Properties of aqueous alkaline sodium borohydride solutions and by-products formed during hydrolysis

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Outline

- Review of ASU tasks
- Review of basic solution properties of aqueous borohydride solutions
- Current Research
  - Hydrogen storage
  - Hydrolysis of borohydride
  - Water and by-products, $NaB(OH)_4$
  - Characterizing by-products
    - Identity
    - Solution properties
- Conclusions

Review of ASU tasks

Task 1: ASU will support the Univ. of Illinois (UIUC) in reporting and participate in technical meetings.

Task 4.3: Optimize $NaBH_4$ performance

Task 4.3.1: ASU will develop an energy dense (>2100 Wh/liter or Wh/Kg) hydrogen storage solution component consisting of >30% sodium borohydride in aqueous >1M NaOH solution.

Task 4.3.2: ASU will develop a means of separating the hydrogen gas from the liquid hydrogen storage solution, so that only the hydrogen gas is supplied to the fuel cell anode.

Task 11.3: Refine $NaBH_4$ performance

Task 11.3.1: Design and construction of catalytic hydrogen generation reactor with catalyst inside a micro-channel in multi-channel reaction zone. Hydrogen generation will occur only when hydrogen storage solution passes over a heterogeneous catalyst in the micro fluidic reactor. Packed bed and wall coated catalyst zones will be tested.

Subtask 3.1a: Design and construct a setup for determining the rate of hydrogen gas generation.

Subtask3.1b: Design and construct an apparatus for determining the activity of hydrogen gas generation catalyst on heterogeneous support.

Task 11.3.2: ASU will develop a means to integrate the hydrogen gas to a fuel cell stack.

Task 11.1: ASU can assist oxidant storage/supply to fuel cell and regeneration a team members and resources allow.

Today's talk is about borohydride/boron-oxide solution stability. Relates to Tasks 4.3, maximizing hydrogen storage & optimizing fluidics.

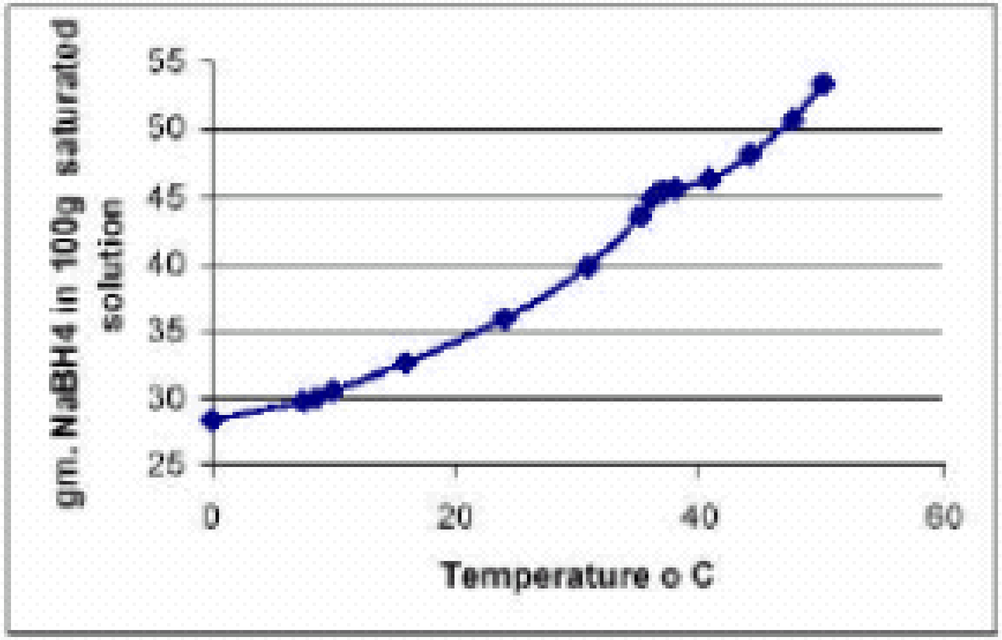
Solubility of Sodium Borohydride in Various Solvents

