Hydrogen Storage by Reversible Hydrogenation of Liquid-phase Hydrogen Carriers

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Overview

Timeline

- 2/04 – 2/08
- 80% complete

Budget

- Total project $6,121,242
  - DOE share $4,346,082 (71%)
- FY06 funding $1,000,000
- FY07 funding $1,025,000

Barriers

- Technical Barriers- Hydrogen Storage:
  - A. System Weight and Volume
  - C. Efficiency
  - E. Charging/Discharging Rates
  - R. Regeneration Processes

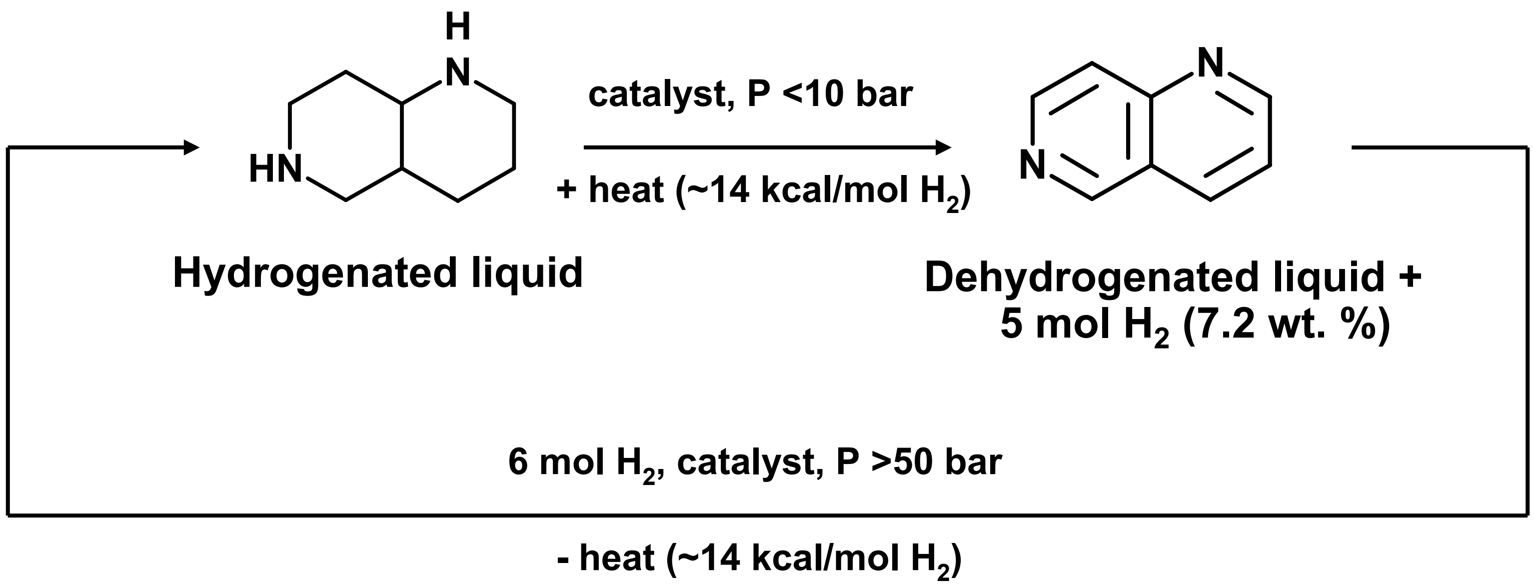
Interactions

- Current interactions: Auto OEM's, Argonne National Laboratory
- Anticipated interactions: Chemical hydrides COE

Objectives

- Development of liquid-phase hydrogen storage materials (liquid carriers) with capacities and thermodynamic properties that enable hydrogen storage systems meeting 2010 DOE system-level targets. Optimization of dehydrogenation and hydrogenation catalysts.
  - Selective, reversible catalytic hydrogenation and dehydrogenation. Multiple cycles of use with no significant degradation of the materials.
  - Optimal heat of dehydrogenation (10-13 kcal/mole H_2), enabling the catalytic dehydrogenation at unprecedented temperatures (<200 ^{o}C).
  - Multi-functional liquid carriers that enable autothermal dehydrogenation.
  - Low volatility (b.p. > 300 ^{o}C), enabling the use of these liquids in simplified systems onboard vehicles and reducing exposure to vapors.
  - Enhanced rates of catalytic dehydrogenation with wash coat catalysts.

