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Hydrogen Storage and Delivery in a Liquid Carrier Infrastructure

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Air Products' Hydrogen Experience

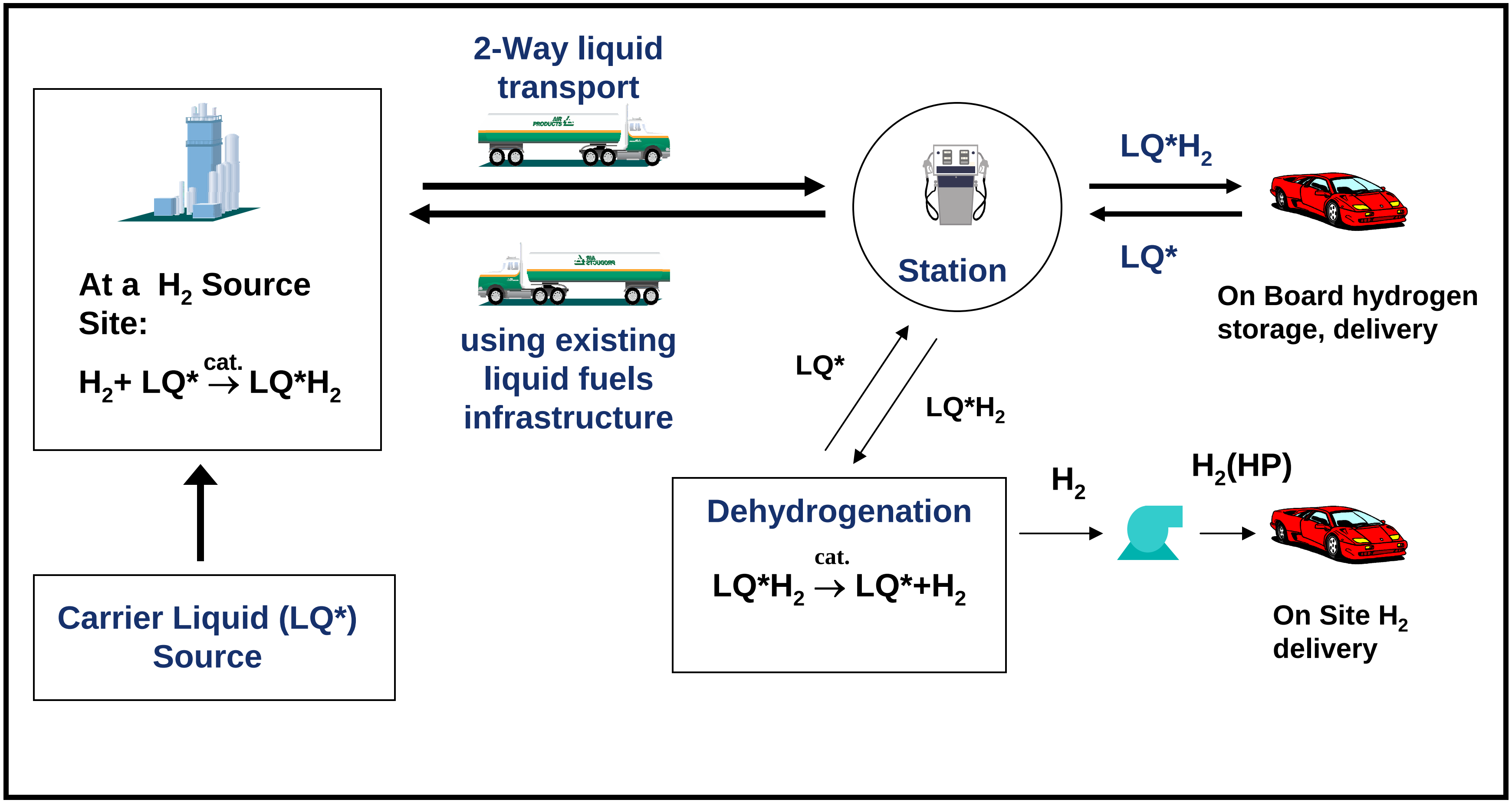
- **World leader in industrial hydrogen supply**
  - **Own, operate, and distribute hydrogen – Americas, Europe, Asia**
  - **Operate over 60 plants, 7 pipelines, produce over 1.25 million tons/year**
- **Demonstration leader in hydrogen fueling infrastructure**
  - **30 fueling stations - Americas, Europe, Asia**
  - **Technology advances include mobile fueling, underground liquid storage, dispensing, onsite generation, storage**
  - **Global safety leader**

Hydrogen Storage Methods

- Physical methods
  - compression (350, 700 bar)
  - liquid hydrogen (20 K)
- Physical adsorption (H-H bond remains intact)
  - adsorption on high surface area materials
    - activated carbon, carbon nanotubes, zeolites
- Chemisorption (H-H bond broken)
  - metal hydrides ($LaNi_5$, FeTi)
  - advanced hydrides ($NaAlH_4$)
  - “chemical hydrides” - hydrolysis ($NaBH_4$), benzene $+3H_2 \rightleftarrows$ cyclohexane

Hydrogen storage is one of the key technical barriers to the use of hydrogen as an energy carrier

An Integrated Production, Storage and Delivery of Hydrogen – Using Reversible Liquid Carriers (LQ^*H_2)



At a H_2 Source Site:

$$H_2 + LQ^* \xrightarrow{cat.} LQ^*H_2$$

Carrier Liquid (LQ^*) Source

2-Way liquid transport

using existing liquid fuels infrastructure

Station

On Board hydrogen storage, delivery

Dehydrogenation

$$LQ^*H_2 \xrightarrow{cat.} LQ^* + H_2$$

On Site H_2 delivery

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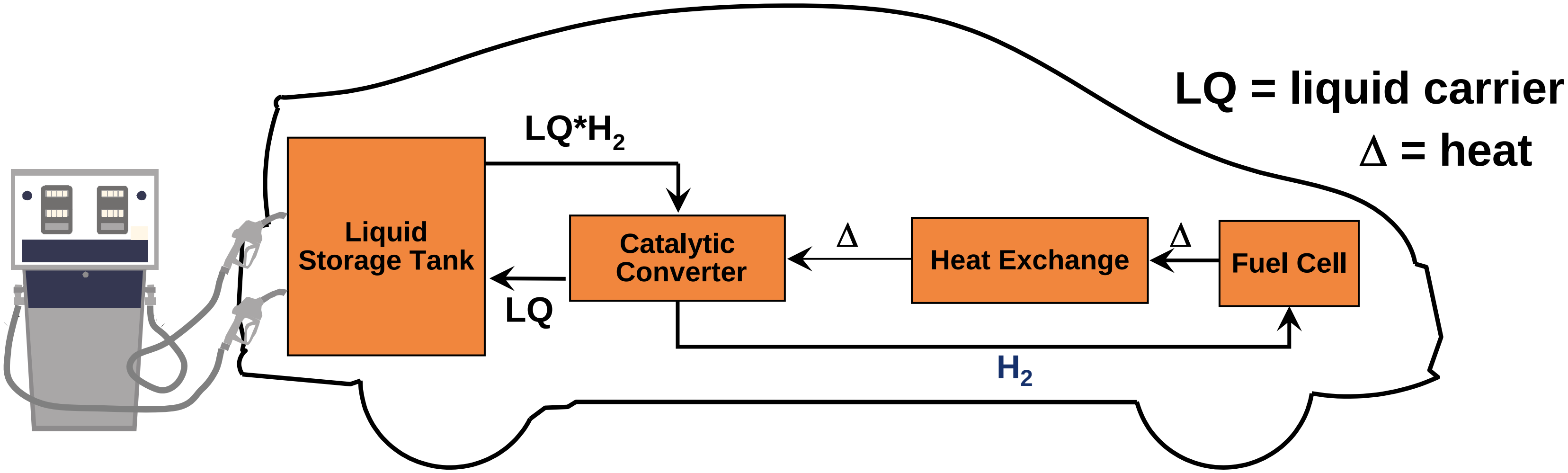
Approach:

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



LQ = liquid carrier

Δ = heat

Liquid Storage Tank

$LQ*H_2$

Catalytic Converter

LQ

Δ

Heat Exchange

Δ

Fuel Cell

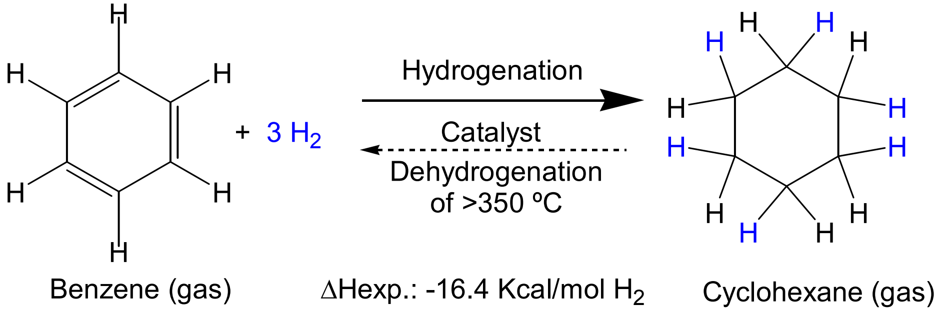
H_2

- Conformable shape liquid tank with design to separate liquids; 22.5 gallons for 5 kg hydrogen at 6 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)