Table III NaBH$_4$ Solubility in Various Solvents
(g/100g of solvent)

Solvent	Temp(°C)	Solubility
Water	0	25.0
	25	55.0
	60	88.5
Liquid Ammonia	25	104.0
Methylamine	-22.0	27.6
Ethylamine	17	20.9
N-Propylamine	28	9.6
Iso-Propylamine	28	6
N-Butylamine	28	4.9
Cyclohexylamine	28	1.8
Morpholine	25	1.4
	75	2.5
Aniline	75	0.6
Pyridine	25	3.1
	75	3.4
Monoethanolamine	25	7.7
Ethylenediamine	75	22.0
Methanol	20	16.4 (reacts)
Ethanol	20	4.0 (reacts slowly)
Iso- Propanol	25	0.37
	60	0.88
Tert-Butanol	25	0.11
	60	01.8
2-Ethylhexanol	25	0.01
Tetrahydrofurfuryl Alcohol	20	14.0 (reacts slowly
Ethylene glycol dimethyl ether	0	2.6
	20	0.8
Diethylene glycol dimethyl ether	0	1.7
	25	5.5
	45	8.0
	75	0.0
Triethylene glycol dimethyl ether	0	8.4
	25	8.7
	50	8.5
	100	6.7
Tetraethylene glycol dimethyl ether	0	8.7
	25	9.1
	50	8.4
	75	8.5
	100	4.2
Dimethylformamide	20	18.0
Dimethylacetamide	20	14.0
Dimethylsulfoxide	25	5.8
Acetonitrile	28	2.0
Tetrahydrofuran	20	0.1

From Rohm and Haas Borohydride digest www.Rohm&Haas.com

Solubility of Sodium Borohydride in Water withTemperature



From Rohm and Haas Borohydride digest www.Rohm&Haas.com

Stability of Sodium Borohydride with pH

Table V: pH Vs Half life of SBH

pH	$NaBH_4$ Half life
4.0	0.0037 sec.
5.0	0.037 sec
5.5	0.12 sec
6.0	0.37 sec
7.0	3.7 sec.
8.0	36.8 sec.
9.0	6.1 mins
10.0	61.4 mins
11.0	10.2 hours
12.0	4.3 days
13.0	42.6 days
14.0	426.2 days

Current Research

OVERALL GOAL:

Maximize hydrogen storage capacity of aqueous alkaline sodium borohydride solution and solubility of hydrolysis by-product solution.

Hydrolysis of Borohydride: $NaBH_4 + 2\ H_2O \rightarrow 4\ H_2 + NaBO_2$

SUB-GOALS:

* Characterize hydrolysis of sodium borohydride ($NaBH_4$) using:
- ^{11}B Nuclear Magnetic Resonance (NMR) Spectroscopy
- X-ray diffraction (XRD)
- Fourier Transform Infrared (FTIR) spectroscopy.

*Ascertain the chemical structure of the by-product(s) formed during hydrolysis.

*Determine the mechanism of the catalytic hydrolysis of NaBH4 in alkaline solution

*Evaluate the effect of additives on:
- the hydrolysis of sodium borohydride and the
- solubility of the resulting boron-oxide by-products.

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Hydrogen Content of alkaline sodium borohydride solutions

- Goal: use as high a concentration of borohydride in solution as possible

Gravimetric storage density:

% H2 by weight

Solid NaBH4 10.6 %

NaBH4-20 solution (20 wt% NaBH4, 3 wt% NaOH, 77 wt% H 2O) 4.3 %

NaBH4-25 solution (25 wt% NaBH 4, 3 wt% NaOH, 72 wt% H2O) 5.3 %

NaBH4-30 solution (30 wt% NaBH 4, 3 wt% NaOH, 67 wt% H2O) 6.4 %

NaBH4-35 solution (35 wt% NaBH4, 3 wt% NaOH, 62 wt% H2O) 7.5 %

Volumetric storage density:

1 Liter NaBH4-20 solution 44 grams or 526 Standard Liters

1 Liter NaBH 4-25 solution 55 grams or 658 Standard Liters

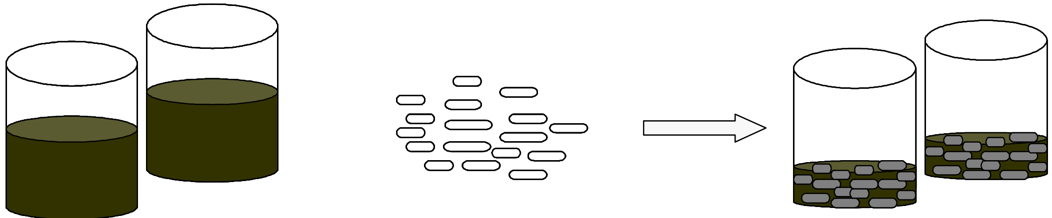
1 Liter NaBH4-30 solution 66 grams or 789 Standard Liters

1 Liter NaBH4-35 solution 77 grams or 921 Standard Liters

From Millenium Cell website, www.milleniumcell.com

Ru on Alumina: a Catalyst for Borohydride Hydrolysis

Prep of Catalyst for H_2 Generation

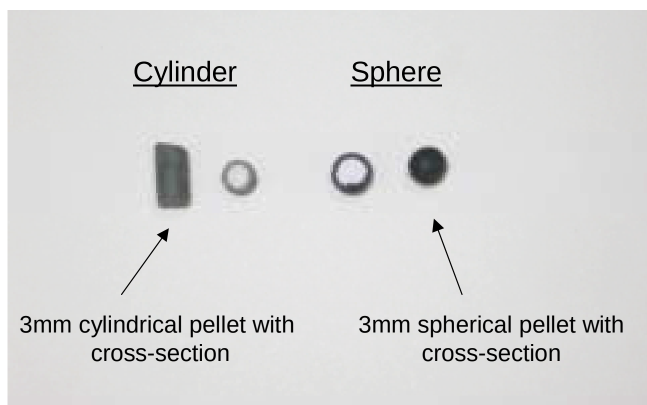


2wt.% and 5wt.% Ru Cl_3 solutions in DI water

High surface area gamma alumina pellets for catalyst support

Alumina pellets soaked in the Ru Cl_3 solutions.

Solution soaked $RuCl_3$ on alumina pellets, decanted, air dried.
Samples were heated under 5% hydrogen, balance helium.
heated at 100°C/hr to 150°C or 700°C, no dwell and 6 hour dwell

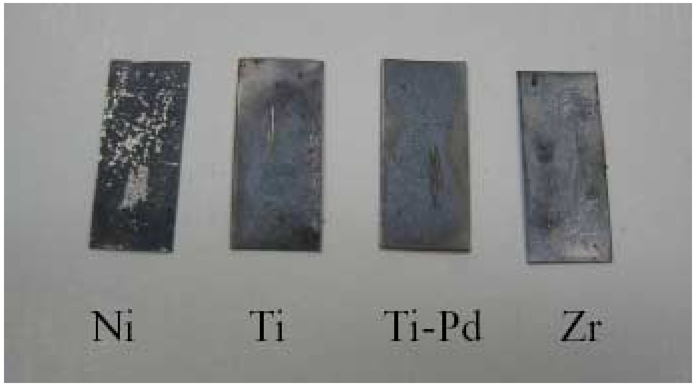


- *Catalyst support features: High surface area (220m^2/g) g-alumina with total pore volume of 0.62cc/g.*
- *Improved packing of catalyst bed with spherical alumina support*

Precipitates during catalytic hydrolysis

Ru on alumina Not Stable in aqueous alkaline sodium borohydride hydrogen-storage solution !

Alumina-borate solid lump that forms in hydrogen generation reactor from alumina dissolution 30wt% sodium borohydride in aqueous 1M NaOH solution.



Ru on various metal supports
Ti best support:
- **stable**
- **Ru adheres.**

Ru on metal Ti support is stable in aqueous alkaline sodium borohydride solution!