Approach: A regenerable organic liquid carrier for hydrogen storage onboard vehicles and stationary H_2 delivery



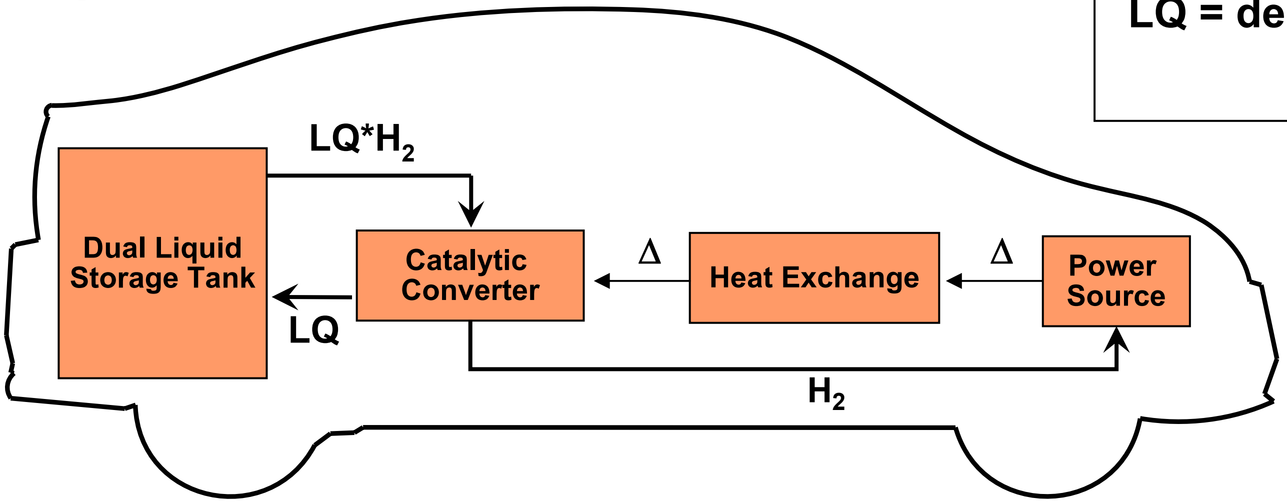
- 19 gallons of hydrogenated liquid carrier will reversibly store 5 kg hydrogen at 7 wt. % and 1g/cc density

