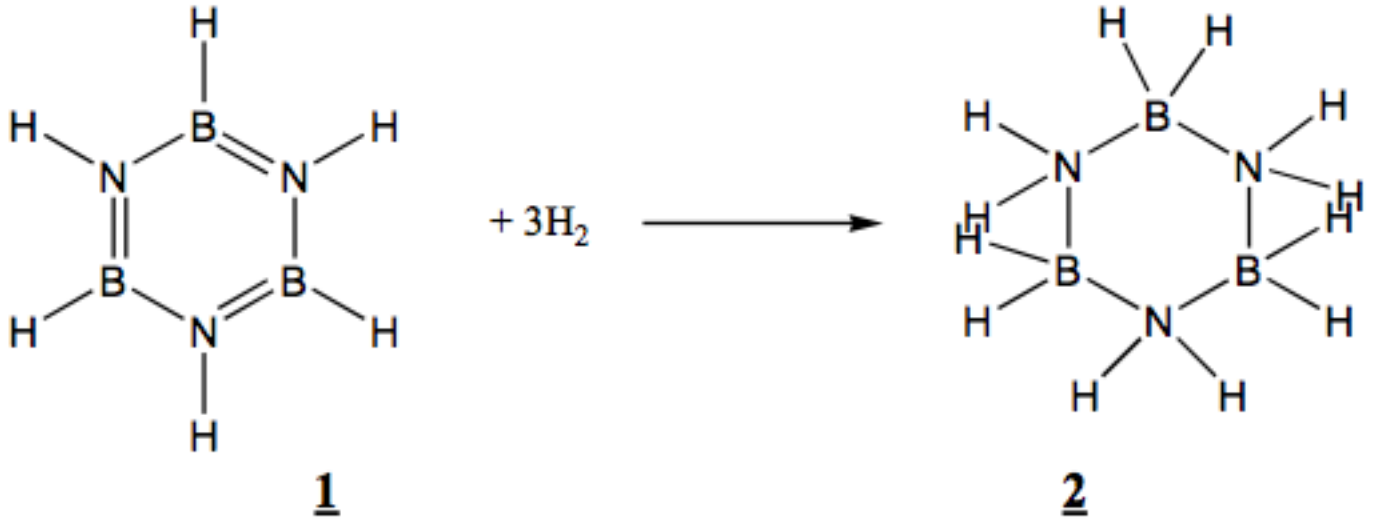
process of hydrogenation

- Methods included the use of high pressure cells to introduce hydrogen to the cycloborazine compounds.
- Authors used three samples (ball-milled) to ensure even distribution of borazine and palladium catalysts. Note: "All precautions for working with moisture- and air-sensitive compounds were observed."

Sample	Composition	Hydrogen Pressure (psi)	Hydrogenation Duration (hrs)
PB1	PB (0.2g) 5% Pd on $BaCO_3$ (0.002g)	250	12
PB2	PB (0.2g) 5% Pd on $BaCO_3$ (0.002g)	1010	24
PB3	PB (0.2g) 5% Rh on C (0.002g)	250	12

results of hydrogenation

- Borazine was hydrated under pressure and in the presence of Pd and Ni catalysts. Hydrogenation was not successful in each case.
- A proposed scheme is presented below



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Scheme 1- Borazine hydrogenation to cyclotriborazane.

other methods of hydrogenation of ammoniaborane

- Another method has been introduced that could provide a means of hydrogenating borazine and other byproducts into ammonia borane.
- One research group is looking at regeneration via ammonia and hydrazine.
  - "[This method] regenerates ammonia borane from a hydrogen depleted "spent fuel" form (called polyborazylene) back into usable fuel via reactions taking place in a single container. This "one pot" method represents a significant step toward the practical use of hydrogen in vehicles by potentially reducing the expense and complexity of the recycle stage. Regeneration takes place in a sealed pressure vessel using hydrazine and liquid ammonia at 40 degrees Celsius and necessarily takes place off-board a vehicle.

DOE/Los Alamos National Laboratory. "The drive toward hydrogen vehicles just got shorter." ScienceDaily, 21 Mar. 2011. Web. 30 Jun. 2011.

the future

- Several hurdles need to be overcome before fuel cells are widely used to fulfill our transportation needs.
  - The fuel cells themselves will need to come down in price.
  - The issue of hydrogen storage will need to be addressed; by ammoniaborane or some other method.
  - Recycling methods will need to get better.
  - Government interest directed towards hydrogen power will need increase.

the future is brighter with fuel cells leading the way

Thank you.

questions?