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

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

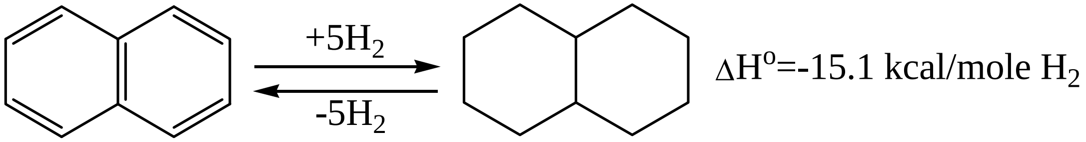
Partial List of Organic “Liquid Carrier” Performance Criteria



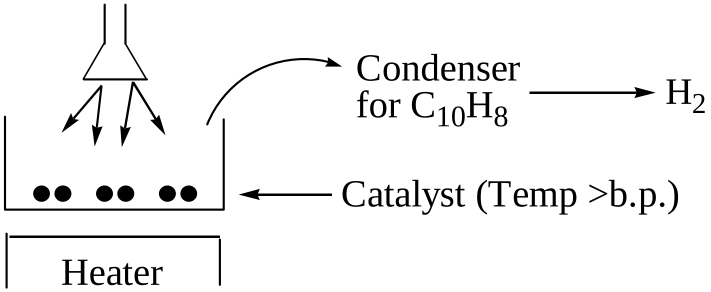
- Optimal heat of dehydrogenation ($\Delta H = 10\text{-}13$ kcal/mole H_2), enabling the catalytic dehydrogenation <u>in an all-liquid state</u> at temperatures (<200 ºC) for utilizing the FC’s or ICE’s waste heat.
- Meet DOE’s hydrogen on board storage and delivery targets
- Low volatility (b.p. > 300 ºC), enabling the dehydrogenation in small compact reactor systems onboard vehicles and reducing exposure to vapors
- Low toxicity and environmental impact
- Clean catalytic hydrogenation and dehydrogenation, enabling multiple cycles of use with no significant degradation of the molecule
- Manufacture of the liquid carriers from low cost, source raw materials.

Prior Art on Organic Liquid Carriers

Hydrogen and energy storage [1] by a reversible catalytic hydrogenation of naphthalene $C_{10}H_8$ to decalin $C_{10}H_{18}$ (a “liquid organic hydride”[2])



High conversion of $C_{10}H_{18}$ in membrane reactor at ~320°C[2]
Efficient H_2 evolution from $C_{10}H_{18}$ from 195°C to 400°C under “wet-dry multiphase”[3] or “superheated liquid film” conditions[4-5].
(Both are two-phase liquid/vapor processes.)



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3. N. Kariya, M. Ichikawa *et al*, Appl. Cat A, 233, (2002), 91-102
5. *S. Hodoshima and Y. Saito,* Int. J. Hy Energy, 28, (2003), 197-204
2. R. O. Loufty *et al*, Proc. Of Int. H_2 Energy Forum, (2000) 335-340
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Fundamental Energetics for Containing Hydrogen

For H_2 (gas) + carrier $\xrightleftharpoons{K}$ H_2 (contained) equilibrium:

$$\Delta G = \Delta H - T\,\Delta S = RT\ln K$$

For containing hydrogen in a spontaneous prcess:

a) For carrier bound, but intact molecular H_2 (physisorption)

$(-\Delta H) <\sim 8$ kcal mole H_2 $(-\Delta S) <\sim 25$ e.u.

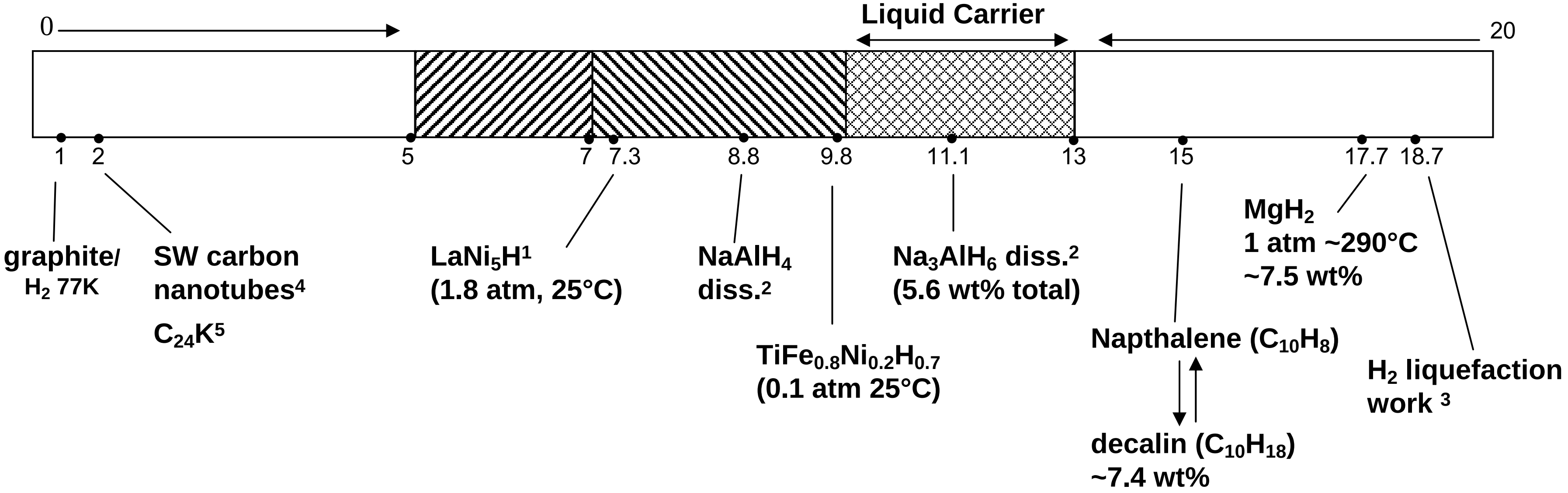
b) For carrier bound dissociated H2 (chemisorption)

$(-\Delta H) >\sim 8$ kcal/mole H_2 $(-\Delta S) \sim 25\text{-}30$ e.u.

and ~30 e.u. for H_2 +aromatics → alkanes

The greater variable contribution to ΔG is from ΔH

Observed and Desirable H_2-Containment Enthalpies (-ΔH, kcal/mole H_2)



graphite/ H_2 77K

SW carbon nanotubes[4]

$C_{24}K$[5]

$LaNi_5H$[1] (1.8 atm, 25°C)

$NaAlH_4$ diss.[2]

$TiFe_{0.8}Ni_{0.2}H_{0.7}$ (0.1 atm 25°C)

Na_3AlH_6 diss.[2] (5.6 wt% total)

MgH_2
1 atm ~290°C
~7.5 wt%

Napthalene ($C_{10}H_8$)

$\downarrow\uparrow$

decalin ($C_{10}H_{18}$)
~7.4 wt%

H_2 liquefaction work [3]

Desired (-ΔH) ranges : 5-7 kcal/mole H_2-Strong Physisorption
: 7-13 kcal/mole H_2 – Weak to Moderate Chemisorption
: 10-13 kcal/mole H_2 – optimal for liquid carrier