Question…Do sodium borohydride and hydrolysis by-products stay in solution? Or Precipitate?

Answer…it depends on hydrolysis by-product(s)

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Possible By-Products formed during $NaBH_4$ Hydrolysis

The reaction of hydrogen generation from sodium borohydride is nominally written as:

$$NaBH_4 + 2\ H_2O \rightarrow 4\ H_2 + NaBO_2$$

Actually many boron oxides can form, dictating the amount of water needed as seen below.

Boron Oxide	Mole Oxygen (per $NaBH_4$)	H_2O Needed (30% sol'n)	Volume H_2O (milliliter)
*$NaB(OH)_4$	4 moles	32 moles	576
$NaBO_2 \cdot x$ H2O	2+x	16	288
Na2B4O7	7/2	28	504
$Na_2B4O_7 \cdot 10$ H2O	17/2	68	1224
$Na_2B_4O_6(OH)_2 \cdot 3\ H_2O$	11/2	44	792
$Na_2B_4O_7 \cdot 5\ H_2O$	12/2	48	864
$Na_2B_4O_5\ (OH)_4 \cdot 3\ H_2O$	12/2	48	864
$Na_2\ B_4O_5\ (OH)_4 \cdot 8\ H_2O$	17/2	68	1224

* *ASU X-ray diffraction data indicate that $NaB(OH)_4$ is the by-product of hydrolysis reaction.*

Specific Case: Hydrolysis of 30% $NaBH_4$ to $NaB(OH)_4$

In 1000 g of fuel (NaBH4-30), there are:

- 2.8 g NaOH or 0.07 moles of NaOH per kilo of solution

- 700 g H_2O or 39 moles of free water per kilogram of solution.

- 300 g $NaBH_4$ or 8 moles of $NaBH_4$ per kilo of solution.

$$NaBH_4 + 4\ H_2O \rightarrow 4\ H_2 + NaB(OH)_4$$

After hydrolysis as given in above reaction, there are:

- 32 moles or 571 g of water consumed

- 8 moles or 807.5 g of $NaB(OH)_4$ formed

- 0.07 or 2.8 g of NaOH remain

- 125 ml of free water remains.

Questions for Future Work

Q1: Is $NaB(OH)_4$ the only hydrolysis by-product?

Q2: Does NaOH react with $NaB(OH)_4$?

Q3: What is pH before and after?

