DOE Hydrogen Program

Development of Regenerable, High-Capacity Boron Nitrogen Hydrides For Hydrogen Storage

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RTI International

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Intematix

Project ID# STP 5

RTI INTERNATIONAL

Overview

Timeline

- Project start – 3/15/2005
- Phase I end – 11/30/2008
- Phase I – 70 % complete

Budget

- Total project funding
  - DOE share - $ 1.6M
  - Contractor share - $ 0.4M
- Phase I Funding through FY08
  - DOE share - $ 0.75M
  - Contractor share - $ 0.2M

Barriers

Barriers Addressed

- A – System weight and volume
- B – Energy efficiency
- R – Regeneration process

Partners

- Intematix Corporation – Discovery of catalysts

Objectives

Overall – Develop a boron-nitrogen hydride-based hydrogen storage system to meet U.S. DOE's 2010 technical (6 wt%) and cost targets ($4/kWh).

Hydrogen Release – Develop an energy efficient process of on-board thermal decomposition of ammonia-borane (AB) (NH_3BH_3) to produce pure hydrogen suitable for PEM fuel cells. Discover catalysts to improve efficiency of hydrogen release and to produce decomposition products that are amenable to regeneration.

Regeneration – Develop an energy efficient process for catalytic regeneration of AB decomposition products. Discover catalysts to promote regeneration of partially dehydrogenated products, preferably using only H_2 pressure and temperature.

Phase I Milestones

	Milestone or Go/No-Go Decision	Status
Milestone	Conduct full cycle energy balance for the original chemical regeneration approach and change scope of work if necessary	Changed Scope of work
Milestone	Demonstrate hydrogen release greater than 6% by wt of AB material	Achieved
Milestone	Demonstrate lab-scale synthesis of pure AB starting from AB decomposition byproducts by catalytic hydrogenation	On going Work
Go/No Go to Phase II	Demonstrate hydrogen release from AB at temperatures < 500 ^{o}C	Achieved
Go/No Go to Phase II	Demonstrate >70% yield and > 60% energy efficiency in Regeneration	On going Work

Full Cycle Energy Balance for Chemical Regeneration

Chemical Regeneration Energy Requirement (*+ve = endothermic, -ve = exothermic)*

Reaction	Reaction Enthalpy	Free Energy Change
1) $2\ BN + 3\ Cl_2 \xrightarrow{800\ ^oC} 2\ BCl_3 + N_2$	- 36.5 kcal/mole BN	- 46 kcal/mole BN
2) $2\ BCl_3 + 6\ H_2 \xrightarrow{400\ ^oC} B_2H_6 + 6\ HCl$	+ 31.7 kcal/mole BCl_3	+37.3 kcal/mole BCl_3
3) $B_2H_6 + 2NH_3 \xrightarrow{30\ ^oC} 2\ BH_3NH_3$	- 20.9 kcal/mole AB	- 15.8 kcal/mole AB
4) $6\ HCl \rightarrow 3\ H_2 + 3\ Cl_2$	+ 66.2 kcal/mole BCl_3	+ 68.4 kcal/mole BCl_3
5) $3\ H_2 + N_2 \xrightarrow{500\ ^oC} 2NH_3$	- 12.5 kcal/mole AB	+ 14.2 kcal/mole AB
$2\ BN + 6\ H_2 \rightarrow 2\ BH_3NH_3$	+ 28 kcal/mole AB	+ 58.1 kcal/mole AB

- Although overall reaction sequence appears to be >60% energy efficient it will require thermal integration between individual reactions e.g. Reactions 1 and 2
- The large number of reaction steps increases overall energy requirement significantly due to inefficiencies involved in each reaction
- Electrolysis of HCl is a single most energy intensive step not suitable for thermal integration with others and will likely require ~ 95 kcal/mole AB (~55% AB energy)
- Chemical regeneration is not likely to meet 60% energy efficiency target.

Approach

Task 1 – Hydrogen release

- Characterize non-catalytic thermal decomposition of ammonia borane – complete
- Conduct combinatorial high-throughput screening of the catalyst libraries to identify catalysts to a) lower H_2 release temperature, b) increase hydrogen yield and c) produce products amenable to regeneration – Methodology developed, catalyst screening on-going
- Evaluate promising catalysts and process conditions (temperature) for hydrogen release in a larger scale reactor – just began

Task 2 - Regeneration

- Conduct combinatorial high-throughput catalyst screening to identify promising catalysts and process conditions (H_2 pressure and T) for regeneration – Methodology developed, screening on-going
- Evaluate promising catalysts and process conditions for regeneration of decomposition products (with up to 2 moles of hydrogen released) in a larger scale reactor – just began

Significant Accomplishments

- Characterized non-catalytic hydrogen release from AB for hydrogen yield, impurities, heat released, and release kinetics for AB decomposition at 100 – 500 ^{o}C.
- Demonstrated hydrogen yield of up to 16.3 wt% AB
- Established methodology and techniques for combinatorial screening of catalyst activity for dehydrogenation of AB and regeneration of decomposition products.
- Conducted screening of one set of catalyst compositions each for hydrogen release from ammonia borane (identified two catalyst leads) and for regeneration of decomposition products generated with loss of one mole of hydrogen/mole AB (identified several catalyst leads)
- Bulk catalytic dehydrogenation/regeneration reactor assembled and evaluation of promising catalysts has just begun.

Task 1 - Hydrogen Release

- Two Possible modes of AB System design:
  - a) “Heat to material”: Conventional with fixed AB cartridge with heat directed to progressive zones – compartmentalized cartridge design – slow heating and hydrogen release rate, controlled heating pattern.
  - b) “Material to heat”: Dispensing of AB in to a fixed hot zone – fast heating and hydrogen release rate, controlled solid powder/ pellet dispensing system, may need separate product storage.
- Two possible modes of supplying heat: direct hydrogen combustion, Resistive heating using fuel cell power.