$LQ*H_2$ = hydrogenated liquid

LQ = dehydrogenated liquid

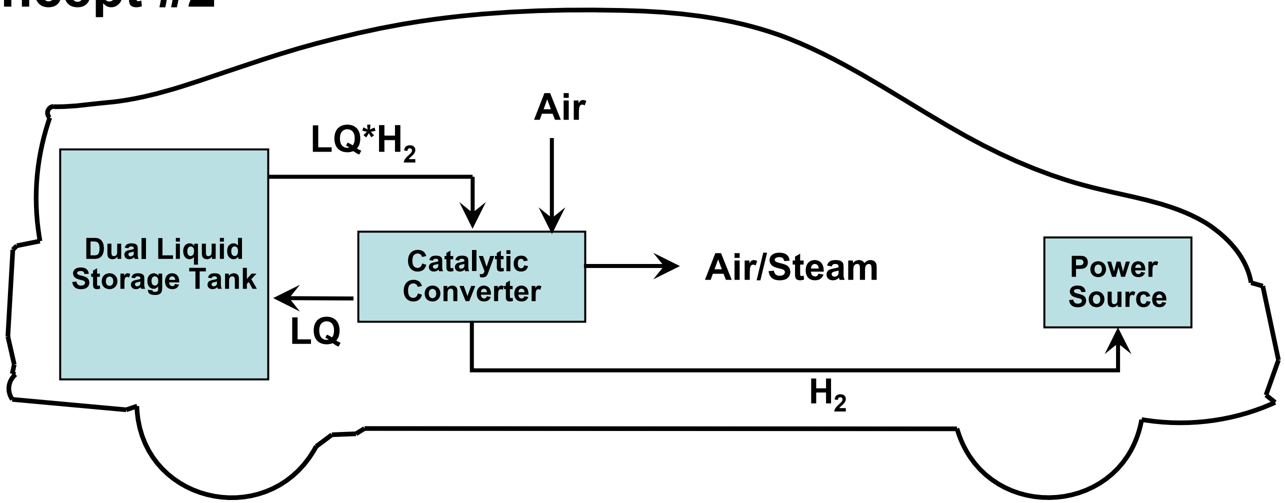
Δ = heat

Concept #1



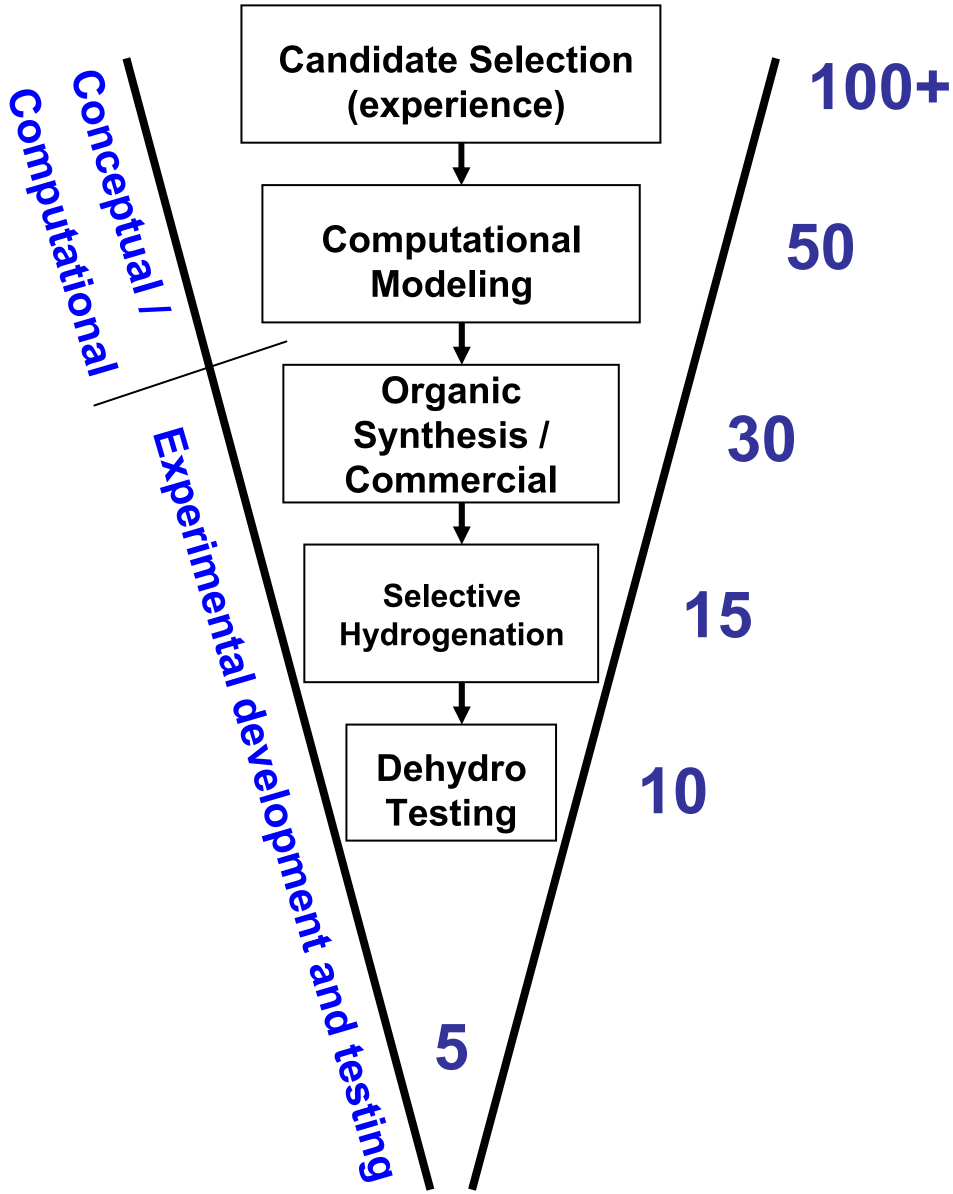
Maximum energy efficiency:
by (a) recovering the exothermic ($-\Delta H$) of hydrogenation and (b) utilizing the waste heat from the power source to supply the ΔH for the endothermic dehydrogenation.