Note: Lower Heating Value for H_2(LHV) = 57 kcal/mole

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3. W. Peschka, "Liquid Hydrogen Fuel of the Future" Springer-Verlag p. 65
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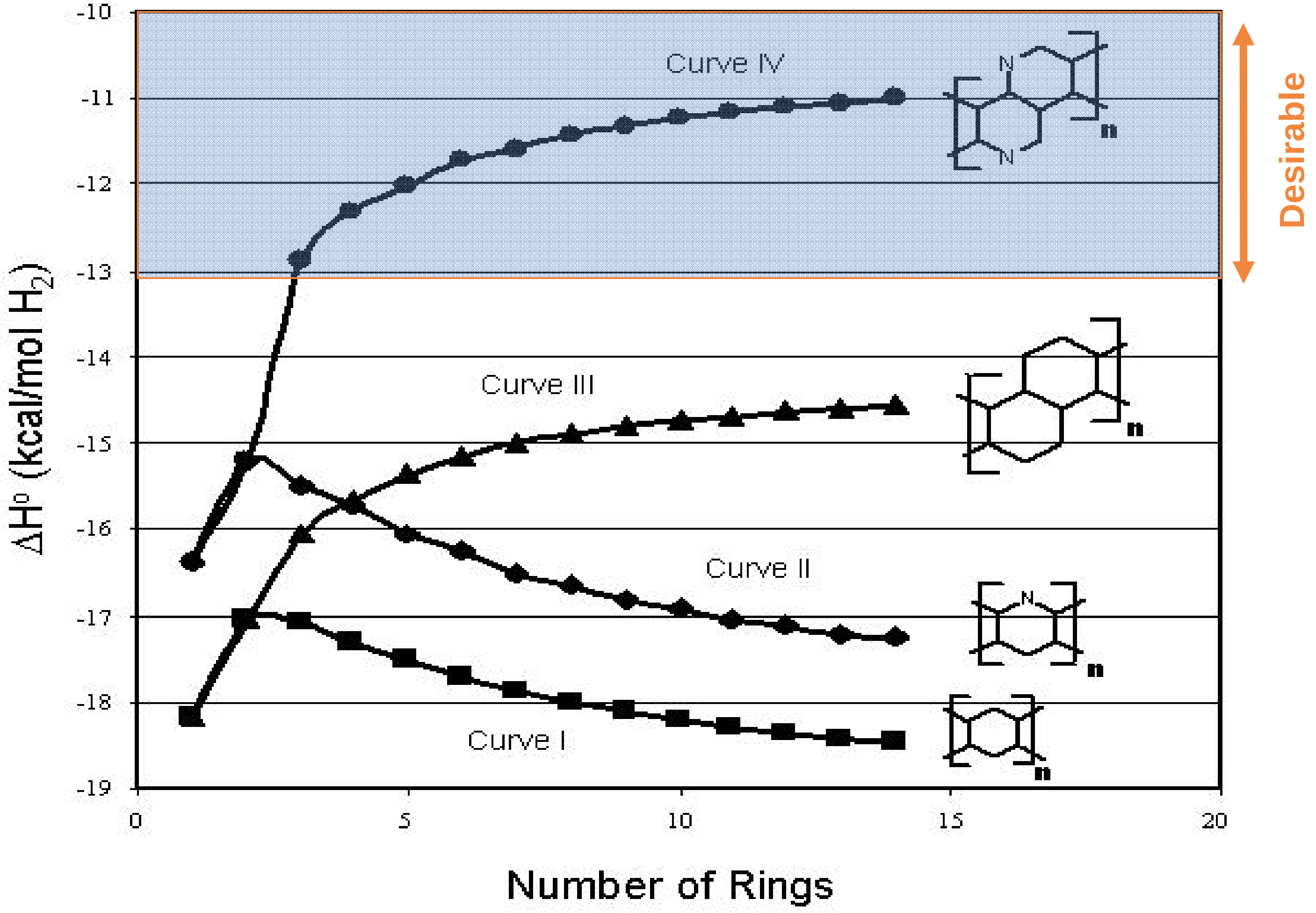
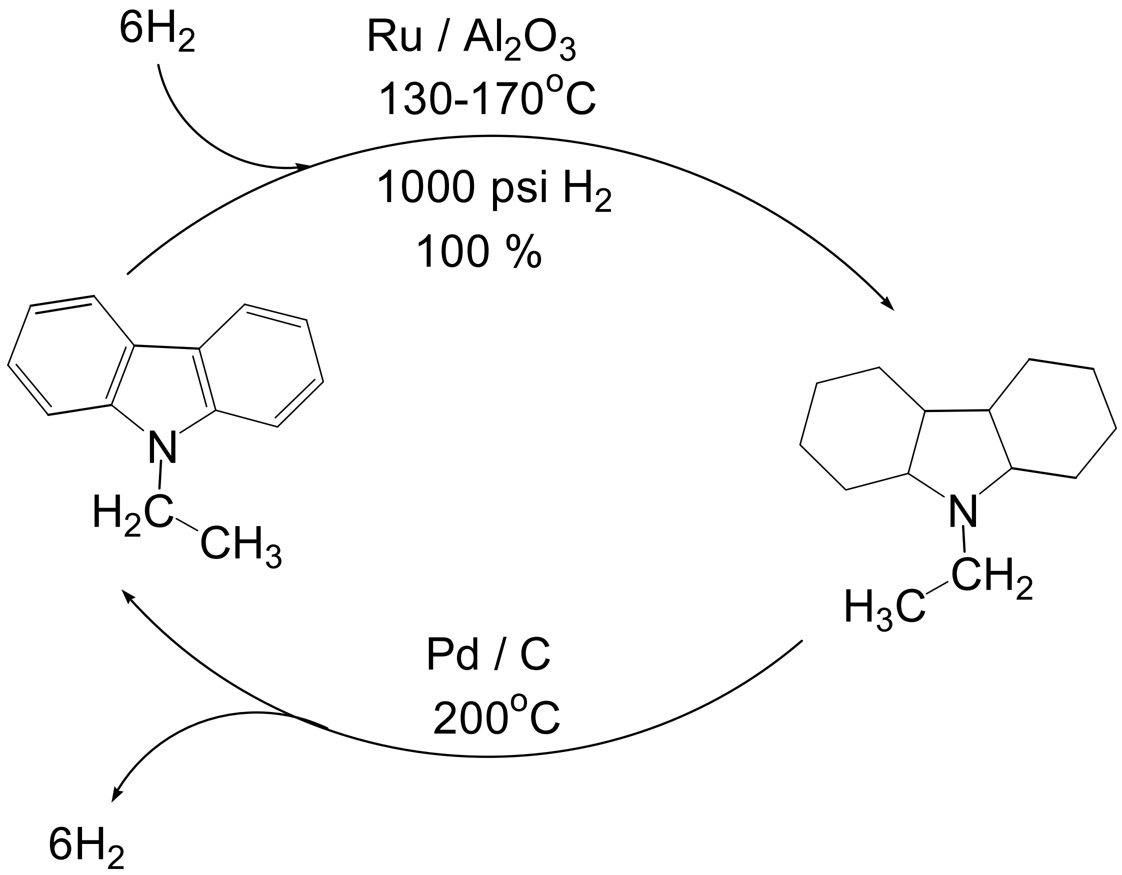
Enthalpies of Hydrogenation as Function of N Substitution