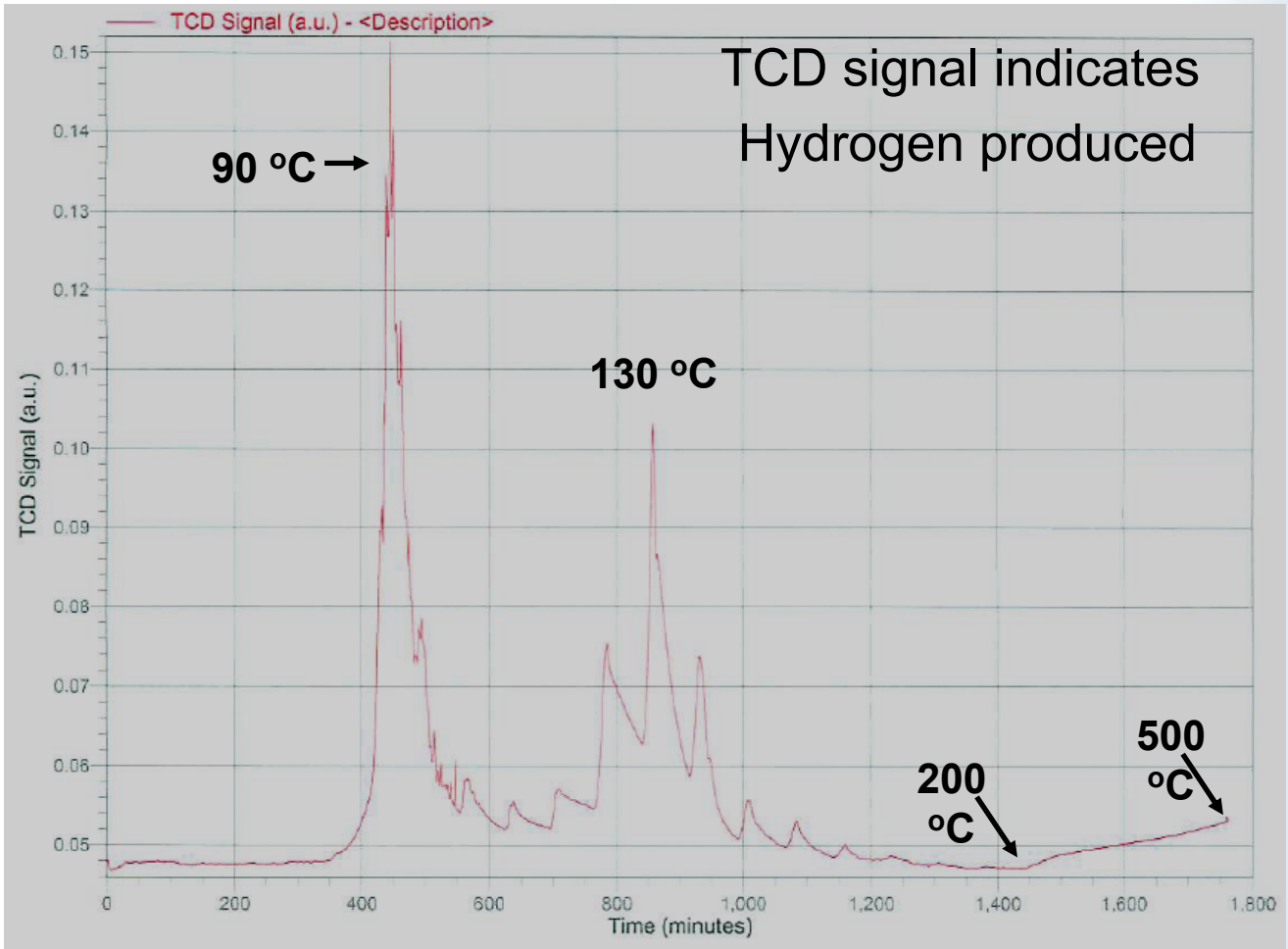
We are looking at two possible rates of heating for thermal decomposition of AB for ultimate design.

Task 1 – Temperature Programmed Decomposition (TPD) Studies – non-catalytic

- Simulation of slow and progressive heating of AB.
- controlled: ramp rate, hold times, and final Temperature.
- AB sample (~ 20 mg) wrapped in nickel foam.
- Species released during heating are identified by mass spectrometer analysis.
- Total amount of hydrogen gas released is determined by thermal conductivity detector (TCD).
- Heat produced during hydrogen release determined by DSC

These experiments determined effect of slow heating parameters on hydrogen release

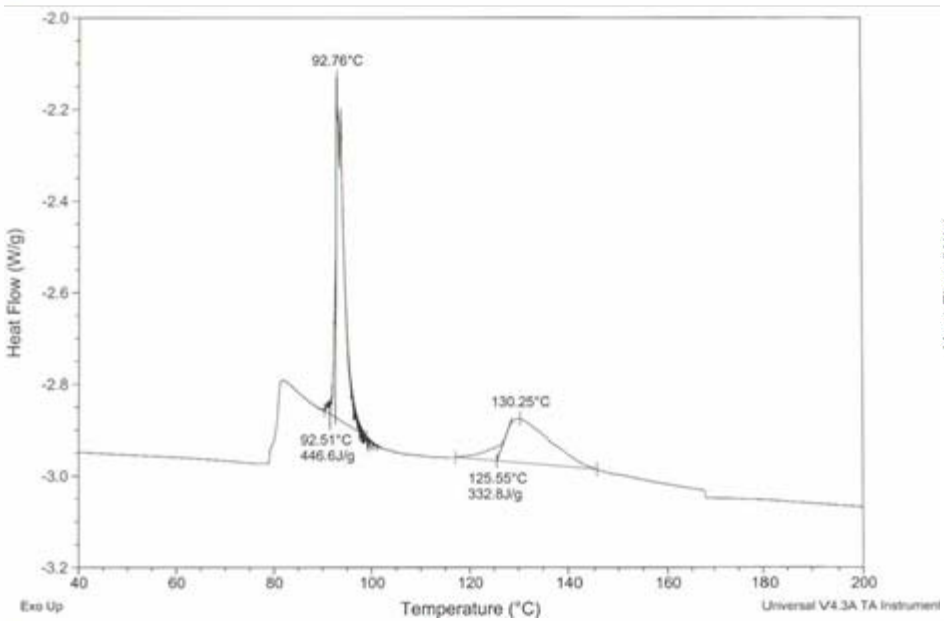
TCD Signal – 25 – 500 °C



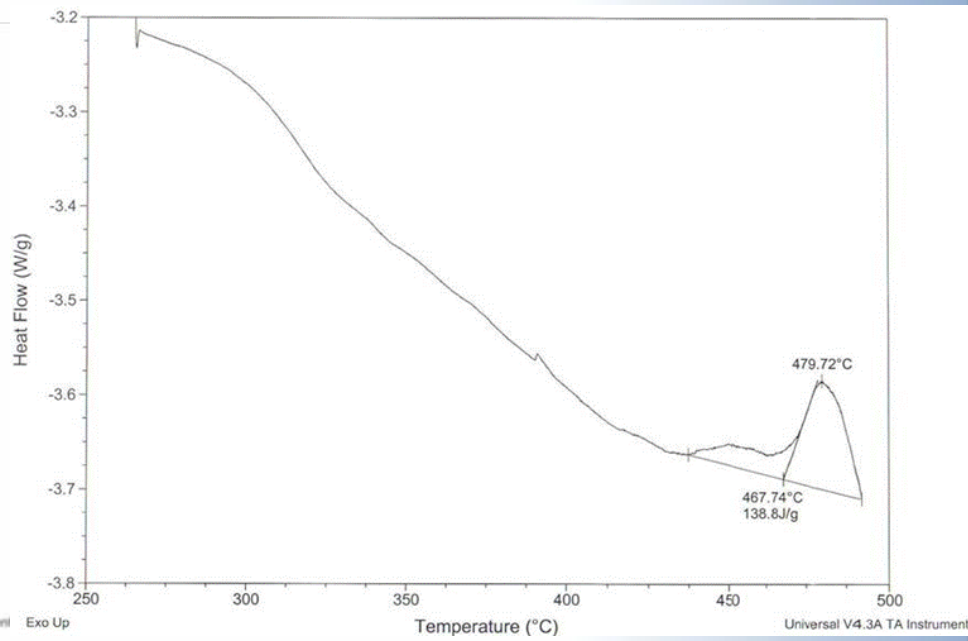
hydrogen released in slow heating ~ 67% in first two stages, ~ 1% in the third stage