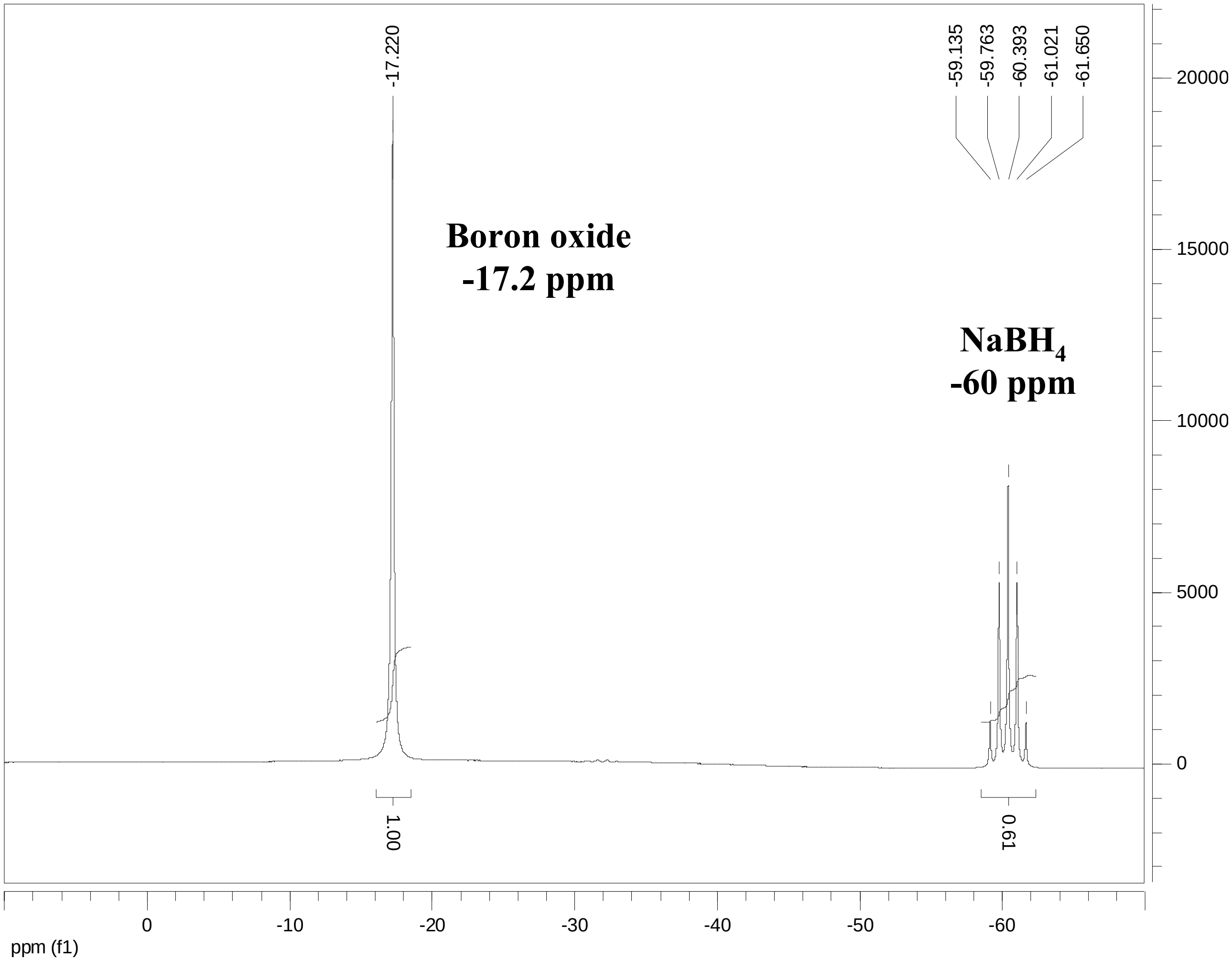
Q4: Can 800 g of $NaB(OH)_4$ dissolve in 125 ml of pure water? With 0.07 moles of NaOH?

Q5: Does the hydrolysis process influence identity of by-product(s)?

- heterogeneous catalytic hydrolysis over Ru? (NMR ex-situ and in-situ)

- electrolysis on Pt electrode? (NMR ex-situ and in-situ)

