Hydrogen Storage by Reversible Hydrogenation of Liquid-phase Hydrogen Carriers

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ST-9

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Overview

Timeline

- 2/04 – 2/08
- 60% complete

Budget

- Total project $6,121,242
  - DOE share $4,346,082 (71%)
- FY05 funding $812,000
- FY05 funding $1,000,000

Barriers

- Technical Barriers- Hydrogen Storage
  - A. Cost
  - B. Weight and Volume:
  - 6.0 wt. % and 45 g H_2/L (2010)
  - C. Efficiency
  - E. Refueling time
  - R. Regeneration Processes

Interactions

- Current interactions: Auto OEM's, Academic researchers
- Anticipated interactions: Chemical hydrides COE, Catalyst companies

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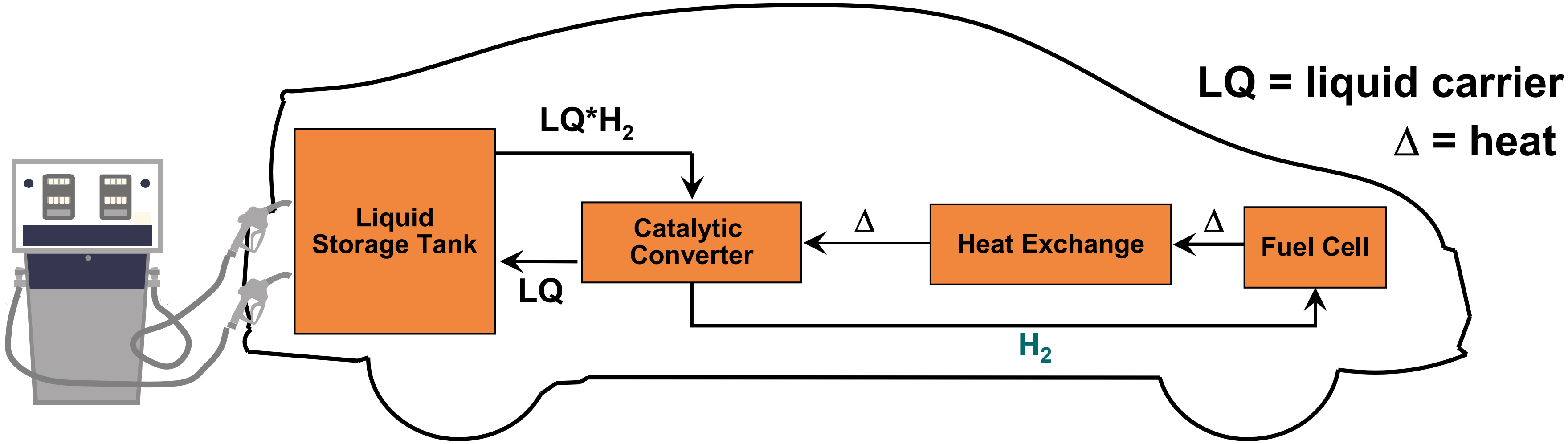
Objectives

- Development of liquid-phase hydrogen storage materials with capacities of >7 wt. % and >60 g H_2/L and associated dehydrogenation and hydrogenation catalysts. Scale up of liquid carriers for further evaluation.
  - Selective, highly reversible catalytic hydrogenation and dehydrogenation, enabling multiple cycles of use with no significant degradation of the molecule - barriers A, R (cost, regeneration processes)
  - Optimal heat of dehydrogenation (10-13 kcal/mole H_2), enabling the catalytic dehydrogenation at unprecedented temperatures (<200 °C) – barriers B, C (weight/volume, efficiency)
  - Low volatility (b.p. > 300 °C), enabling the use of these liquids in simplified systems onboard vehicles and reducing exposure to vapors – barrier E (refueling time)
  - Acceptable cost for the liquid carrier and the hydrogenation process – barriers A, R (cost, regeneration processes)

Approach: An off-board regenerable liquid carrier for vehicles and stationary H_2 gas delivery



- Conformable shape liquid tank with design to separate liquids; 18.9 gallons for 5 kg hydrogen at 7 wt. % and unit density
- Heat exchange reduces the vehicles' radiator load by *ca.* 40% (for ΔH of 12 kcal/mol H_2 and 50% FC efficiency)

$$LQ^*H_2 + \text{heat}\ (\Delta H) \underset{\text{P > 50 atm., Catalyst}}{\overset{\text{Catalyst, P < 10 atm.}}{\rightleftharpoons}} LQ + H_2$$

Maximum energy efficiency: by (a) recovering the exothermic ($-\Delta H$) of hydrogenation and (b) utilizing the waste heat from the power source to supply the ΔH for the endothermic dehydrogenation.

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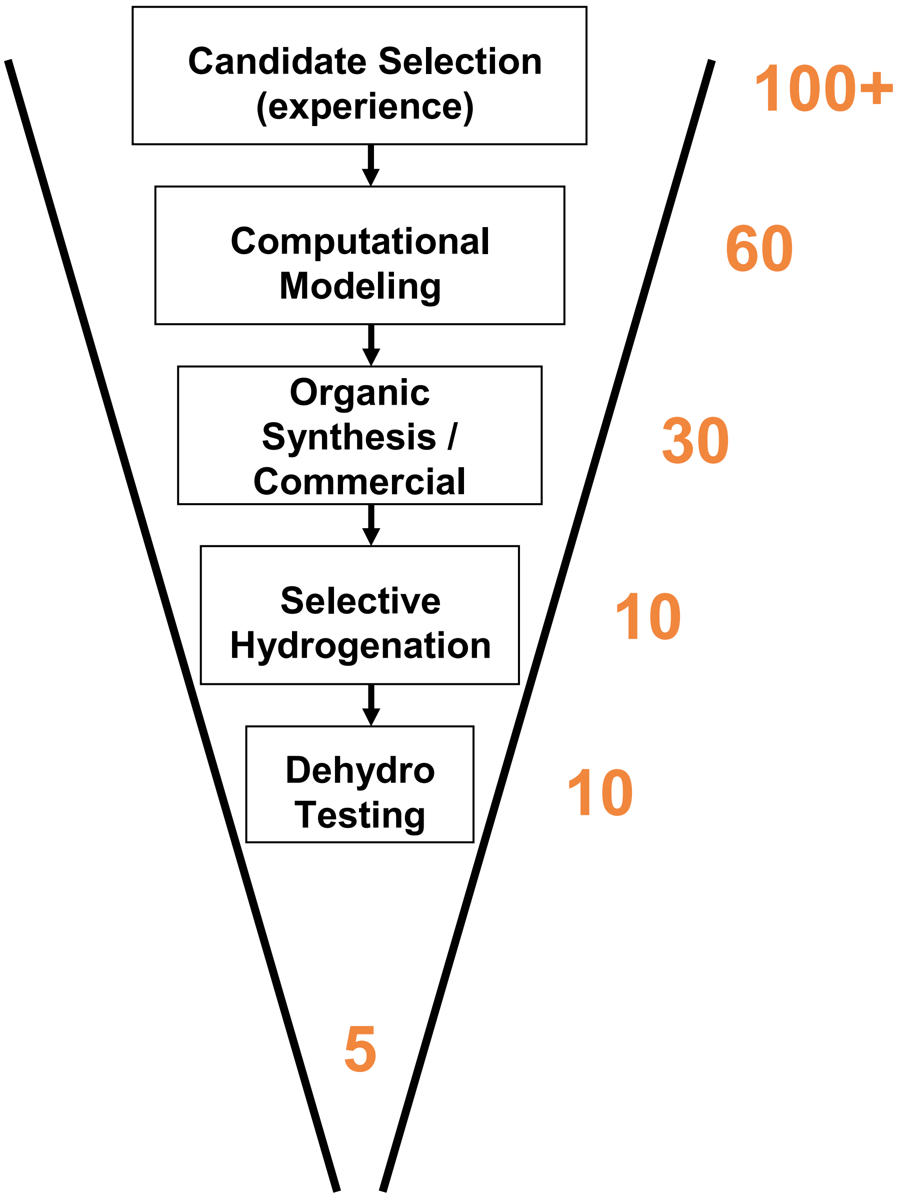
Experimental Discovery Approach