Fused Multi-Ring Aromatics and Inclusion of N-Heteroatoms can greatly lower ΔH

US and non-US patents pending

Hydrogenation/Dehydrogenation of N-Ethylcarbazole



$6H_2$

Ru / Al_2O_3
130-170°C
1000 psi H_2
100 %

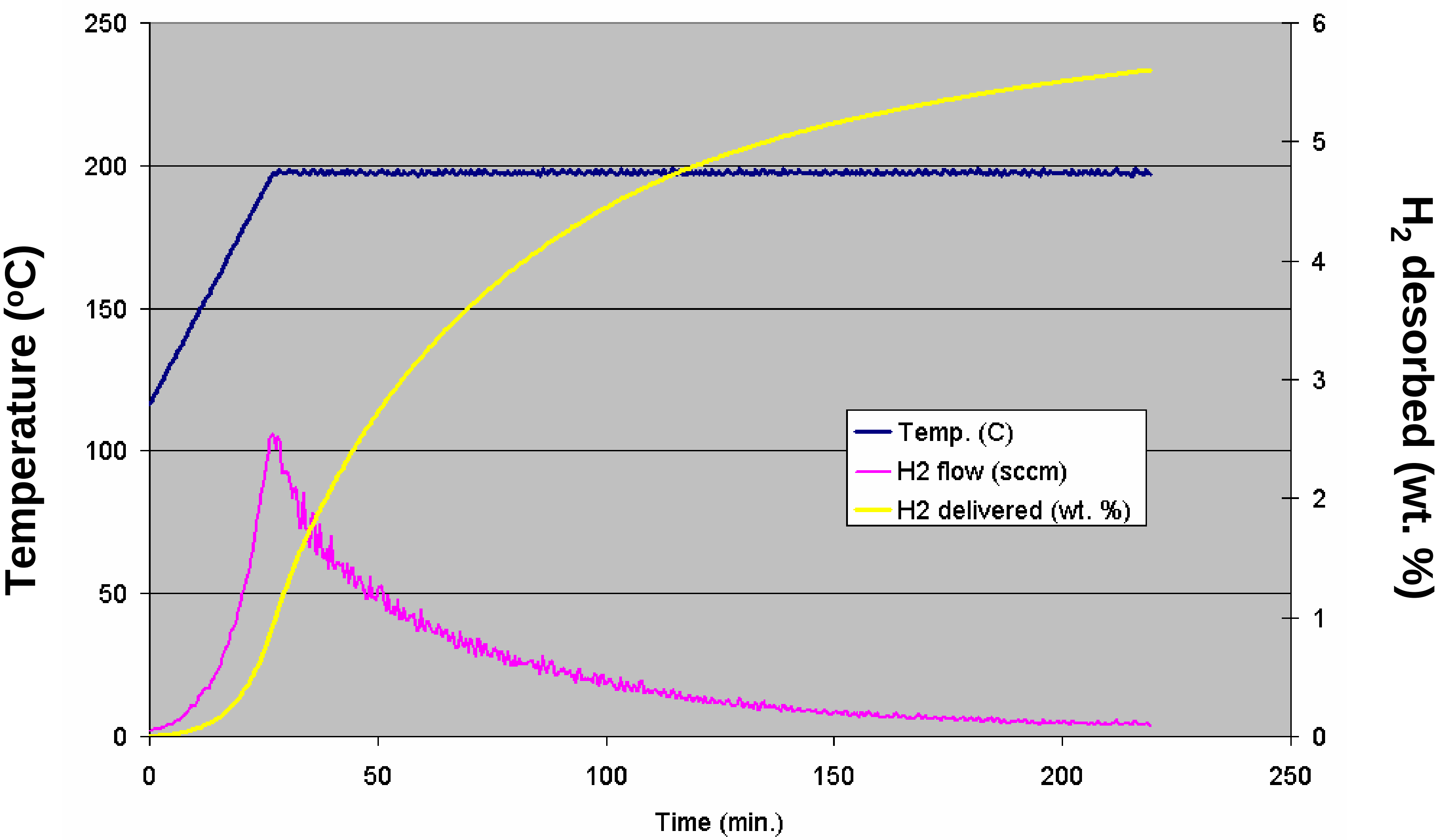
Pd / C
200°C

$6H_2$

Hcalc.= -12.4Kcal/mole H_2
Hesc. = -12.2Kcal/mole H_2

apacity : 5.8 %

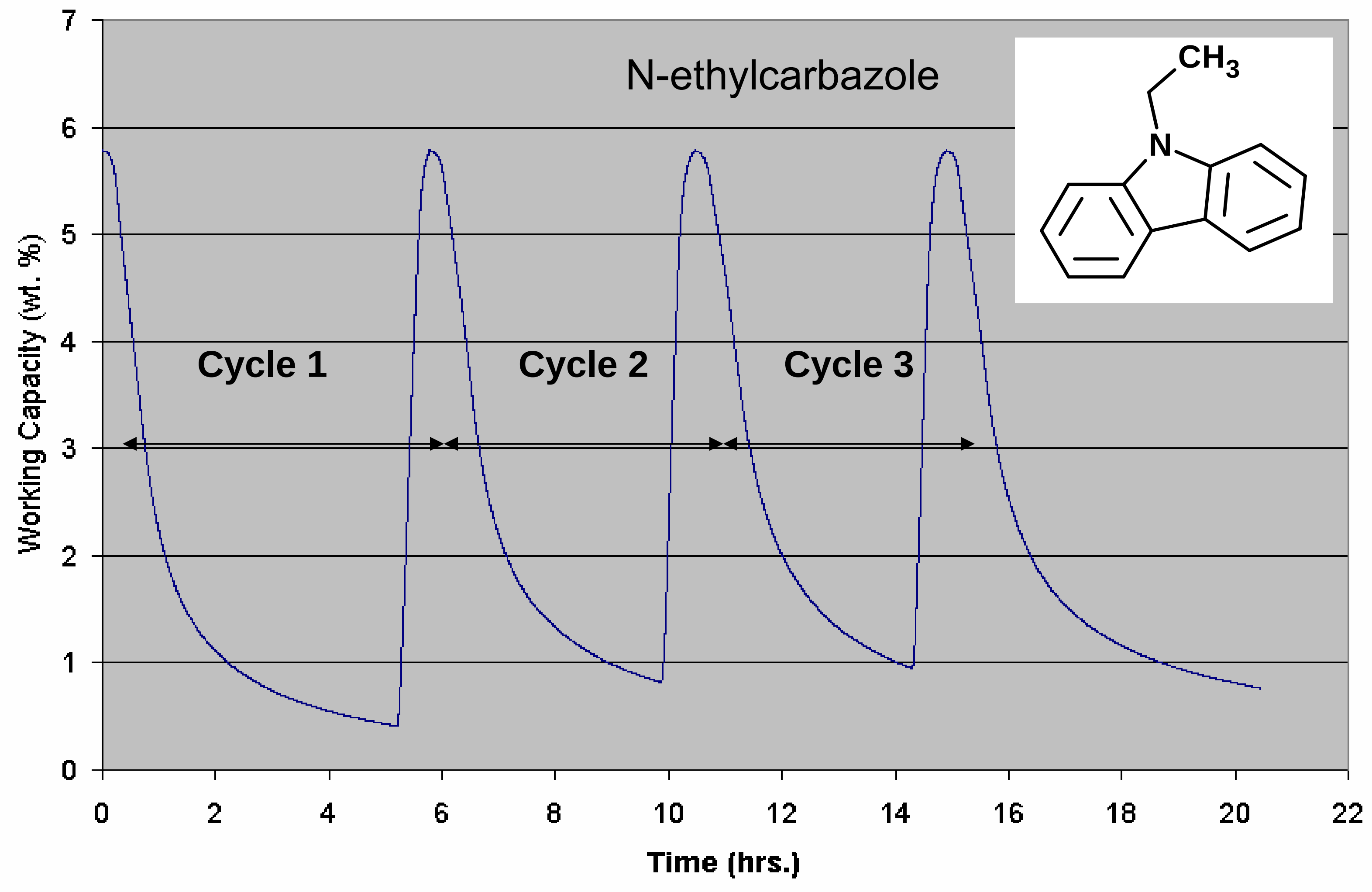
Flow Measurement of Hydrogen Generation from N-ethylcarbazole (Ramp from 25°C to 200°C, 1 atm. H_2, 40:1 substrate/catalyst)



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

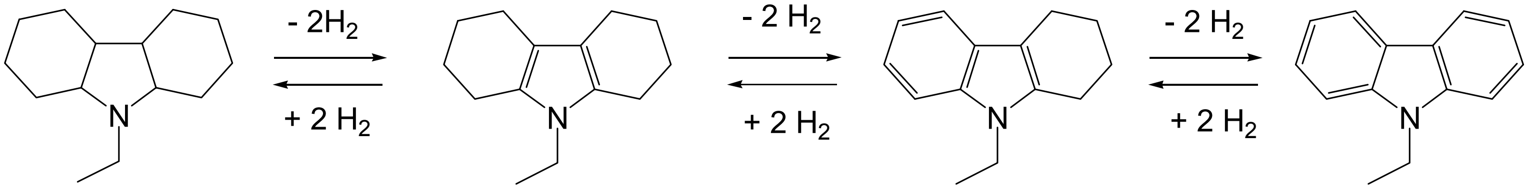
Cycling Studies

Dehydrogenation: Ramp from 25 °C to 200 °C, 15 psia H_2
Hydrogenation: 170 °C, 1200 psia H_2