Differential Scanning Calorimetry (DSC)

Heating Rate 0.2 °C/min
between 80 to 170 °C



Heating Rate 1 °C/min



Release of heat during first stage, close to AB m.p., causes foaming and expansion of solid mass

Release of final third of hydrogen does not occur till ~ 480 °C,

Conclusions from TPD/DSC studies

- Product hydrogen contained borazine as the primary impurity.
- ~ 2/3 of the hydrogen released through 150 ^{o}C (13% of AB wt).
- Only partial release of H_2 in third stage (200 – 500 ^{o}C) ~ 1%
- DSC scan indicated third exothermic hydrogen release at 480 ^{o}C
- Heat released in first two stages ~ 24 kJ/mole AB (5.8 kcal/mole)
- Rate of hydrogen release in 1st stage was about 3x faster than 2nd stage
- At a constant temperature, rate of hydrogen release decreases with time
- Hydrogen release rate is sensitive to T as well as the hold time
- Careful control of temperature, heating rate, and hold times at different temperatures would be needed for on-board implementation
- Exothermic hydrogen release in the first stage close to AB melting point causes foaming and expansion of decomposing mass

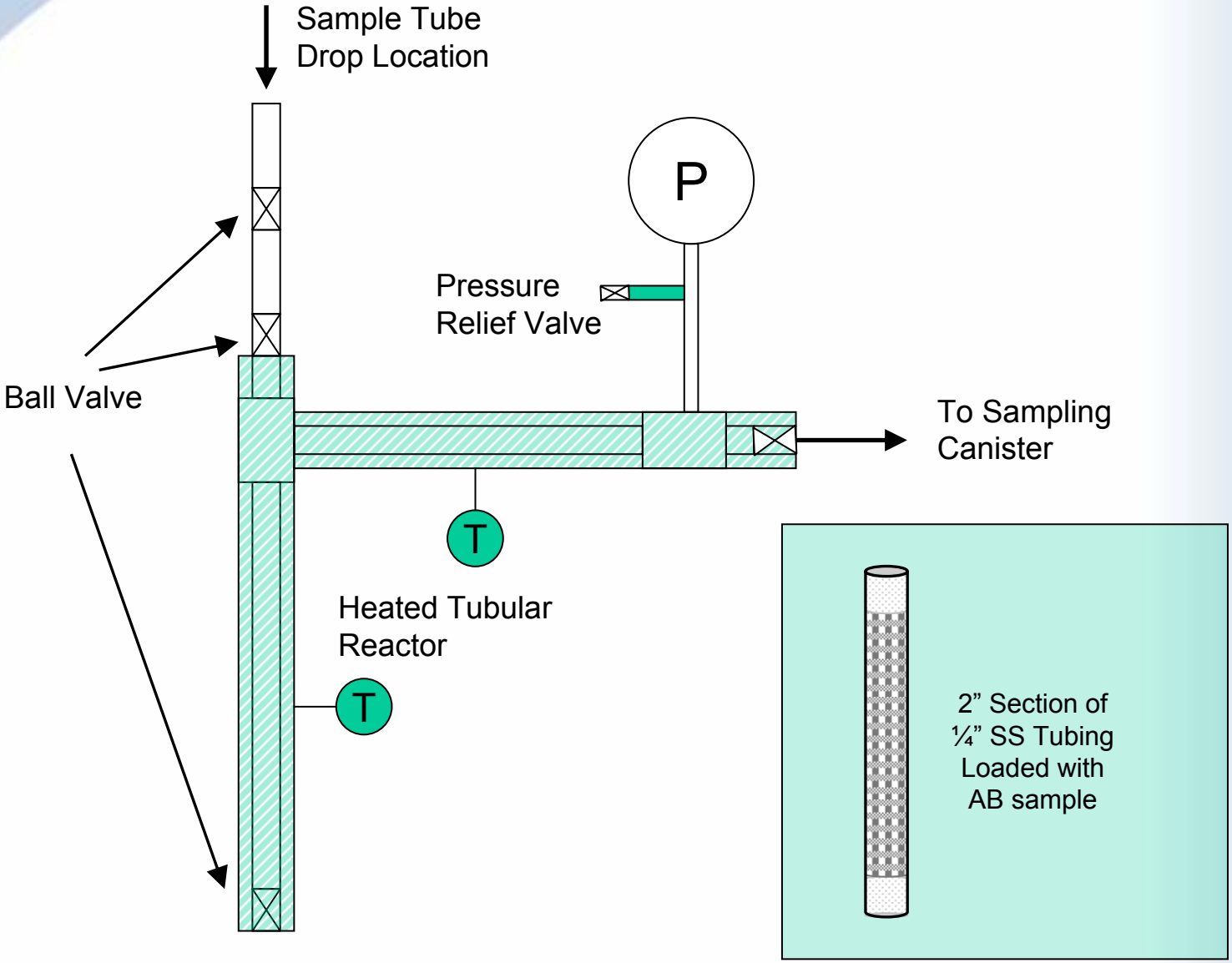
These results indicate that conventional fixed cartridge approach may not work well

Task 1 – Decomposition Reactor Studies (non-catalytic)

- Simulation of rapid heating of AB by dropping material in a pre-heated reactor.
- High temperature tubular reactor is used for quantitative determination of hydrogen released as a function of reactor temperature.
- Reactor temperature was varied from 100 to 500 ^{o}C and pressure rise was monitored with time to determine hydrogen release kinetics.
- The gas produced was analyzed for impurities (borazine and diborane) by GC/Mass Spectrometer

These experiments determined effect of rapid heating parameters on hydrogen release