- Carrier Selection
  - Rational selection based upon experience
- Computational Modeling
  - Must use proper models
- Organic Synthesis
  - High purity compounds
- Selective Hydrogenation
  - 99+% selective!
  - Many different types of molecules
  - Some at low temperatures
- Dehydrogenation Testing
  - Large variation in rates between catalysts
  - Must also be 99+% selective

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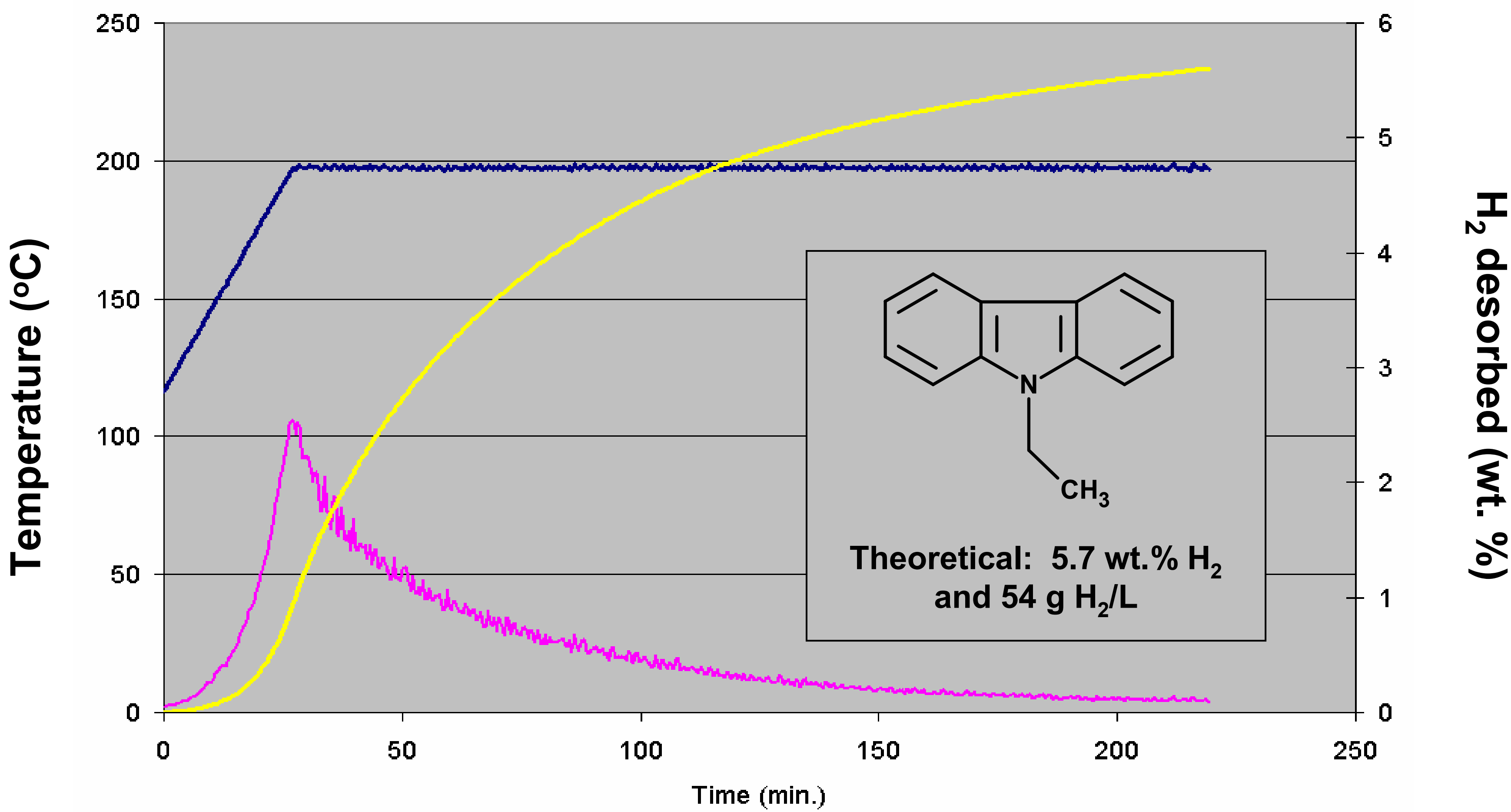
Prior Year Results: Hydrogen Generation from N-ethylcarbazole