Rapid hydrogenation and cycling stability

Understanding the Mechanism

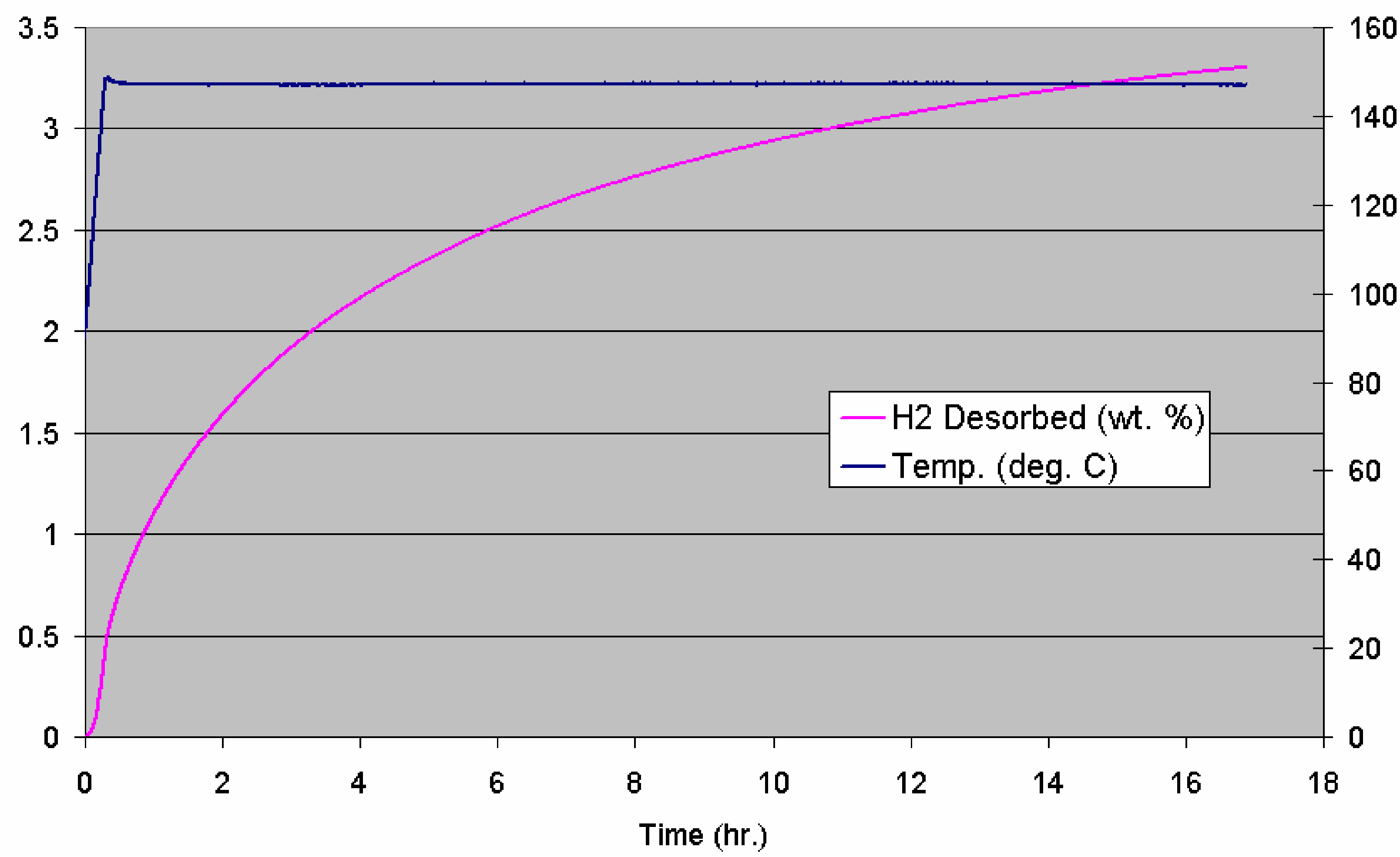


(11.3)* (12.4)* (12.8)*

( )* : $\Delta H_{calc.}$(B3LYP/G-311G**) in Kcal/mol H_2

$\Delta H_{exp.}$ (overall) = 12.2 kcal/mole H_2

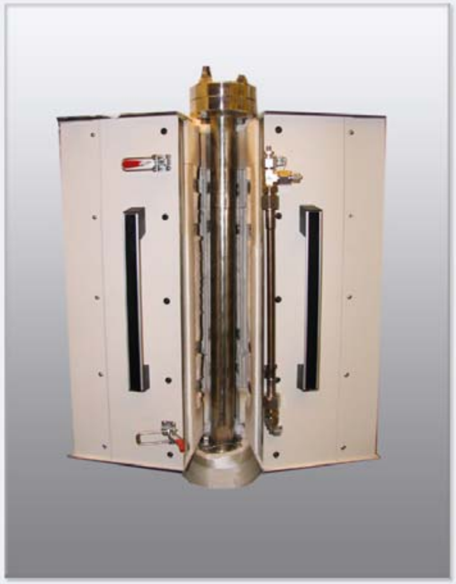
N-ethylcarbazole Dehydrogenation: (Ramp from 25 ^oC to 150 ^oC, 15 psia H_2)



Slow catalytic dehydrogenation rate at 150 ^oC

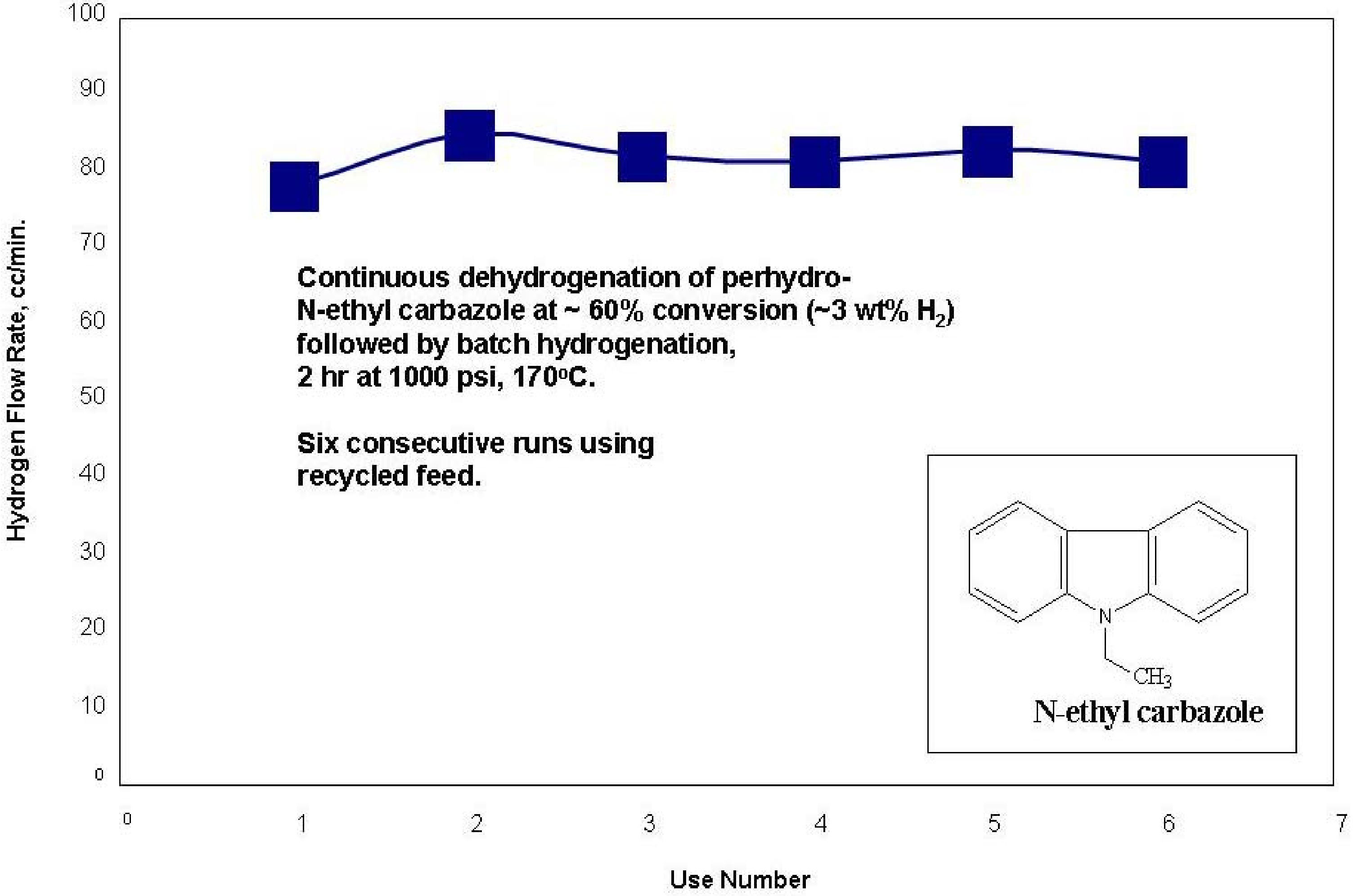
Dehydrogenation Flow Reactor Test System

2” Packed Bed Reactor



Packed Bed Reactor Dehydrogenation/ Hydrogenation Cycling Demonstration

190°C; 0.25 ml./min/ Liquid Flow



Continuous dehydrogenation of perhydro-N-ethyl carbazole at ~ 60% conversion (~3 wt% H_2) followed by batch hydrogenation, 2 hr at 1000 psi, 170°C.

Six consecutive runs using recycled feed.