Decomposition Reactor Schematic



High Temperature Reactor Test Results

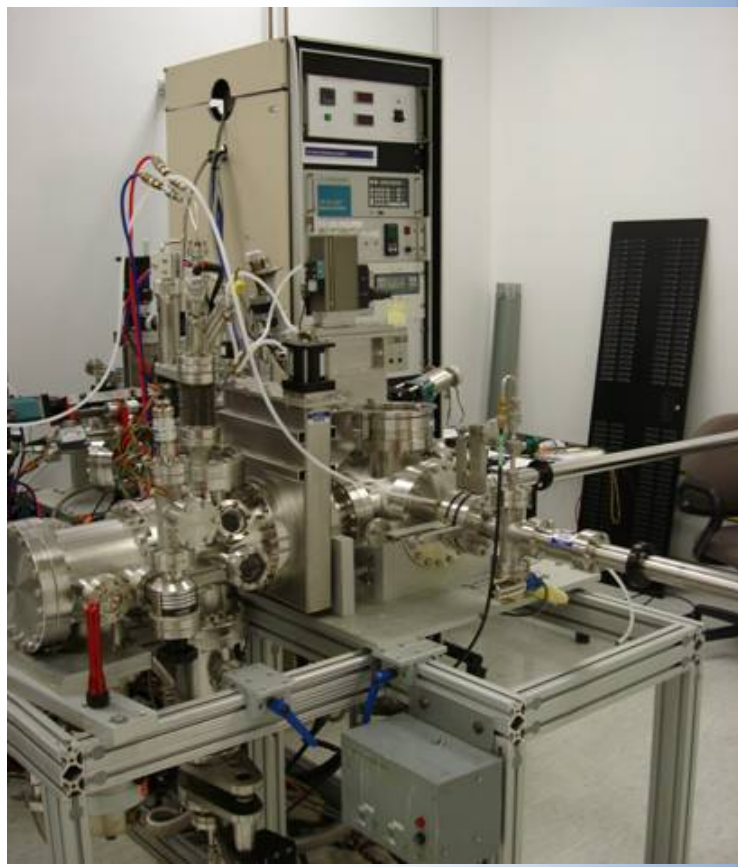
Decomp. Temp., °C	H_2 Released Moles/Mole AB	H_2 yield Wt % AB	Time for Release, s	Borazine Conc., ppm	Diborane Conc., ppm
100	1	6.5	~ 1200	1,110	0
125	1.7	11.2	400 - 500	15,200	320
150	2	13.1	100 - 200	11,800	390
200	2.1	13.7	40 - 60	11,800	300
225	2.1	13.7	35 - 40	14,300	0
300	2.2	14.3	30 - 35	11,100	0
400	2.2	14.3	20 - 25	12,100	0
500	2.5	16.3	15 - 20	7,200	0

Decomposition Reactor Results

- First mole of hydrogen released by 100 °C
- Second mole of hydrogen released by 150 °C
- Increasing temperature from 150 to 400 °C results in faster release of hydrogen but with very little increase in amount
- About 5/6 (~ 83%) hydrogen is released at 500 °C confirmed by residue analysis indicating ~ BNH elemental distribution
- Borazine is predominantly formed during second stage of hydrogen release
- Diborane is formed only during the second stage
- Diborane appears to be decomposed at 225 °C or greater T
- Borazine appears to be stable even at 500 °C
- Borazine readily hydrolyzes by bubbling through water

Catalyst Library Creation
Combinatorial Ion Beam Sputtering

- Intematix's proprietary combinatorial synthesis technology can efficiently generate hundreds of different pure and mixed metal catalyst compositions
- Multi-targets on source carousel & combined shutter/mask system enable creation of discrete or continuous libraries
- Built-in post-deposition annealing chamber turns sputtered thin film into catalyst nanoparticles
- Once the catalyst has been combined with AB or AB decomposition products Intematix's proprietary combinatorial high-throughput screening technologies enable rapid discovery and optimization of catalysts and catalyst compositions



Task 1 – Methodology development for AB dehydrogenation catalyst screening

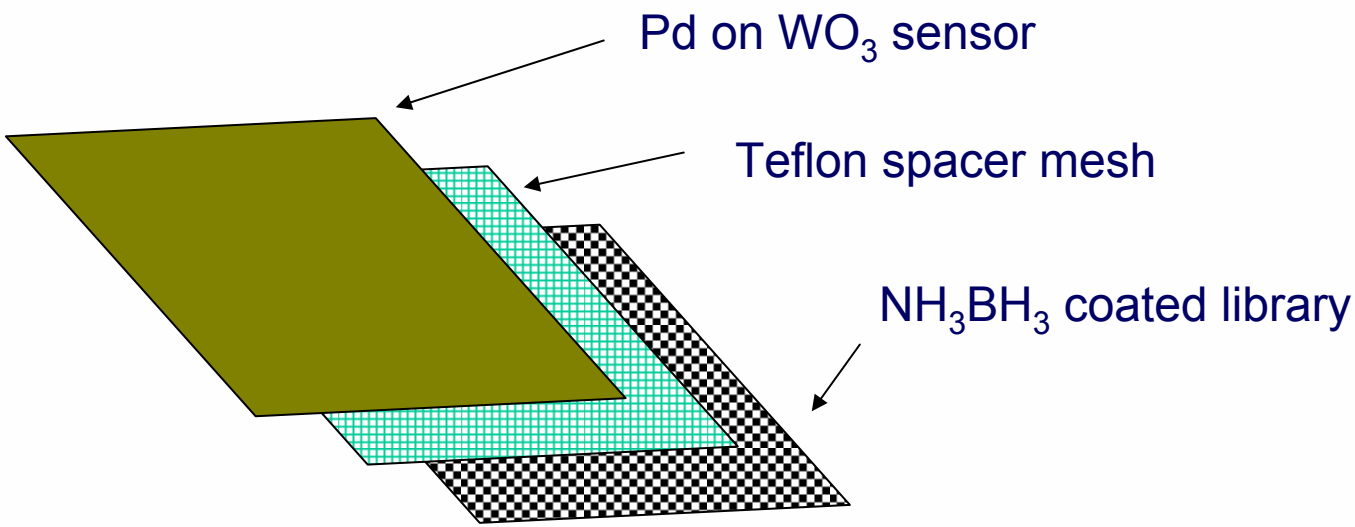
General Method

- Methanolic NH_3BH_3 coated (and MeOH evaporated) on library
- Sensed with Pd on WO_3 reflectivity based H_2 sensor
- Allows library screening of solid state materials

WO_3 system

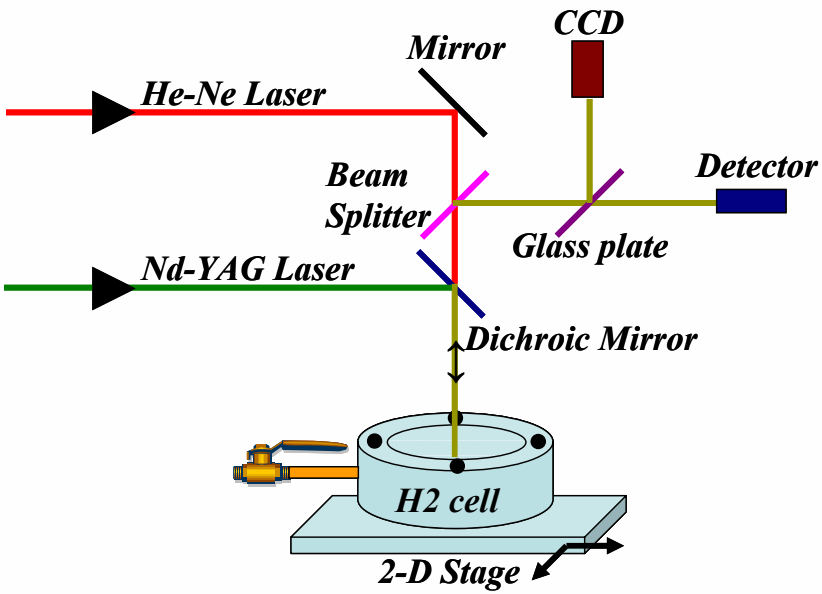
Pd

- $xH_2 + W^{VI}O_3 \rightarrow$ "$H_2W^{IV}O_3$"
- Changes from insulator to metallic behavior
- Monitored by reflectivity
- Semi-quantitative, up through point where all WO_3 is reduced