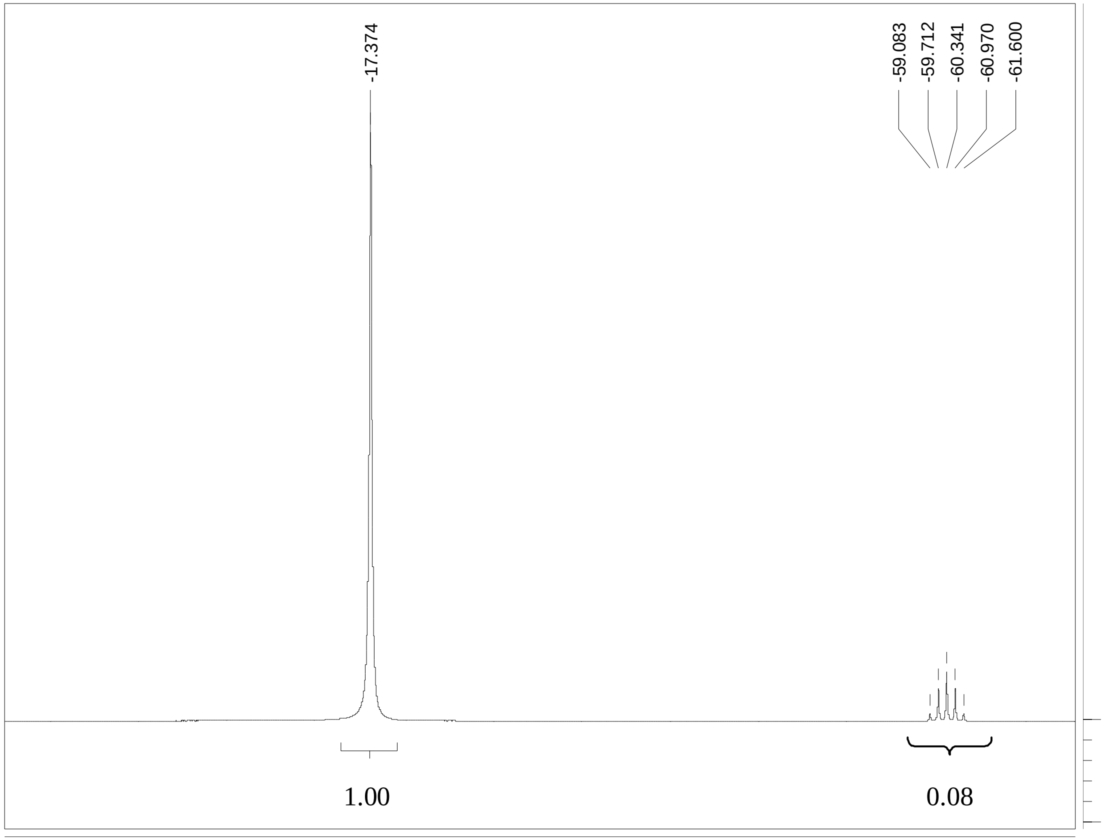
NMR: spectrum of $NaBH_4$ during catalytic hydrolysis



^{11}B NMR, 30% $NaBH_4$ and