N-ethyl carbazole

H_2 Purity from Continuous Flow Dehydrogenation Experiments

Component	Mole %
Hydrogen	99.9+
Methane	0.0013%
Ethane	0.0083%
Carbon Monoxide	ND
N containing compounds	ND
C3’s	ND
C4’s	ND
C5’s	ND
C6’s	ND

ND – Non Detectable

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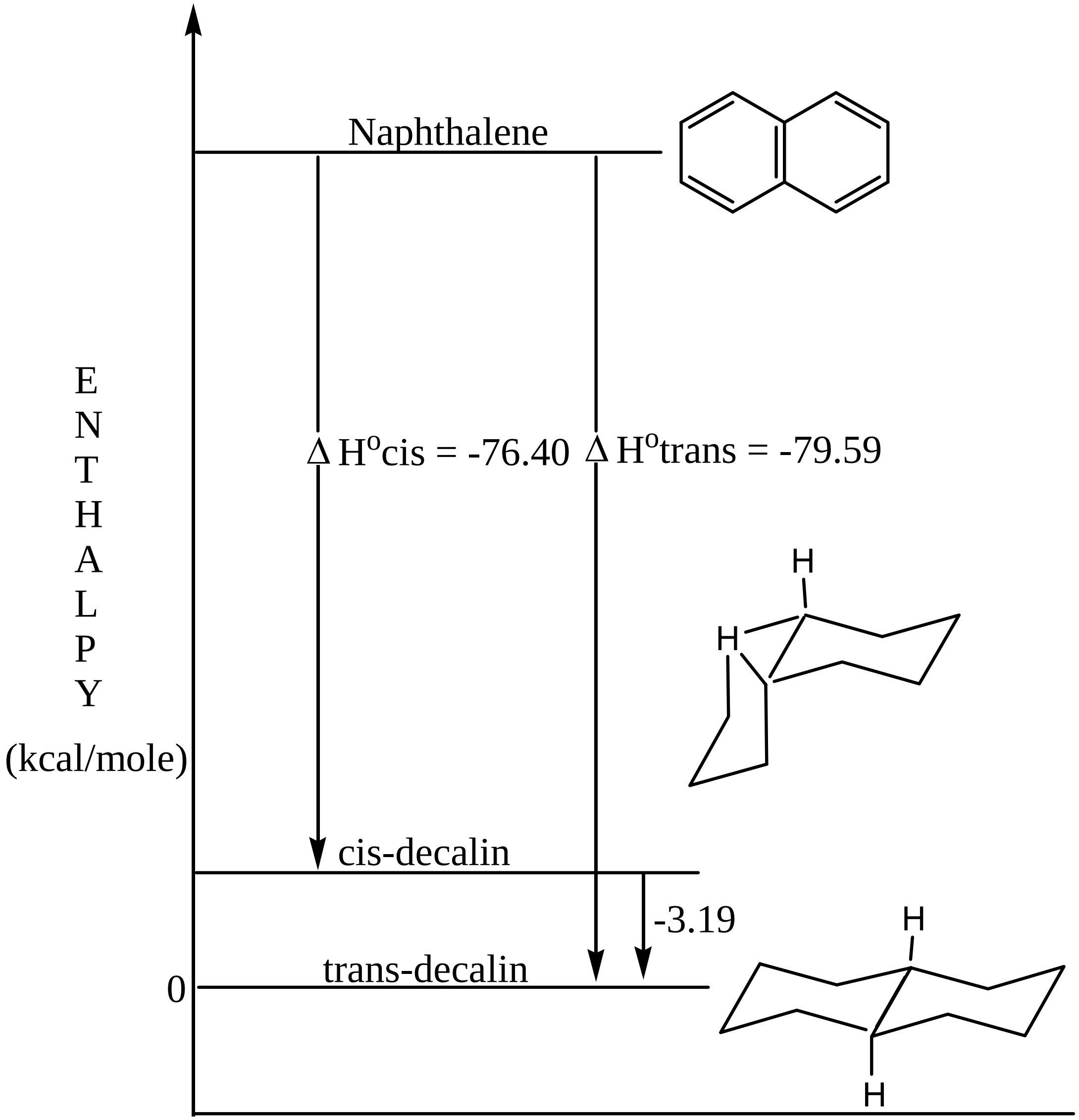
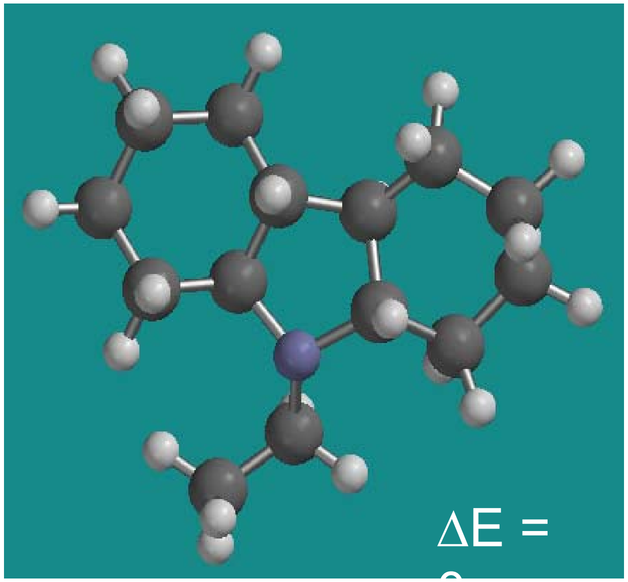
Illustration of Conformers: Decalin