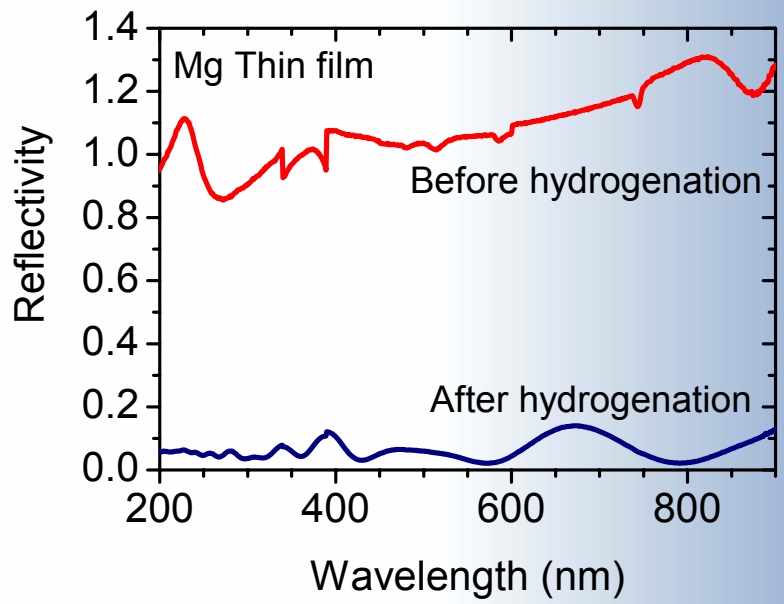


High Throughput Screening of Reflectivity

Reflectivity Measurements



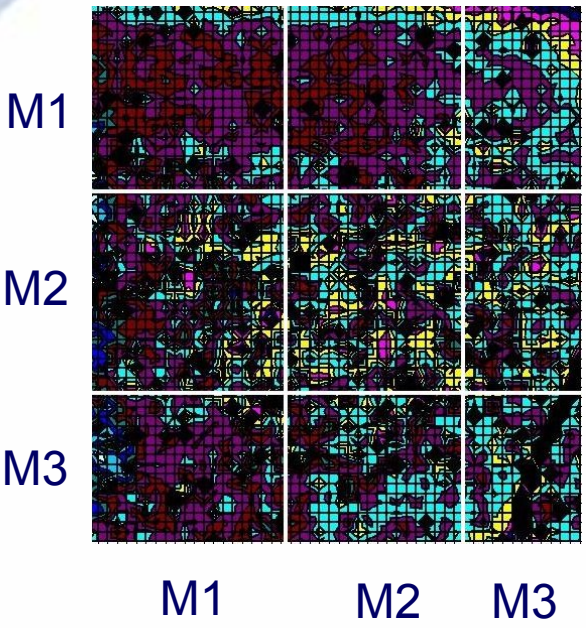
Validation on Mg film

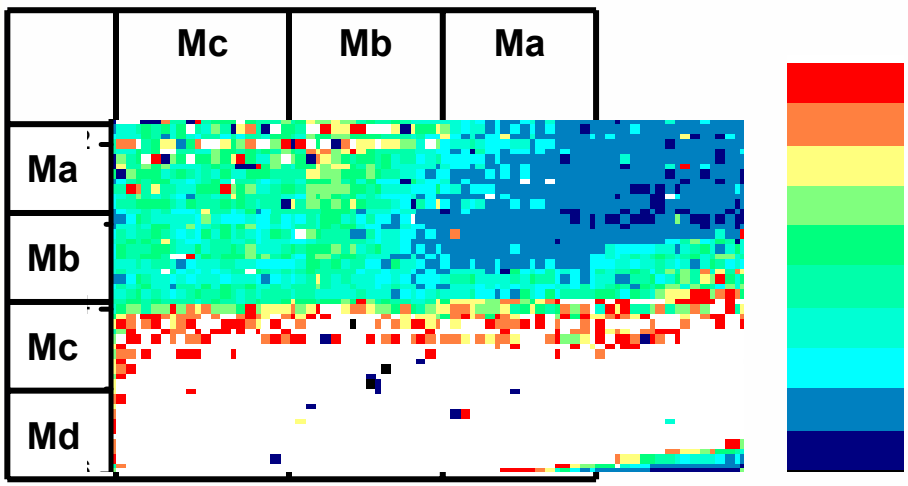


- Data can be spatially correlated via the x-y stage
- Change in reflectivity seen during hydrogenation
- For example, metallic mirror-like Mg film converts to MgH_2 layer
- Method limited to thin film samples – powders cannot be measured

This technique allows evaluation of several pure and mixed metal alloy catalysts simultaneously