catalyst after 15 minutes.

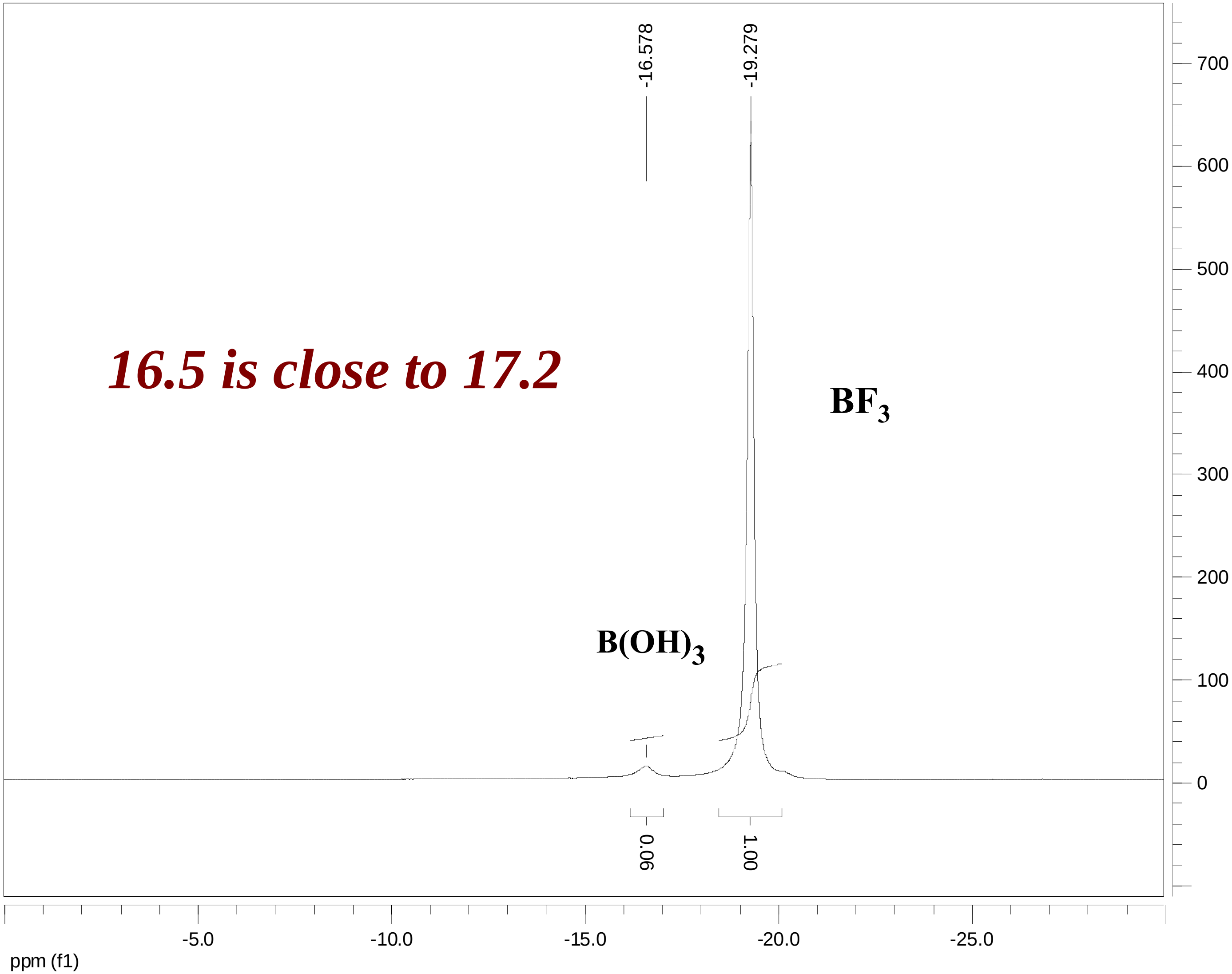
Catalyst: 0.02 g (5wt% Ru on alumina). Boric acid: 0 ppm.