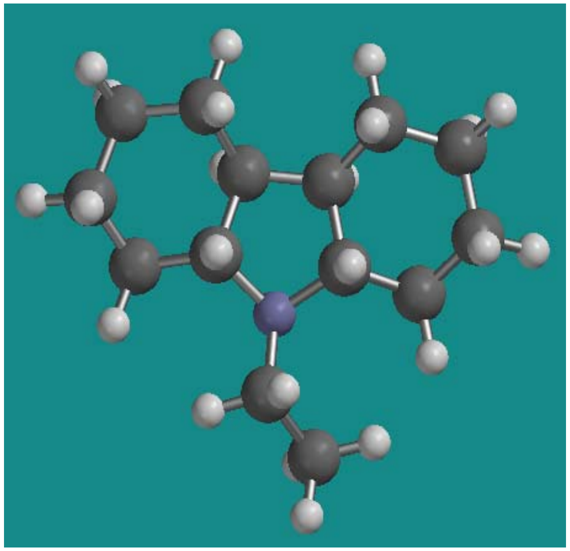


Perhydro-N-ethylcarbazole Conformers

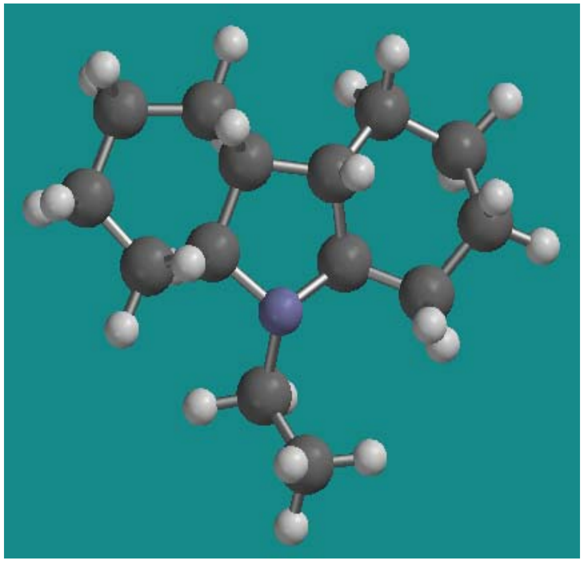
At B3LYP/G-311G** level



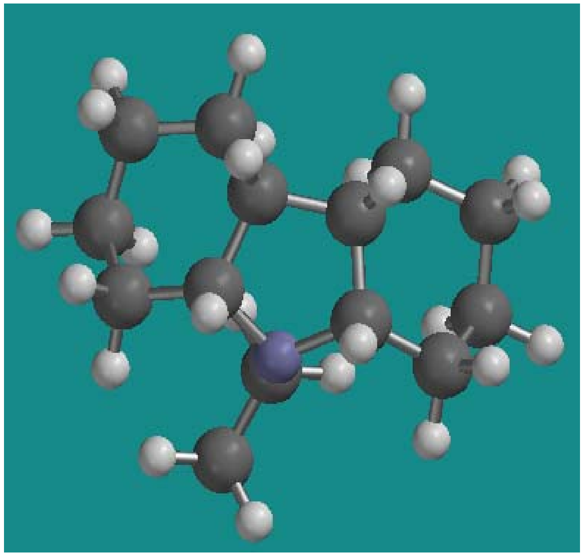
ΔE =



ΔE = 2.6 kcal/mol

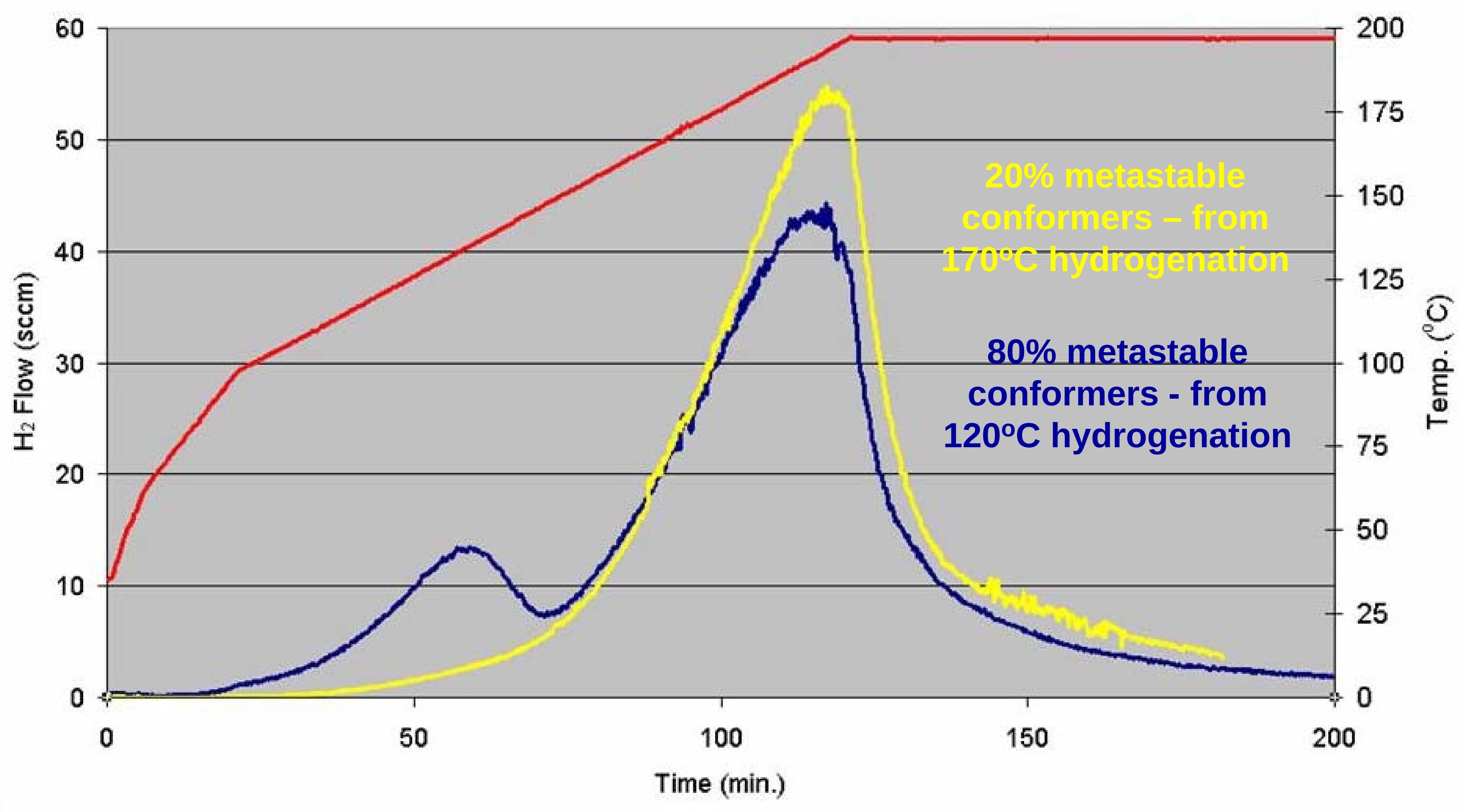


ΔE = 8.6 kcal/mol



ΔE = 14.5 kcal/mol

Flow Measurement of Hydrogen Generation from N-ethylcarbazole: Kinetic versus Thermodynamic Conformers

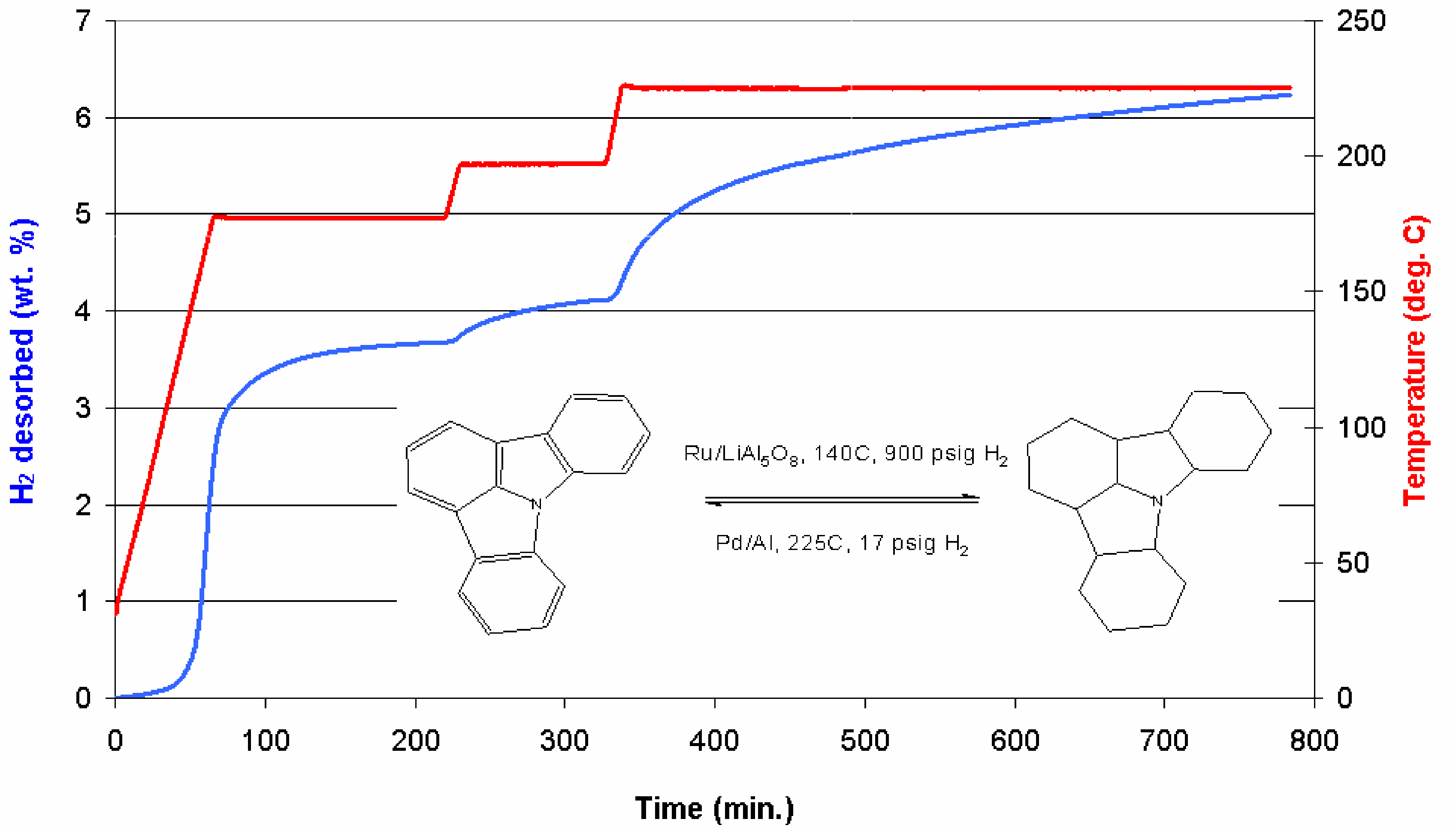


20% metastable conformers – from 170^{o}C hydrogenation

80% metastable conformers - from 120^{o}C hydrogenation

US and non-US patents pending

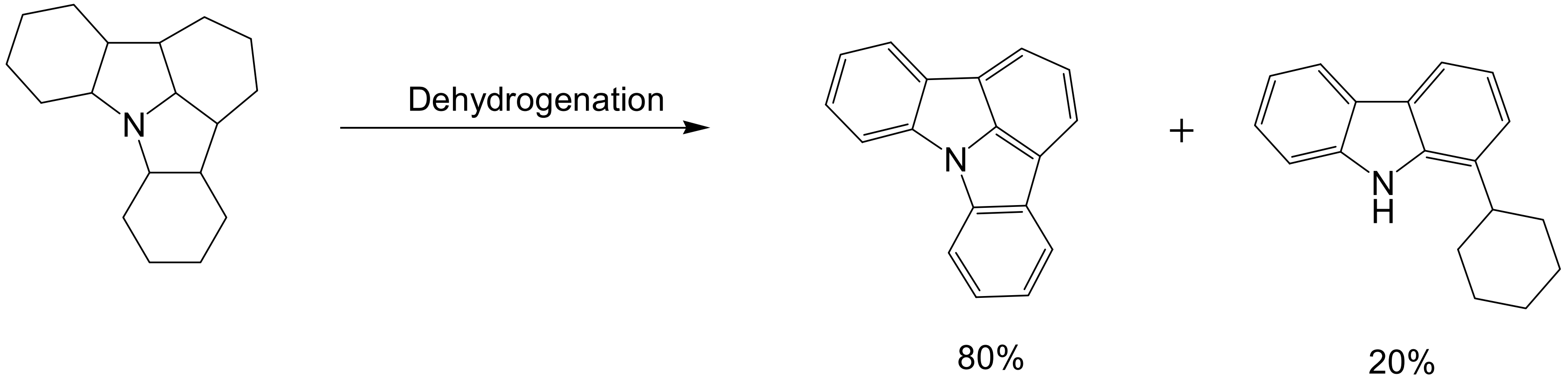
Increasing Capacity: Hydrogen Generation from Phenylenecarbazole