Task 1 - Dehydrogenation Results



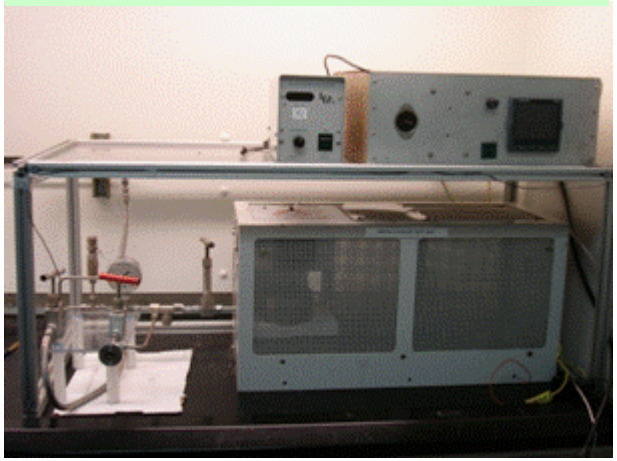


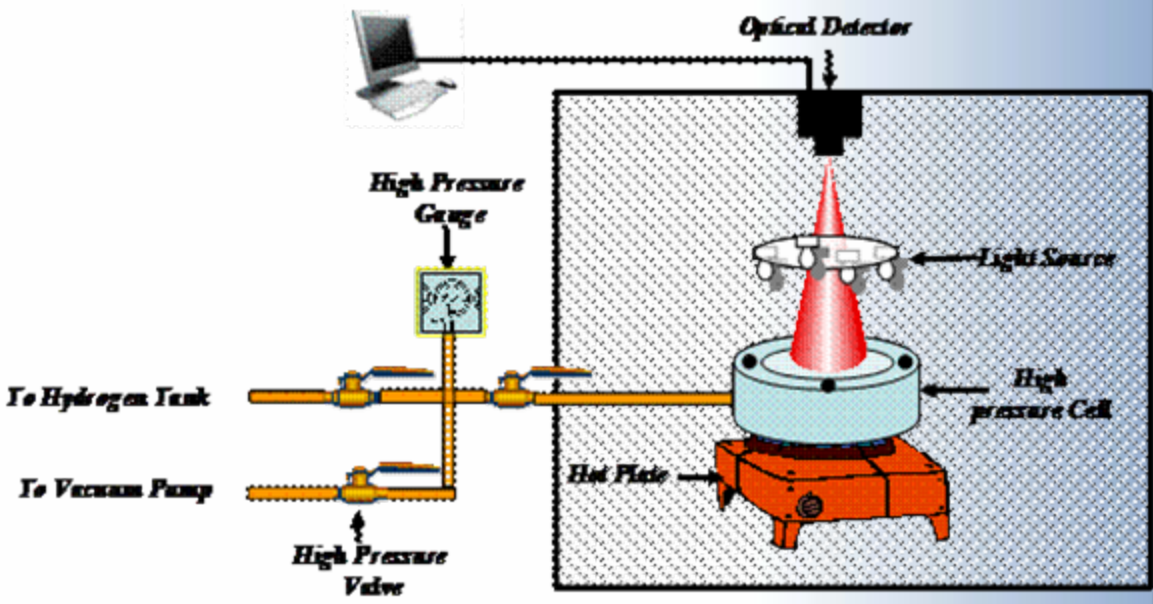
- Results for a segment of a library
- Library heated at 120°C for 20 minutes
- Differences between catalyst entries with same nominal composition (i.e. M1 x M2) may be explained by incomplete annealing at 500 °C (the limit of the in situ oven)
- Differences seen in the reflectivity between library entries, confirming the screening methodology
- Molten AB passed through mesh (capillary action) resulting in smudging seen on Mc, Md rows
- Teflon layer optimized
- Further screenings now necessary

Task 2 - Catalyst screening technique for regeneration of AB decomposition products

- Optical methods, showing changes in the RGB of a sample area, can be tied to changes in reflectivity, absorption and scattering (*Griessen, et al.*)
- Customized pressure cell with an optical window for color variation observation
- Materials color changes during H_2 charging/discharging is an indication of reaction occurrence

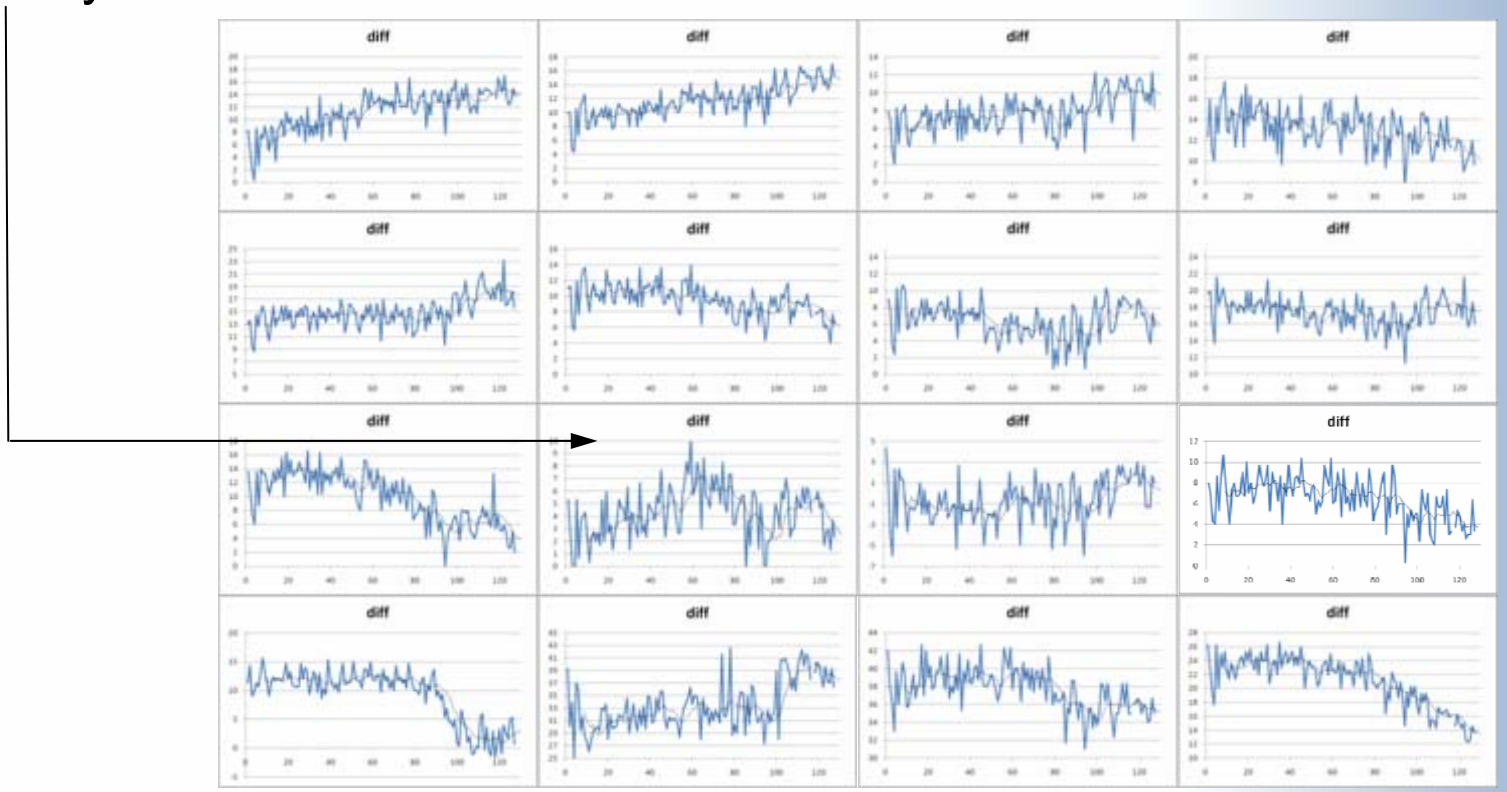
Reaction Cell Parameters:
Max. Pressure: 600 psi
Max. Temperature: 350 ºC