Concept #2



Autothermal hydrogen storage:
Organic liquid carrier provides hydrogen to the power source and supplies the necessary heat of dehydrogenation via selective, H_2-reversible oxidation

Experimental Discovery Approach



- Carrier Selection
  - Selection based upon structure/property relationships
- Computational Modeling
  - Must use proper models
- Organic Synthesis
  - High purity compounds
- Selective Hydrogenation
  - 99+% selective!
  - Many different types of molecules
- Dehydrogenation Testing
  - Large variation in rates between catalysts
  - Must also be 99+% selective

Technical Accomplishments/ Progress/Results

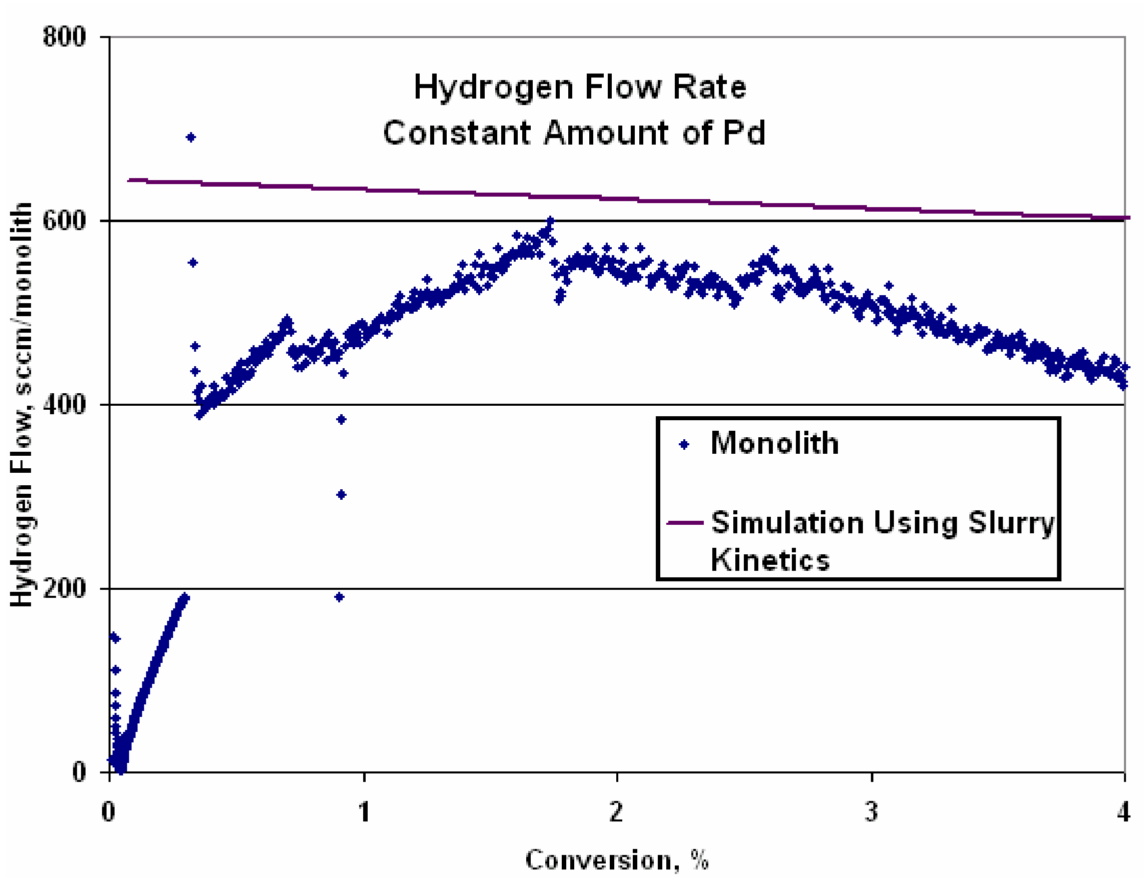
- Dehydrogenation catalyst development
  - Development of wash coated catalysts with high activity
- Organic liquid carrier discovery and testing
  - Towards lowering dehydrogenation temperatures
  - Investigation of new carrier candidates with increased available H_2 capacity
- A new concept: Autothermal hydrogen storage with organic liquid carriers
  - "Bi-functional" liquid carriers
  - Highly selective catalytic oxidation