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

Theory is 6.9% wt H_2

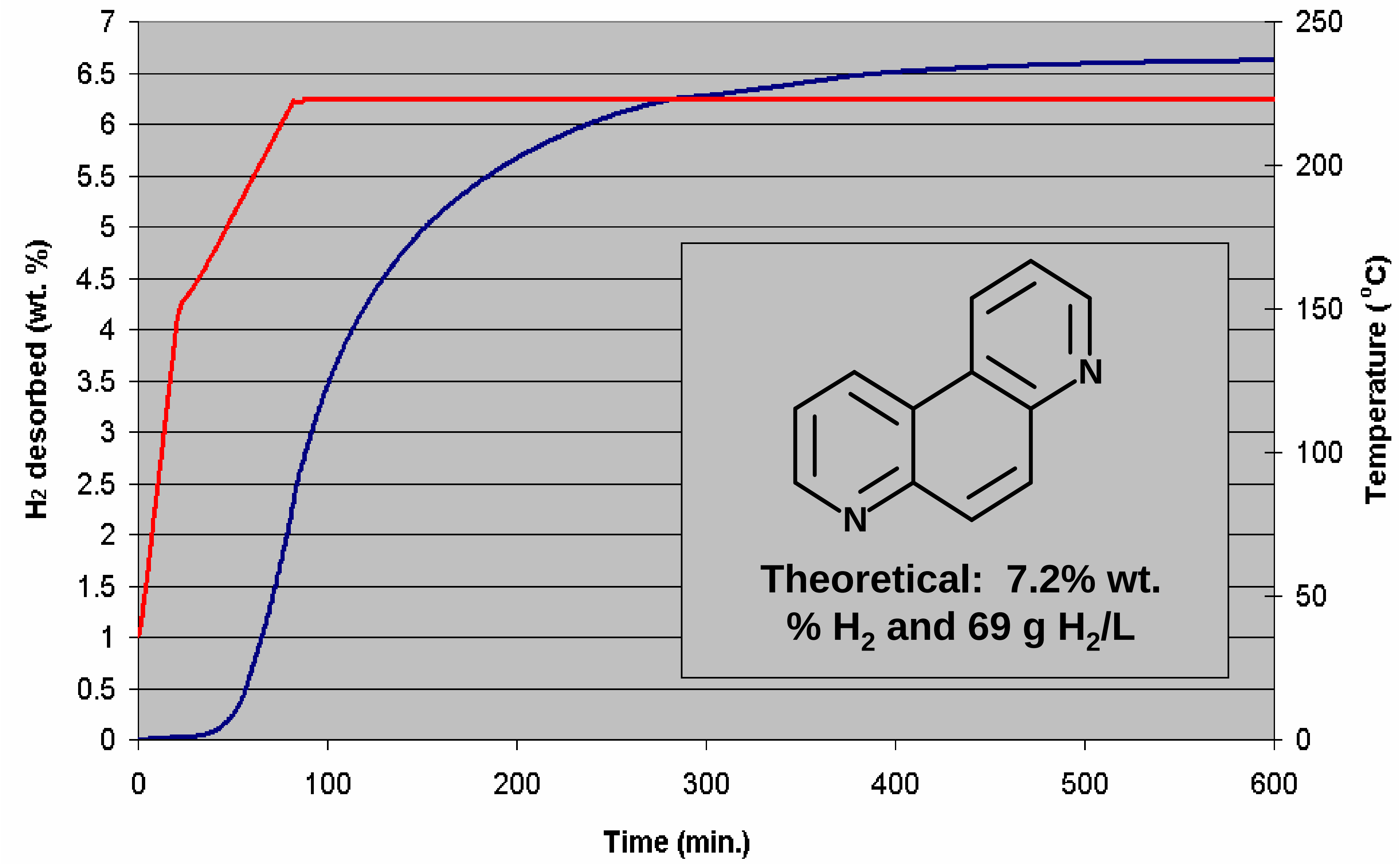
No Perfect World!



Presence of secondary amine confirmed by alkylation and by GC/MS

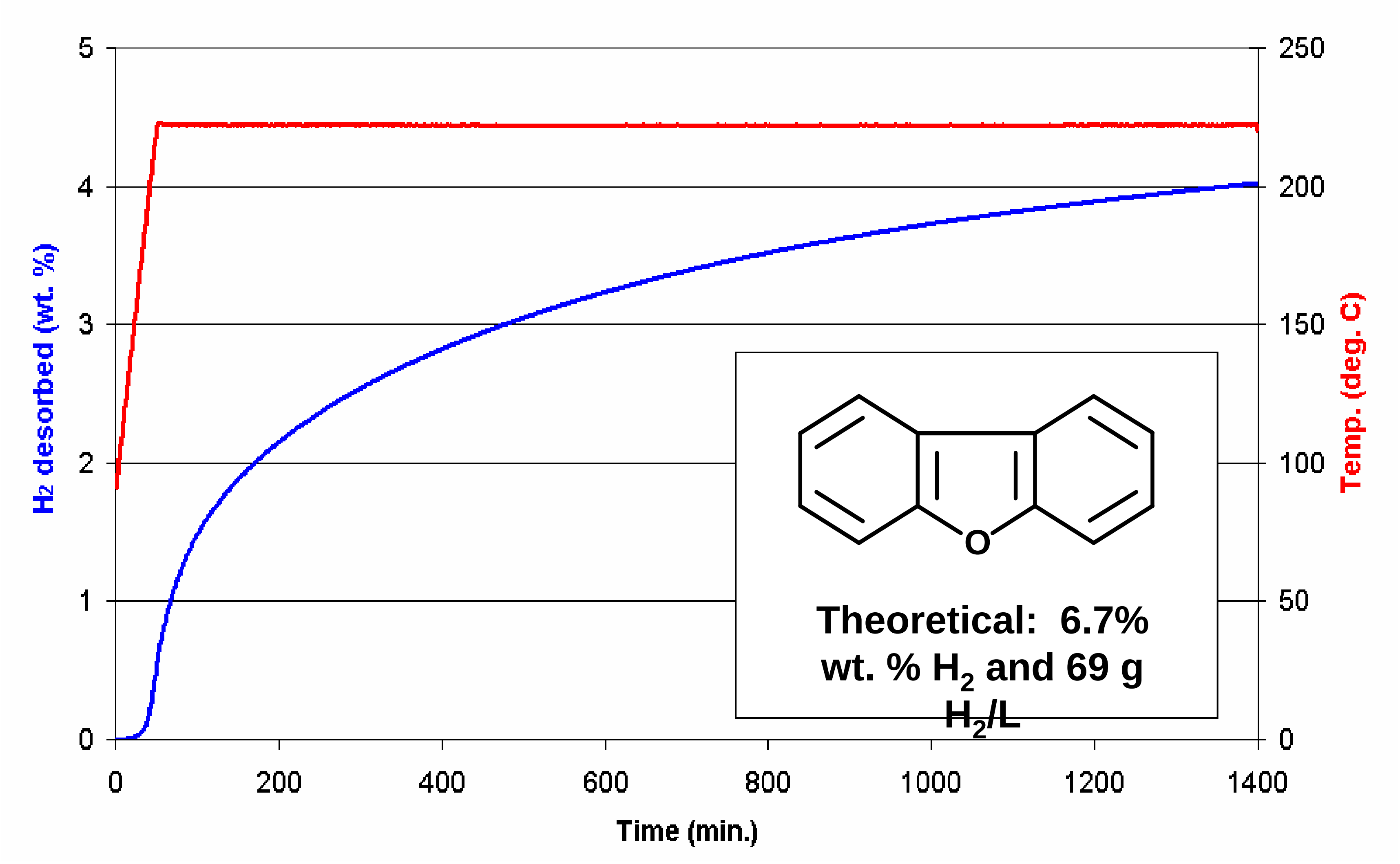
Second fused five-membered rings can cause strain.

Phenanthrolene Dehydrogenation



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

Oxygen-containing Carrier



Theoretical: 6.7% wt. % H_2 and 69 g H_2/L

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

Summary and Conclusions

- Liquid carrier concept provides an integrated hydrogen production, delivery and on-board storage scenario.
  - Maximize use of existing liquids infrastructure
  - Safety
  - Energy efficiency
- Continuing material challenges:
  - Optimal liquid carrier: 9 wt% for system (DOE's 2015 target)
  - Optimal dehydrogenation catalysts for a compact, on-board liquid carrier → H_2 gas conversion reactor

Acknowledgements

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Thank you

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