GC/MS analysis after run termination showed evolution of 5.7 wt. % H_2

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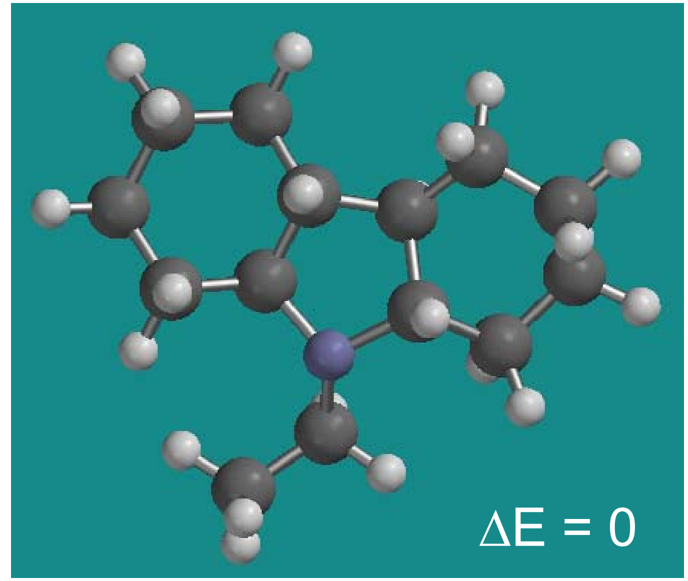
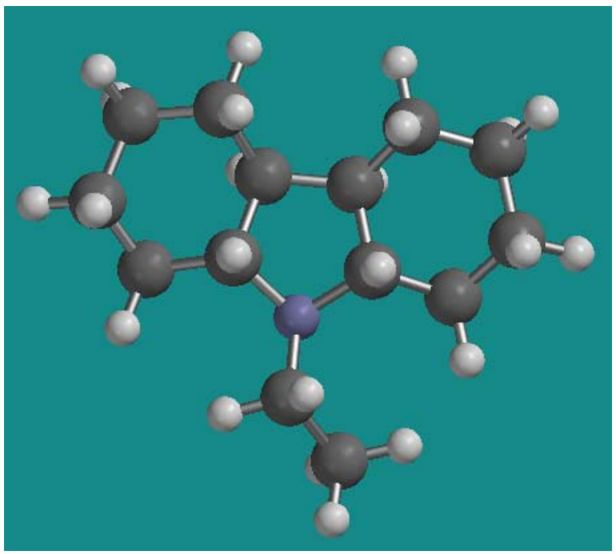
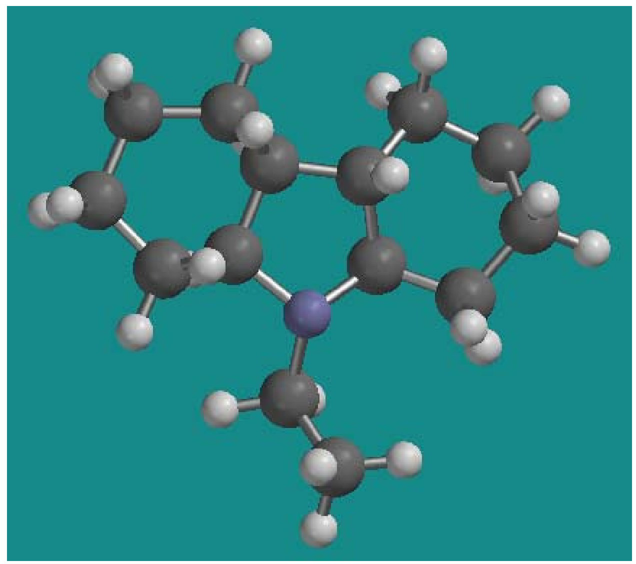
Perhydro-N-ethylcarbazole Conformers