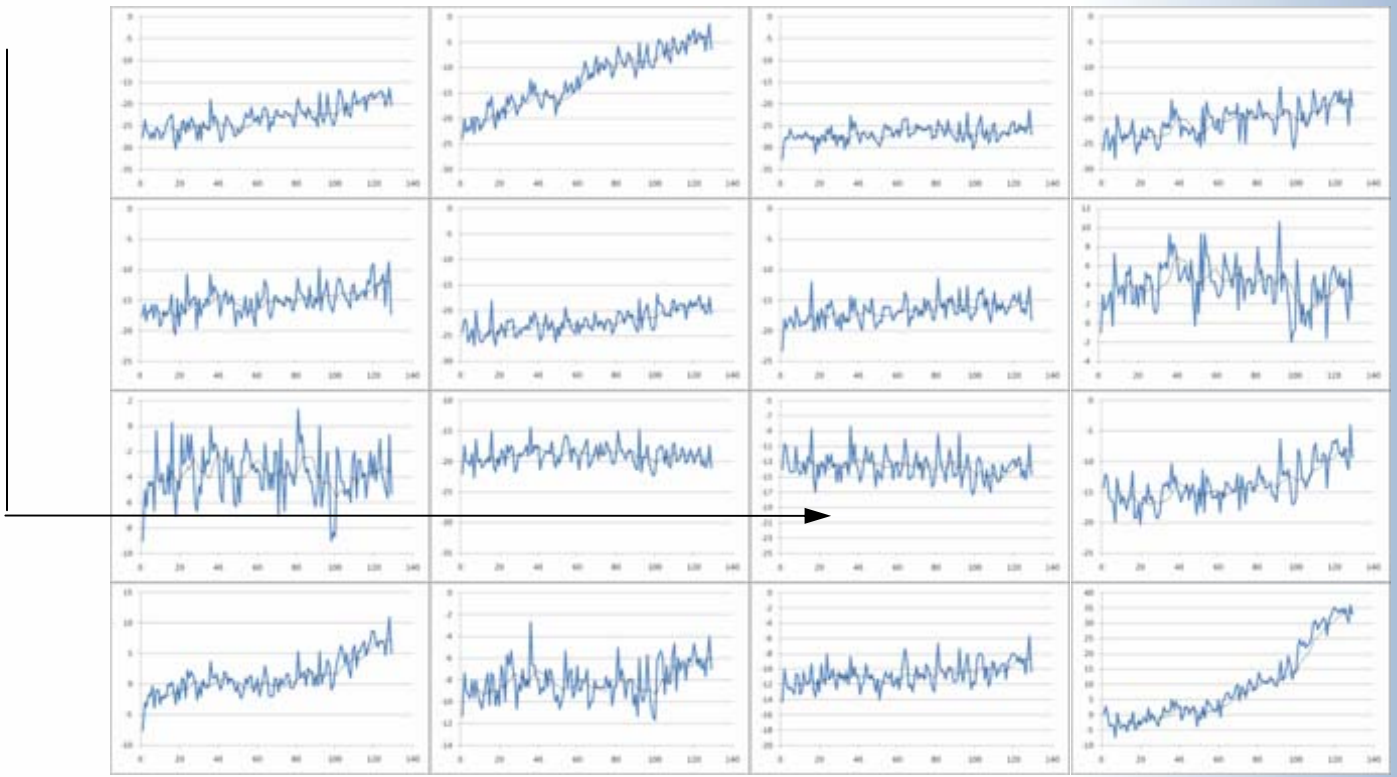
Task 2 - Regeneration results

- Difference between sample and blank signals indicates reactivity
- Mg row (bottom) and column (left) show skewed data due to formation of MgH_2
- Pure M4 and M4 containing catalysts show differences not directly tied to metal hydride formation



AB Dehydrogenation Results

- Bottom right corner is pure Mg, large difference due to MgH_2 formation as H_2 is released from NH_3BH_3
- Pure M4, shown by arrow, shows opposite behavior (slight darkening) as pure M4 in hydrogenation experiment



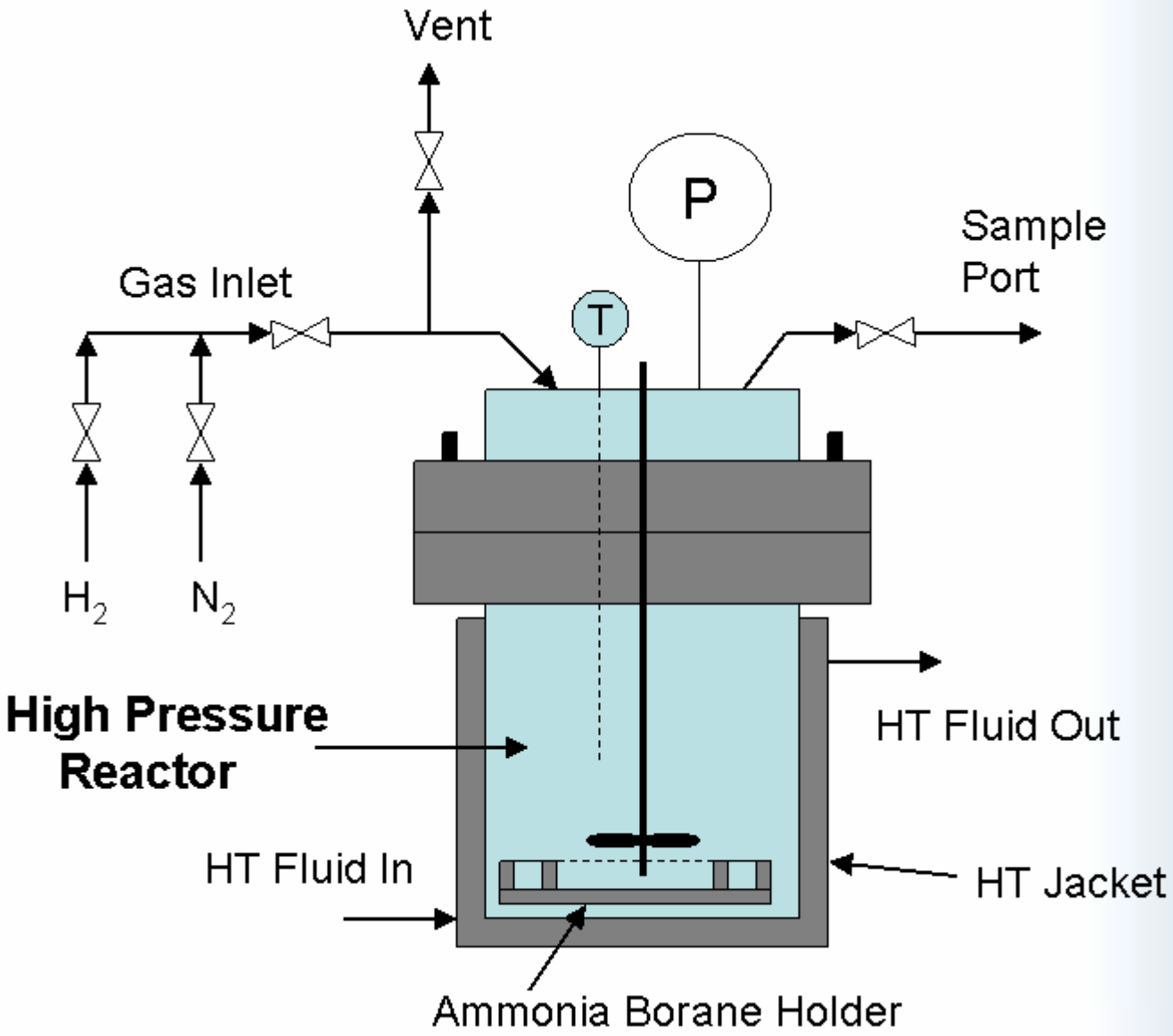
Results of Catalyst Screening

- Screened one set of catalysts for NH_3BH_3 hydrogen release by both direct and indirect methods
  - Will re-examine direct screening under conditions where thermal decomposition is a minor pathway (i.e. <90 °C or for shorter exposure times)
  - Used indirect screening to better understand results of recharge experiments
- Discovered 2 catalyst leads for hydrogen release
  - Require validation at Intematix before submitting to RTI for confirmation
- Screened one set of catalysts for recharge of "NH_2BH_2" (singly dehydrogenated NH_3BH_3)
- Discovered several catalyst leads for spent products regeneration
  - Some of these are confounded by catalyst reactivity with H_2
  - RTI is performing tests on one lead which does not show catalyst reactivity with H_2 (catalyst was in chloride form instead of metallic)