NMR spectrum of $NaBH_4$ during hydrolysis (3 weeks later)



B^{11} NMR of 1 ml 30 wt% $NaBH_4$ in 1M aqueous NaOH with catalyst in after 3 weeks
Mass of catalyst = 0.02g (5% Ru on alumina), Boric Acid: 0 ppm.

B^{11} NMR Spectrum of Boric Acid $B(OH)_3$



^{11}B NMR, neat BF_3 diethyl etherate in external capillary and 0.05M $NaBO_2 \cdot 4H_2O$, 5% D_2O in sample tube. Boric acid: 0 ppm.

Summary of NMR Spectral Data

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Spectrum	Compound	NMR Type	Reference Compound	Chemical Shift (ppm)	Integral	Multiplicity	Assignment
1	$B(OH)_3$	Boron-11	$B(OH)_3$	0.014	1.00	1	
2	Unknown 1M $NaBH_4$ Hydrolysis Product	Boron-11	$B(OH)_3$	-17.666	1.00	1	
3	Unknown 30% $NaBH_4$ Hydrolysis Product	Boron-11	$B(OH)_3$	-17.220	1.00	1	
	$NaBH_4$		$B(OH)_3$	-60.380	4.36	5	
4	Unknown 30% $NaBH_4$ Hydrolysis Product	Boron-11	$B(OH)_3$	-17.690	1.00	1	
5	BBr_3	Boron-11	$B(OH)_3$	18.935	1.00	1	
6	BF_3 diethyl etherate	Boron-11	$B(OH)_3$	-19.181	1.00	1	
7	Unknown 30% $NaBH_4$ Hydrolysis Product w/ Ru catalyst in situ at t=0	Boron-11	$B(OH)_3$	-17.220	1.00	1	
	$NaBH_4$		$B(OH)_3$	-60.395	4.50	5	
8	Unknown 30% $NaBH_4$ Hydrolysis Product w/ Ru catalyst in situ after 15 min	Boron-11	$B(OH)_3$	-17.220	1.00	1	
	$NaBH_4$		$B(OH)_3$	-60.393	0.61	5	
9	Unknown 30% $NaBH_4$ Hydrolysis Product w/ Ru catalyst in situ after 30 min	Boron-11	$B(OH)_3$	-17.225	1.00	1	
	$NaBH_4$		$B(OH)_3$	-60.394	0.60	5	
10	Unknown 30% $NaBH_4$ Hydrolysis Product w/ Ru catalyst in situ after 1 day	Boron-11	$B(OH)_3$	-17.215	1.00	1	
	$NaBH_4$		$B(OH)_3$	-60.375	3.73	5	
11	Unknown 30% $NaBH_4$ Hydrolysis Product w/ Ru catalyst in situ after 1 day, 15 min	Boron-11	$B(OH)_3$	-17.216	1.00	1	
	$NaBH_4$		$B(OH)_3$	-60.374	4.18	5	
12	Unknown 30% $NaBH_4$ Hydrolysis Product w/ Ru catalyst in situ after 1 day, 30 min	Boron-11	$B(OH)_3$	-17.223	1.00	1	
	$NaBH_4$		$B(OH)_3$	-60.372	4.12	5	
13	**SOLID** $B(OH)_3$	Boron-11	$B(OH)_3$	0.033	1.00	1	
14	**SOLID** byproduct from Zr support	Boron-11	$B(OH)_3$	-4.984	1.00	1	
15	**SOLID** byproduct from DSA support	Boron-11	$B(OH)_3$	-5.014	1.00	1	
16	Unknown 30% $NaBH_4$ Hydrolysis Product w/ Ru catalyst in situ after 1 week	Boron-11	$B(OH)_3$	-17.270	1.00	1	
	$NaBH_4$		$B(OH)_3$	-60.364	0.23	5	
17	BBr_3	Boron-11	$B(OH)_3$	18.941	1.00	1	
18	BF_3 diethyl etherate	Boron-11	$B(OH)_3$	-19.199	1.00	1	
19	$B(OH)_3$	Boron-11	$B(OH)_3$	0.069	1.00	1	
	BF_3 diethyl etherate		$B(OH)_3$	-19.207	2.50	1	
20	Unknown 30% $NaBH_4$ Hydrolysis Product w/ Ru catalyst in situ after 3 weeks	Boron-11	$B(OH)_3$	-17.374	1.00	1	
	$NaBH_4$		$B(OH)_3$	-60.341	0.08	5	
21	BBr_3	Boron-11	$B(OH)_3$	18.871	1.00	1	
	$B(OH)_3$		$B(OH)_3$	0.018	0.35	1	
22	$B(OH)_3$	Boron-11	$B(OH)_3$	0.006	0.39	1	
	BF_3 diethyl etherate		$B(OH)_3$	-19.274	1.00	1	
23	$Na_2B_4O_7$	Boron-11	$B(OH)_3$	-9.329	0.10	1	
	BF_3 diethyl etherate		$B(OH)_3$	-19.274	1.00	1	
24	$Na_2B_4O_7$ decahydrate	Boron-11	$B(OH)_3$	-9.529	0.11	1	
	BF_3 diethyl etherate		$B(OH)_3$	-19.274	1.00	1	
25	$NaBO_2$ tetrahydrate	Boron-11	$B(OH)_3$	-16.578	0.06	1	
	BF_3 diethyl etherate		$B(OH)_3$	-19.279	1.00	1	
26		Boron-11	$B(OH)_3$	8.300	1.00	1	1
	SOLID $Na_2B_4O_7$		$B(OH)_3$	-5.214	4.60	1	2
27		Boron-11	$B(OH)_3$	8.327	1.00	1	1
	SOLID $Na_2B_4O_7$ decahydrate		$B(OH)_3$	-5.249	4.21	1	2
28	**SOLID** $NaBO_2$ tetrahydrate	Boron-11	$B(OH)_3$	4.895	1.00	1	

Conclusions

- ***A key problem with the hydrogen generation reactor is keeping the boron oxide (borohydride hydrolysis by-product) from precipitating and obstructing the micro-fluidics in system.***

- ***Once the boron oxide is definitively established through NMR spectroscopy, additives can be tested that are to keep the boron oxide in solution.***

- ***NMR spectroscopy will be used to characterize the effect of additives on the hydrolysis reaction, if any.***