At B3LYP/G-311G** level

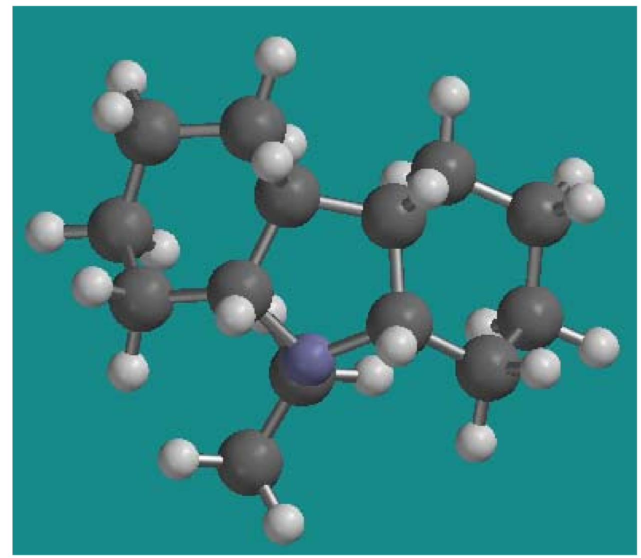




ΔE = 2.6 kcal/mol



ΔE = 8.6 kcal/mol



ΔE = 14.5 kcal/mol

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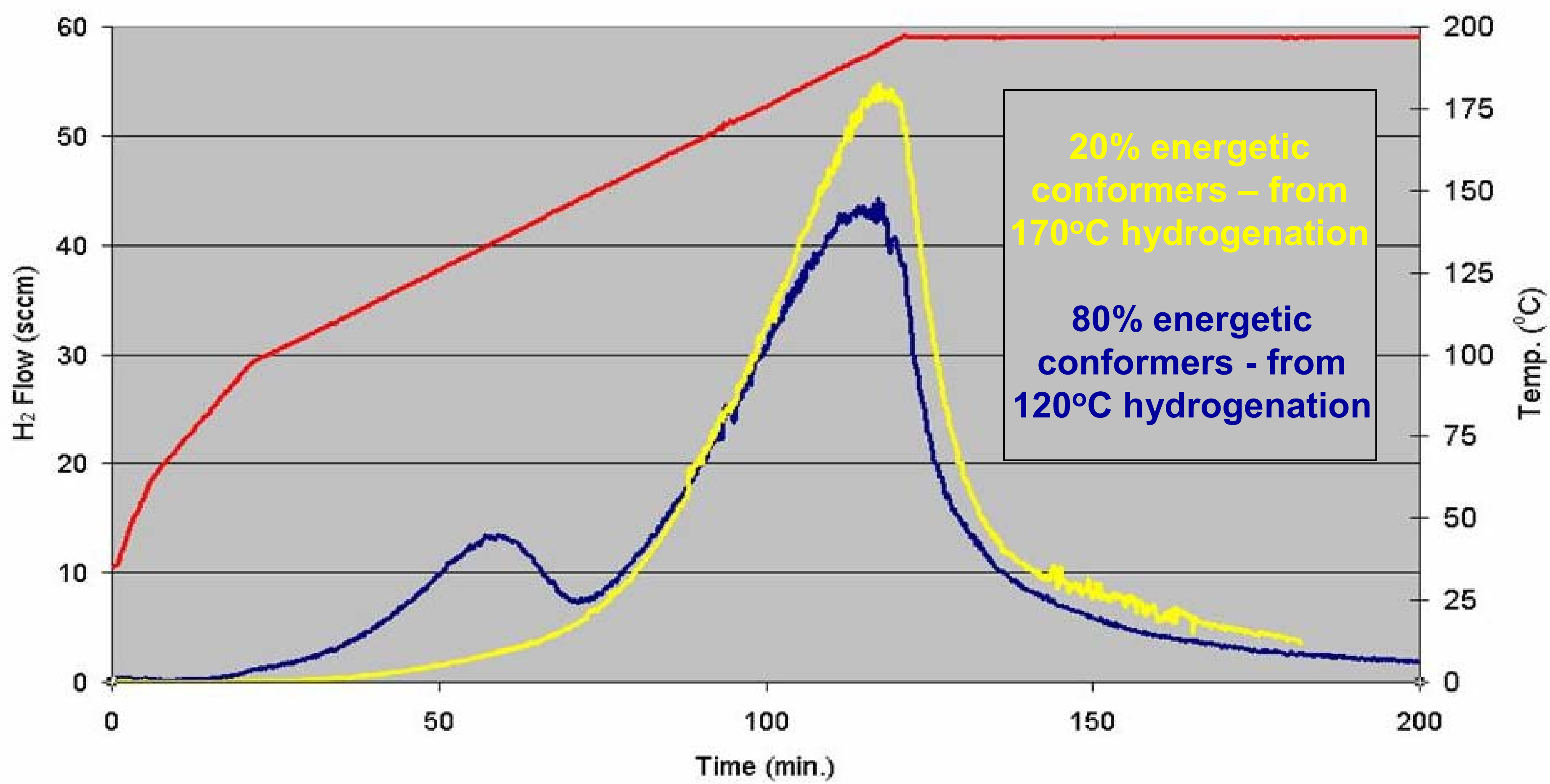
New Results: N-ethylcarbazole Kinetic versus Thermodynamic Conformers



Hydrogen release at 100-125 °C from energetic conformers. Selective formation of energetic conformers could improve the thermodynamics of almost all types of carriers

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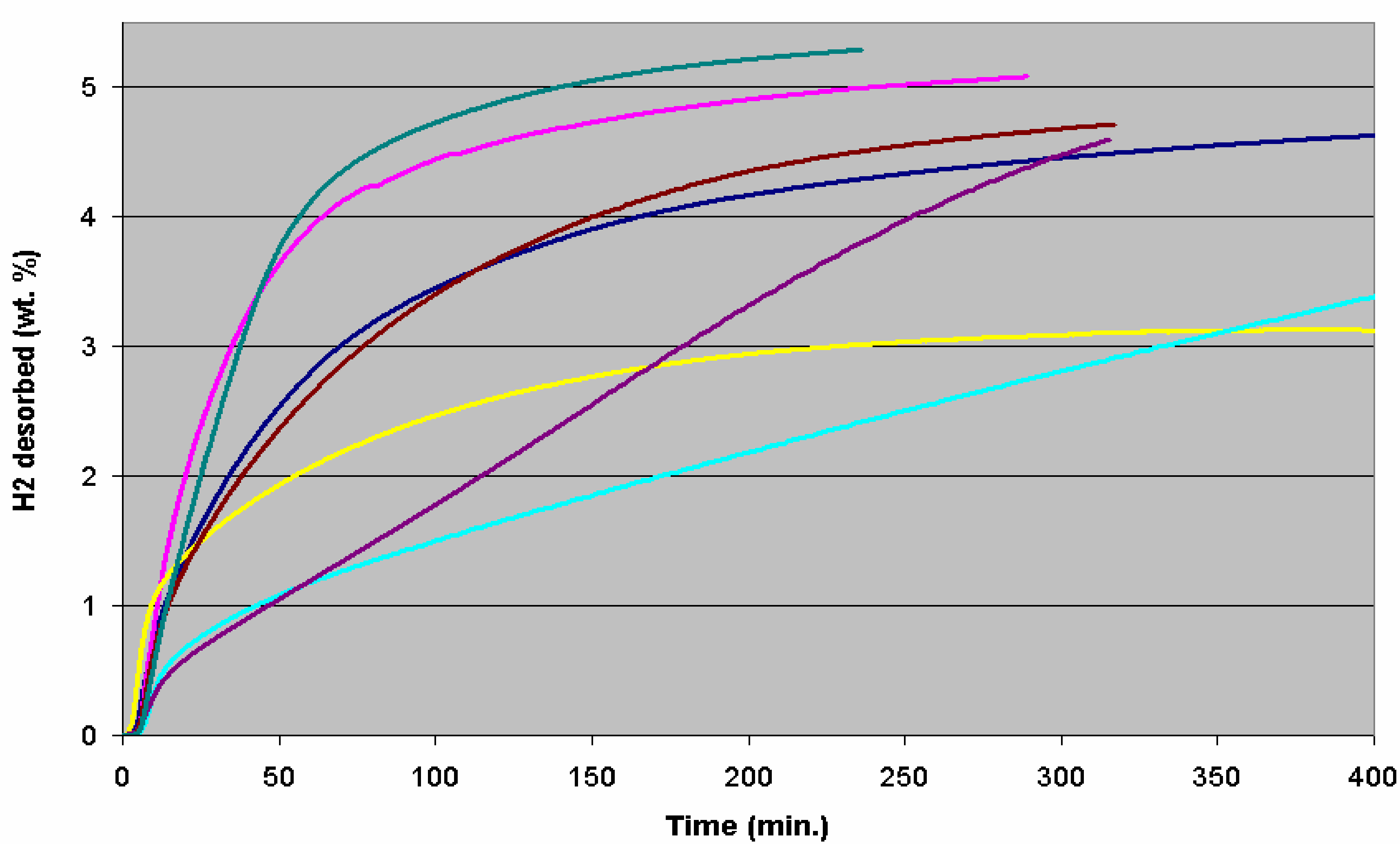
New results: Dehydrogenation Catalyst Screening



Dehydrogenation catalyst discovery – we have designed and tested >100 catalysts in the past year