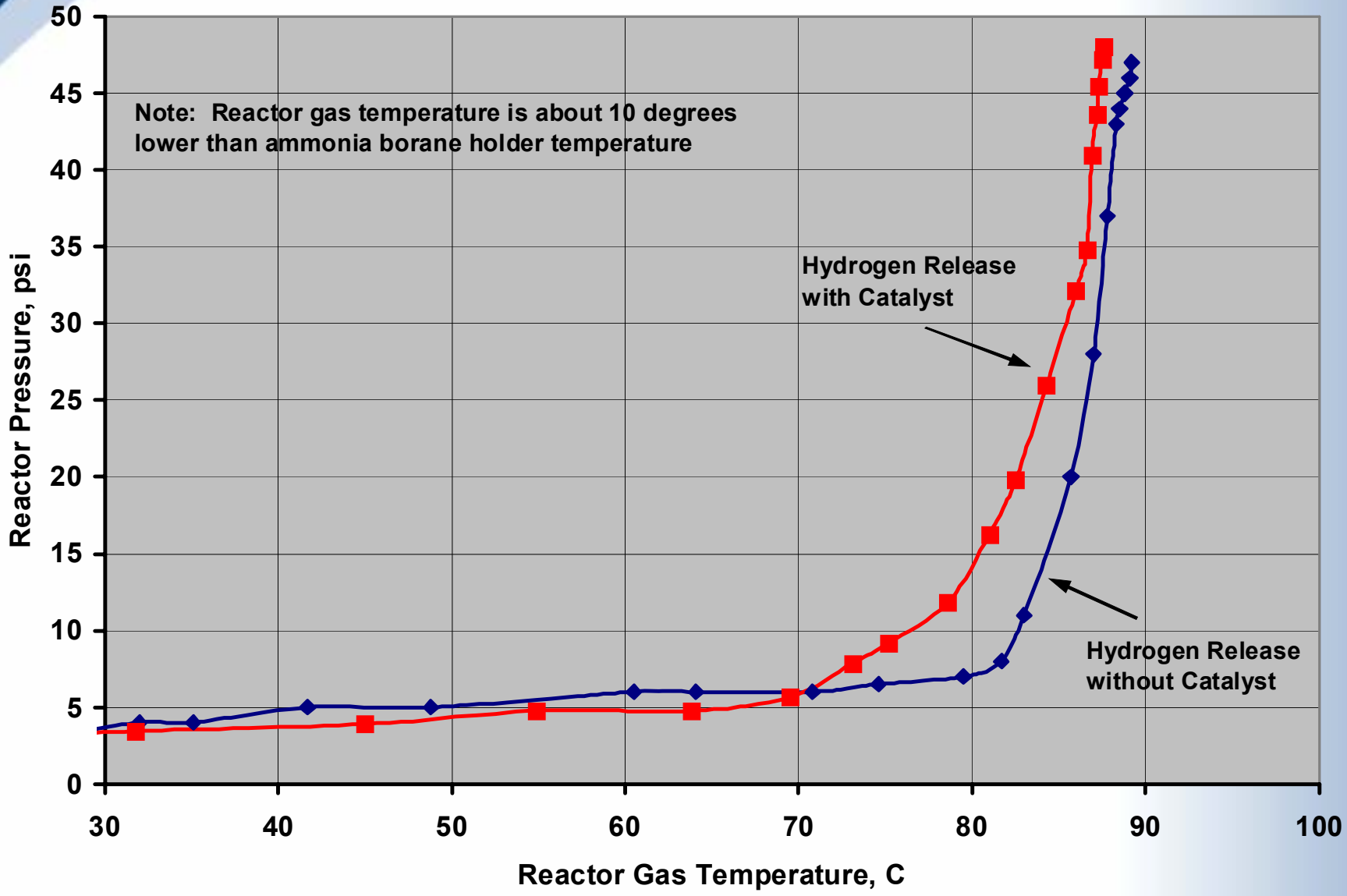
Catalytic Dehydrogenation/Regeneration Bulk Reactor Experiments

- Conducted evaluation of one catalyst composition (M4).
- Metal chloride catalyst dry-mixed with AB (5 % w/w metal).
- Catalytic dehydrogenation indicated hydrogen release at a lower temperature compared with non-catalytic process.
- Catalytic hydrogenation of decomposition residue (generated by releasing one mole H_2) was not successful with ~ 500 psig hydrogen pressure and up to 100 ^{o}C.
- Residue analysis indicated that metal chloride was not reduced to metal as hoped for in the dehydrogenation step.
- Dehydrogenation/Regeneration experiments are ongoing with pure M4 metal powder as catalyst as well as with several other leads identified by screening studies

High Pressure Hydrogenation Reactor



Catalytic Dehydrogenation of AB



Planned Activities

- Task 1 - Hydrogen Release –
  - Additional screenings for dehydrogenation catalysts
    - Optical method (photographic)
    - WO_3/Pd sensor (reflectivity) (more direct screening, as it screens H_2 released)
  - Conduct bulk reactor experiments to quantitatively evaluate effectiveness of selected catalysts for increasing hydrogen yield and/or lower decomposition temperature.

- Task 2 – Regeneration –
  - Additional screenings for hydrogenation catalysts
    - Confirm previous results
    - Generate new leads
    - Alter hydrogenation conditions
  - Conduct bulk reactor experiments to determine process conditions for catalytic regeneration (after releasing 1 and 2 moles of hydrogen.) Quantitatively determine regeneration yield and energy efficiency as well as kinetics for regeneration.

Project Summary

- **Relevance –** Develop a hydrogen storage system to meet DOE's 2010 hydrogen density and cost targets.
- **Approach -** Thermal/catalytic decomposition of ammonia-borane to produce hydrogen on-board efficiently. Catalytic regeneration of AB decomposition products using only H_2 pressure and temperature.
- **Technical Accomplishment –**
  - Characterized non-catalytic hydrogen release from AB for hydrogen yield, impurities, heat released, and release kinetics for AB decomposition at 100–500 ^{o}C. Demonstrated hydrogen yield of up to 16.3 wt% AB. Determined parameters for on-board system design.
  - Established methodology and techniques for combinatorial screening of catalyst activity for dehydrogenation of AB and hydrogenation of decomposition products. Identified catalyst leads for dehydrogenation of AB as well as regeneration of AB decomposition products
  - Bulk catalytic dehydrogenation/regeneration reactor experiments for evaluation of promising catalysts have just begun.
- **Future Activities –** Demonstrate catalytic regeneration of AB decomposition products meeting Phase I goals of > 70% yield and >60% efficiency.

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