Improved Catalyst Efficiency

- Our high-throughput catalyst testing is performed with slurry catalysts in small stirred tank reactors. However, dehydrogenation catalyst must be utilized in a stationary form in end-use application onboard vehicles.
- Dehydrogenation catalysts in pelletized form (eg. in a packed bed reactor) are limited by mass transfer
  - Effectiveness factor (% of available active metal catalyst) only 0.08 (reported last year)
- Thin catalyst coatings (10-20 μm) on a surface should improve effectiveness
- Thin coatings (wash coats) are catalysts used in practical reactors (eg. microreactors and monoliths)

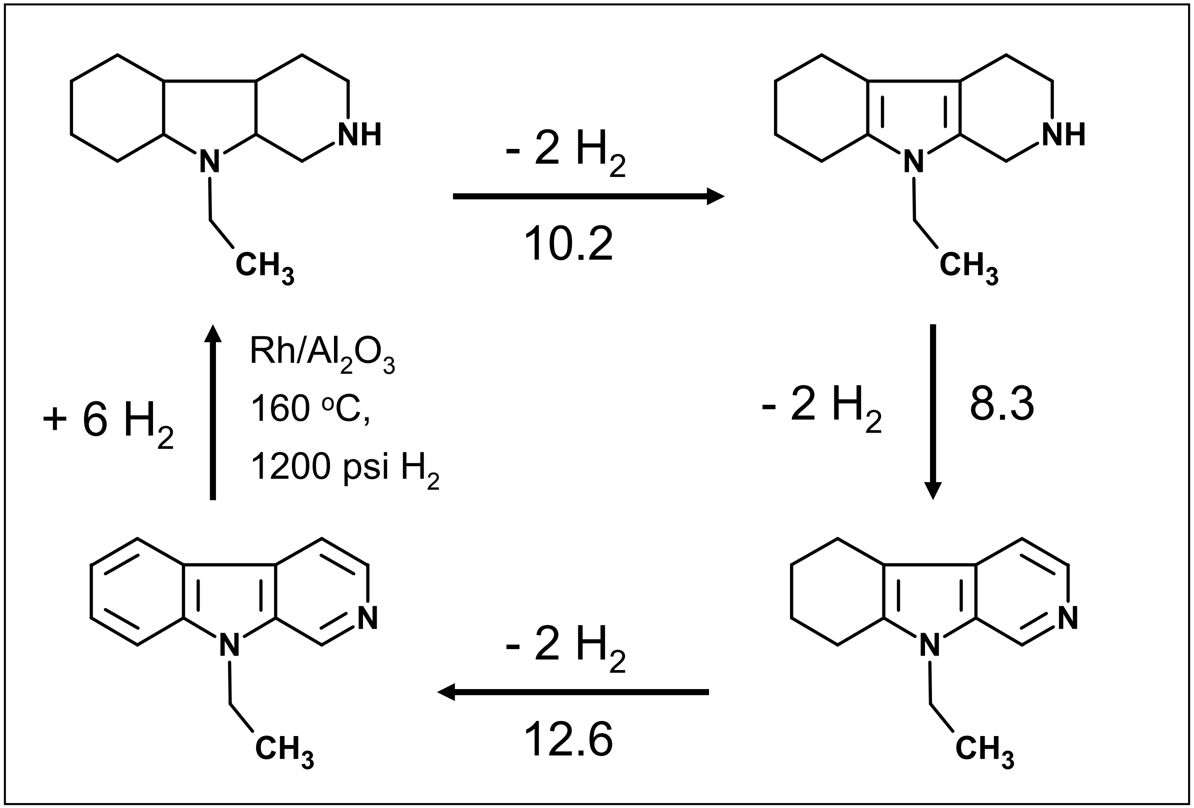
Efficient Wash Coat Catalyst Developed

- Slurry reactors measure intrinsic catalyst activity
- Circulating flow reactor measures wash coat catalyst activity
- Model relates intrinsic activity to wash coat on a monolith
- High catalyst efficiency demonstrated (8X higher than pellets)