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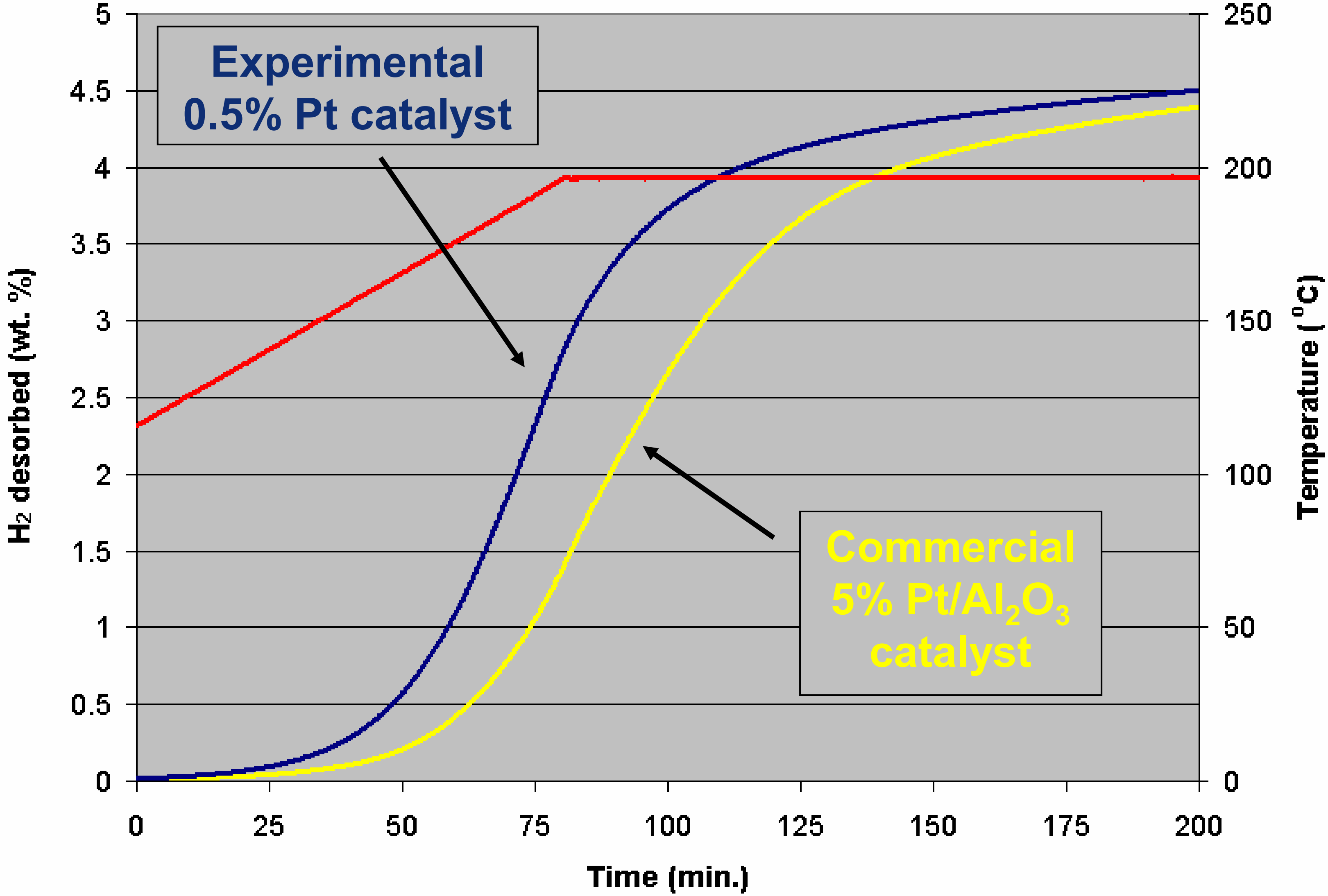
New results: Development of highly active dehydrogenation catalysts



Higher activity than commercial catalyst using 10X less active metal

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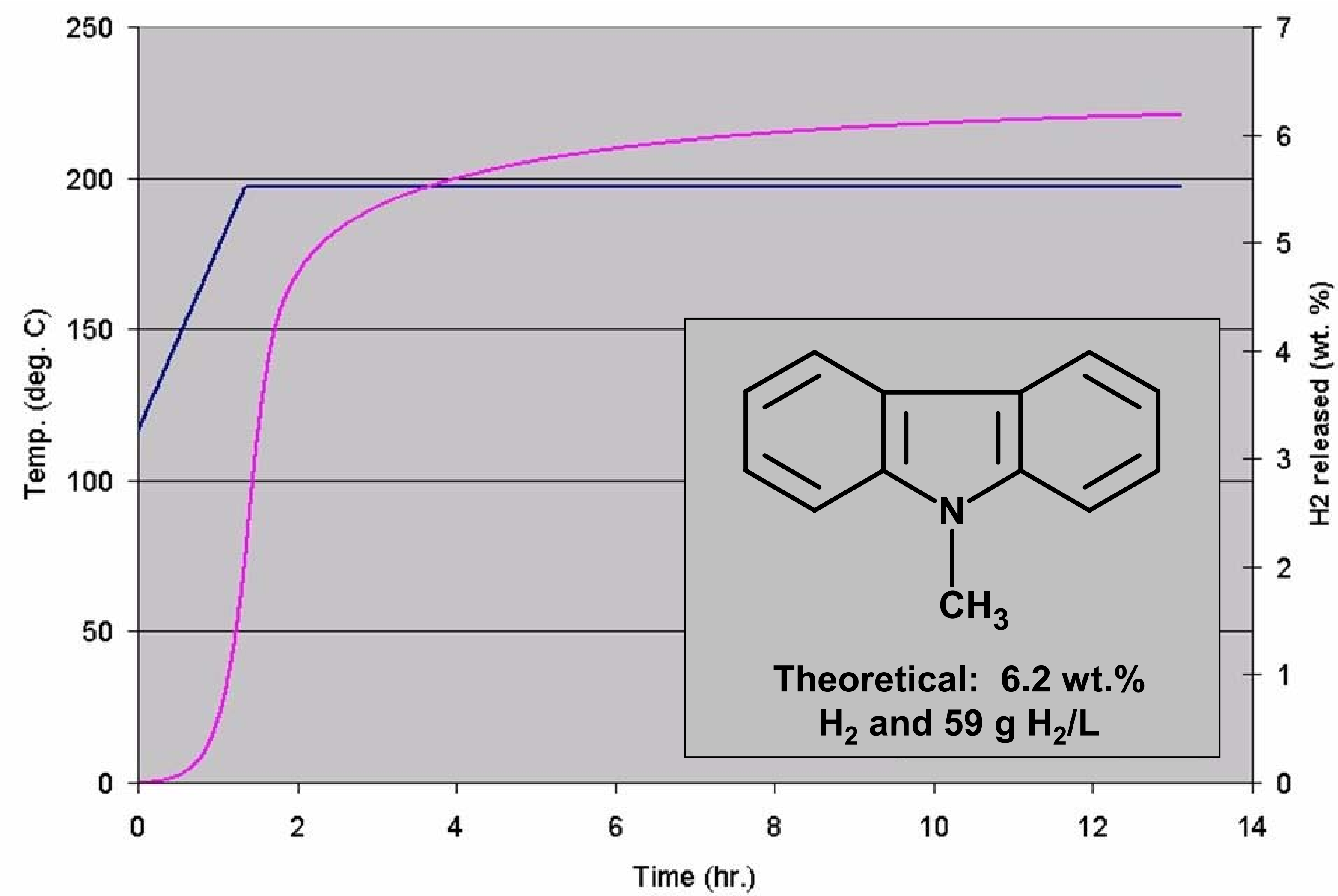
New results: N-methylcarbazole dehydrogenation



An incremental improvement – but additional H_2 density improvements needed to meet goals

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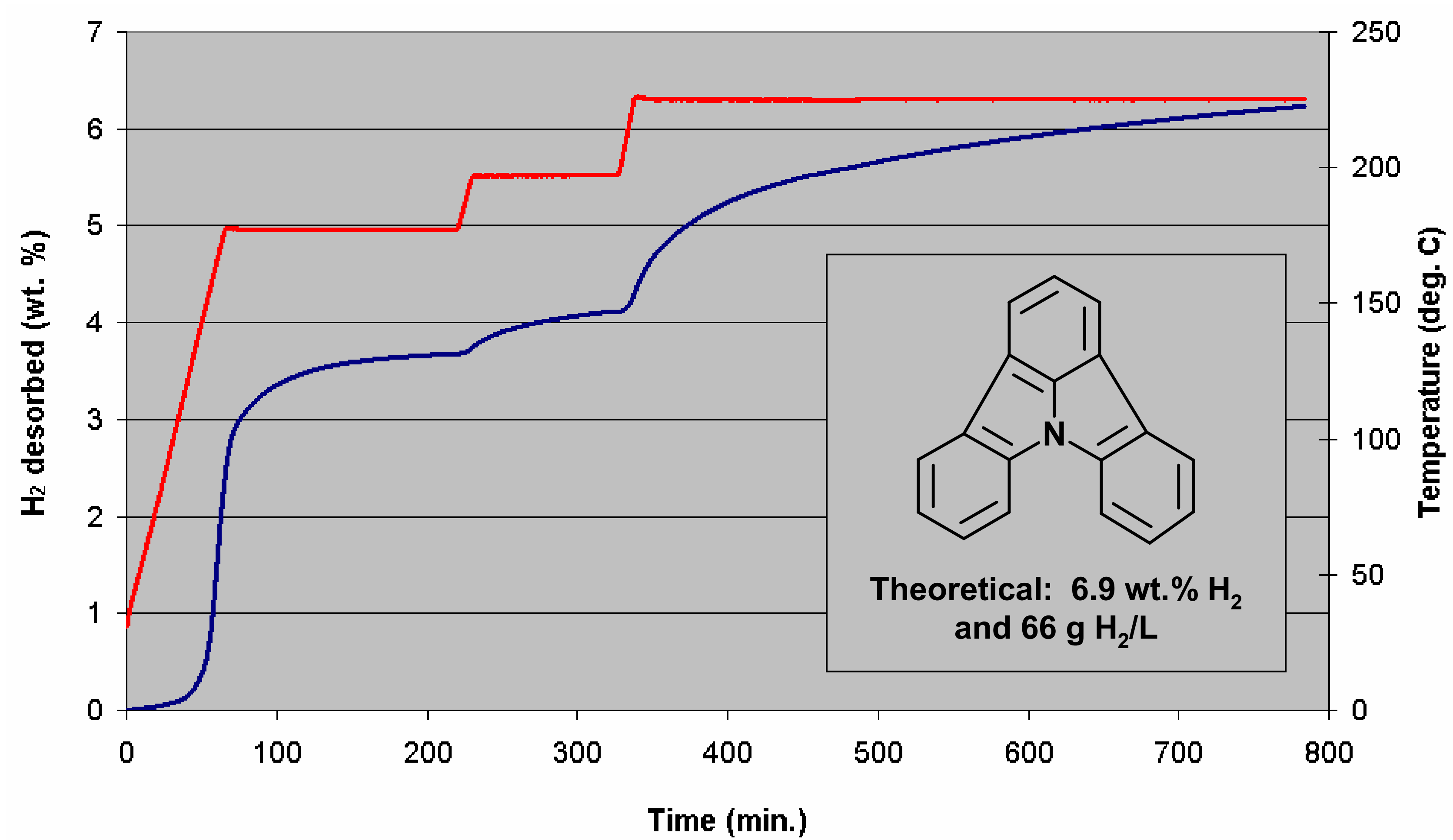
New carrier: Phenylenecarbazole



GC/MS analysis after run termination showed evolution of 6.2 % wt H_2

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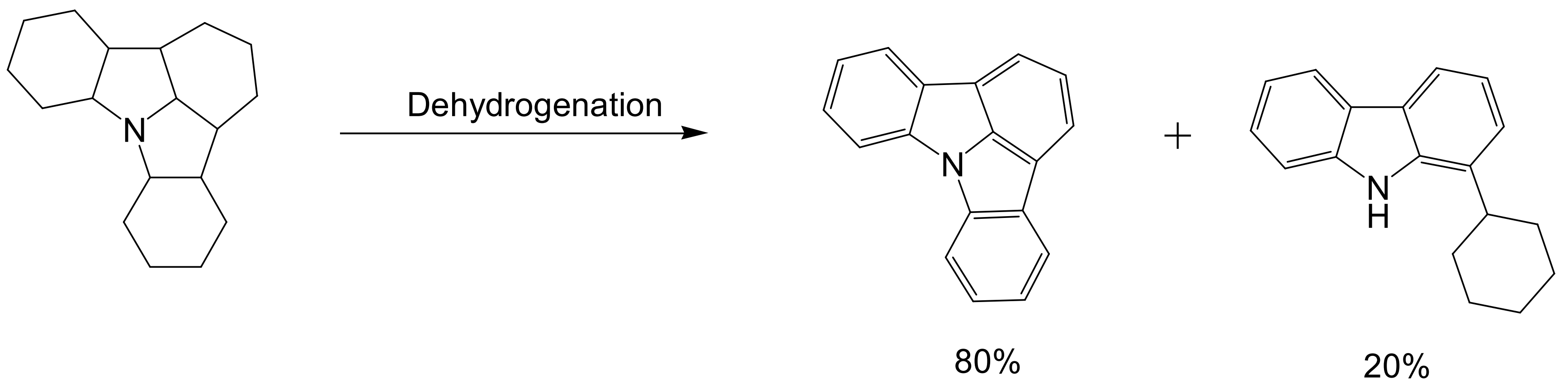
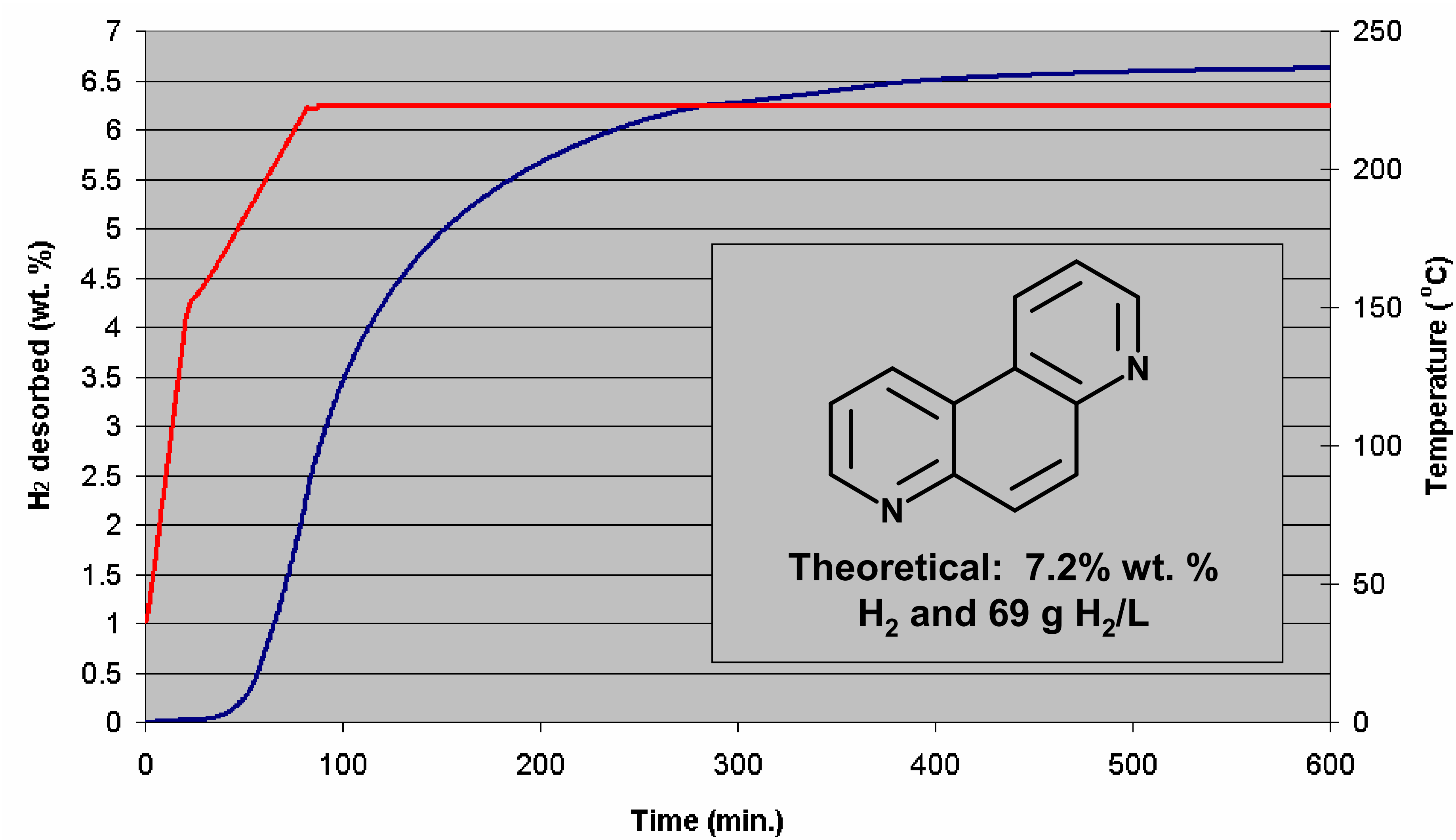
Experimental challenge: Hydrogenolysis of Phenylenecarbazole



High selectivity on hydrogenation

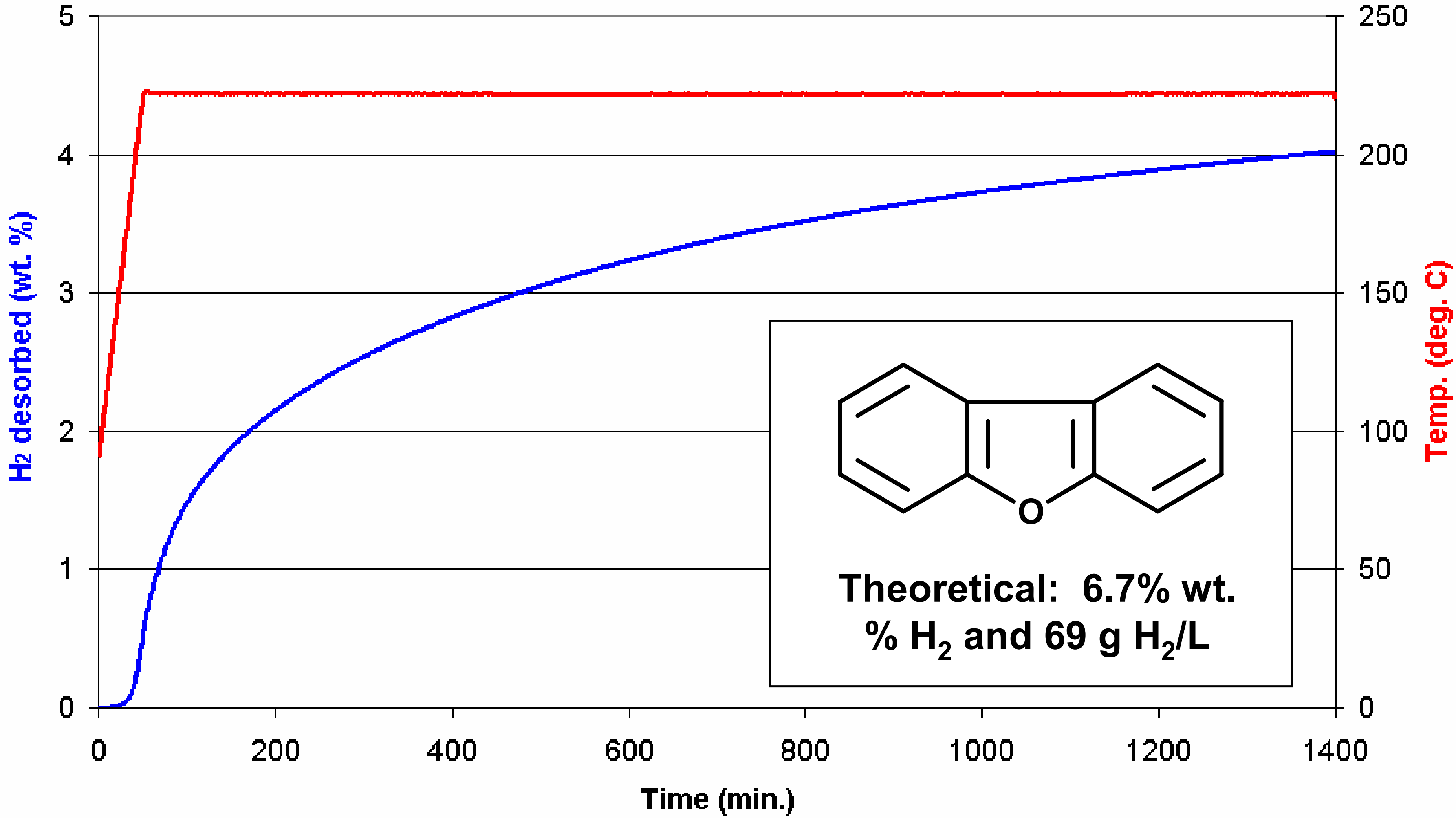
However, presence of secondary amine from ring opening during dehydrogenation confirmed by alkylation and by GC/MS

New results: Phenanthrolene Dehydrogenation



We have demonstrated a 7+ wt. % reversible capacity with this new carrier – a 1.5 wt. % increase over N-ethylcarbazole

New results: Oxygen-containing Carrier



A member of a new class of hydrogen carriers containing only oxygen heteroatoms

Future Work

- Keep focus on fundamentals
- New carrier discovery
  - Focus on carriers with 7+ wt % capacity
    - Investigate carriers with higher unsaturation (>1 H per atom) for >7.2 wt. % theoretical capacity
  - Maintain focus on correct thermodynamics for low temperature dehydrogenation
- New dehydrogenation catalysts
  - combinatorial approach?
- Selection of carriers for lifetime testing and scale-up

Responses to Previous Year Reviewers' Comments

- "Not a great deal of collaboration..."
  - We have a research project with Moscow State University on catalysis. We will be partnering with Pacific Northwest National Laboratory, United Technologies Research Corporation, and Penn State University under a closely related DOE H_2 delivery project.
- "What are prospects for low temperature desorption?"
  - We continue to use computational modeling to identify potential carriers with low heats of hydrogenation. In addition, the fundamental studies on energetic conformers has revealed a mechanism for substantial decease in the dehydrogenation temperature of many potential carriers.
- "...cycling stability demonstrated only over 3 cycles"
  - We have performed additional cycling experiments that have shown stability of both carrier and dehydrogenation catalyst over 6 cycles (see back-up slides). We also performed accelerated lifetime testing by holding liquid carrier for 400 hours at simulated dehydrogenation reactor conditions where multiple fully- and partially-dehydrogenated intermediates were present.

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Summary

- **Relevance: Development of practical hydrogen storage technology with desirable capacity, safety characteristics, efficiency and integration with hydrogen production/delivery**
- **Approach: Reversible, selective hydrogenation of organic liquid carriers**
- **Technical accomplishments: Development of highly active dehydrogenation catalysts, increase of gravimetric and volumetric capacity**
- **Future work: Investigate higher capacity carriers, lower dehydrogenation temperatures**

On-Board Hydrogen Storage System Targets (**Theoretical capacity is based on material only, not system value)				
Storage Parameter	Units	2010 System Target	FY05 materials**	FY06 materials**
Specific Energy	**wt. % H_2**	**6 wt.%**	**5.7 wt.%**	**7.2 wt.%**
Volumetric Energy Capacity	**g H_2/L**	**45**	**54**	**69**
Desorption Temperature	**^{o}C**		**180-200 ^{o}C**	**200-225 ^{o}C**

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Back-up Slides

Acknowledgements

- Aaron Scott
- Don Fowler
- Atteye Abdourazak
- Fred Wilhelm
- Bernard Toseland
- Gian Muraro
- Vyril Monk

Publications and Presentations

- "Hydrogen Storage and Delivery by Reversible Hydrogenation of Liquid-phase Hydrogen Carriers", International Partnership for a Hydrogen Economy Hydrogen Storage Workshop, 6/05, Invited Presentation
- "Integrated Hydrogen Storage and Delivery using Organic Liquid Carriers", Materials Science and Technology Conference, 9/05, Invited Presentation
- "Hydrogen Storage and Delivery in a Liquid Carrier Infrastructure", Materials Research Society Spring Meeting, 4/06, Invited Presentation

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Critical Assumptions and Issues

- In order to utilize fuel cell waste heat for liquid carrier dehydrogenation, dehydrogenation must occur at an acceptable rate at a temperature below the fuel cell waste heat temperature. Carriers at the low end of the 10-13 kcal/mol heat of hydrogenation range and dehydrogenation catalysts that are active at below the fuel cell waste heat temperature must be discovered.
  - Energetic conformers can yield substantial decreases in dehydrogenation temperature. We have identified new, highly active dehydrogenation catalysts.
  - Increase in PEM fuel cell operating temperatures could assist.
- Carriers with higher unsaturation (>1 H per atom) that have >7.2 wt. % theoretical capacity can be identified.
  - We are using our predictive computational capability to identify potential carriers for experimental testing.
- Effective dehydrogenation reactors that can utilize successful carriers and dehydrogenation catalysts from this hydrogen storage program will be engineered.
  - We are awaiting DOE funding to begin the associated H2 delivery project. One aspect of this project is the engineering of novel dehydrogenation reactors that are designed to accommodate carriers and dehydrogenation catalysts from this hydrogen storage program.

Packed Bed Dehydrogenation Cycling Experiments