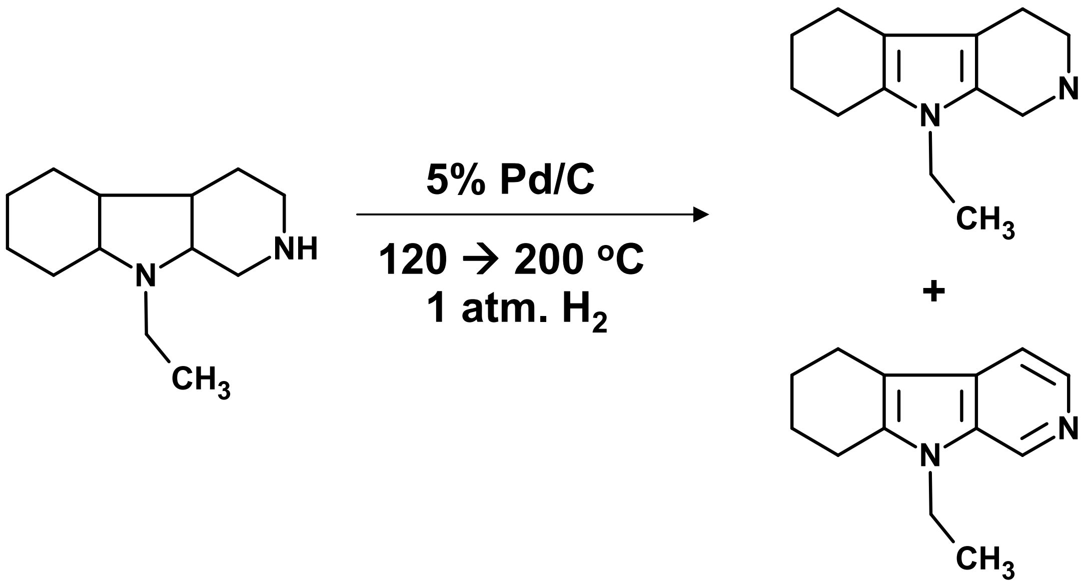
Hydrogen flow vs. conversion for dehydrogenation of perhydro-N-ethylcarbazole in a circulating flow reactor

Energetics of stepwise heat of dehydrogenation ($kcal/mol\ H_2$)



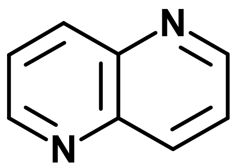
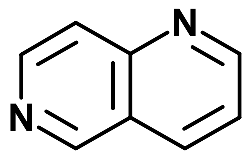
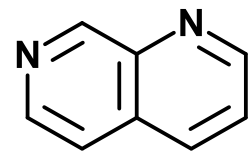
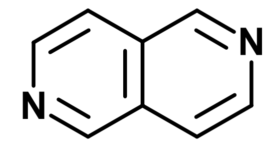
- Average β-carboline ΔH = 10.4 (cf. N-ethylcarbazole average ΔH =11.3)
  - Lower ΔH enables substantial conversion at lower temperatures than N-ethylcarbazole; closer to PEM FC waste heat temperature (Desirable ΔH range is 10-13 $kcal/mol\ H_2$)

Dehydrogenation of β-carboline



- Clean dehydrogenation observed (no byproducts), but only partial conversion – limiting the hydrogen storage capacity
- Temperatures required for dehydrogenation are higher than predicted by calculated dehydrogenation energetics → Conclusion: Catalyst activity is limited at very low temperatures (<150 °C)
- Testing of new catalysts necessary to improve performance

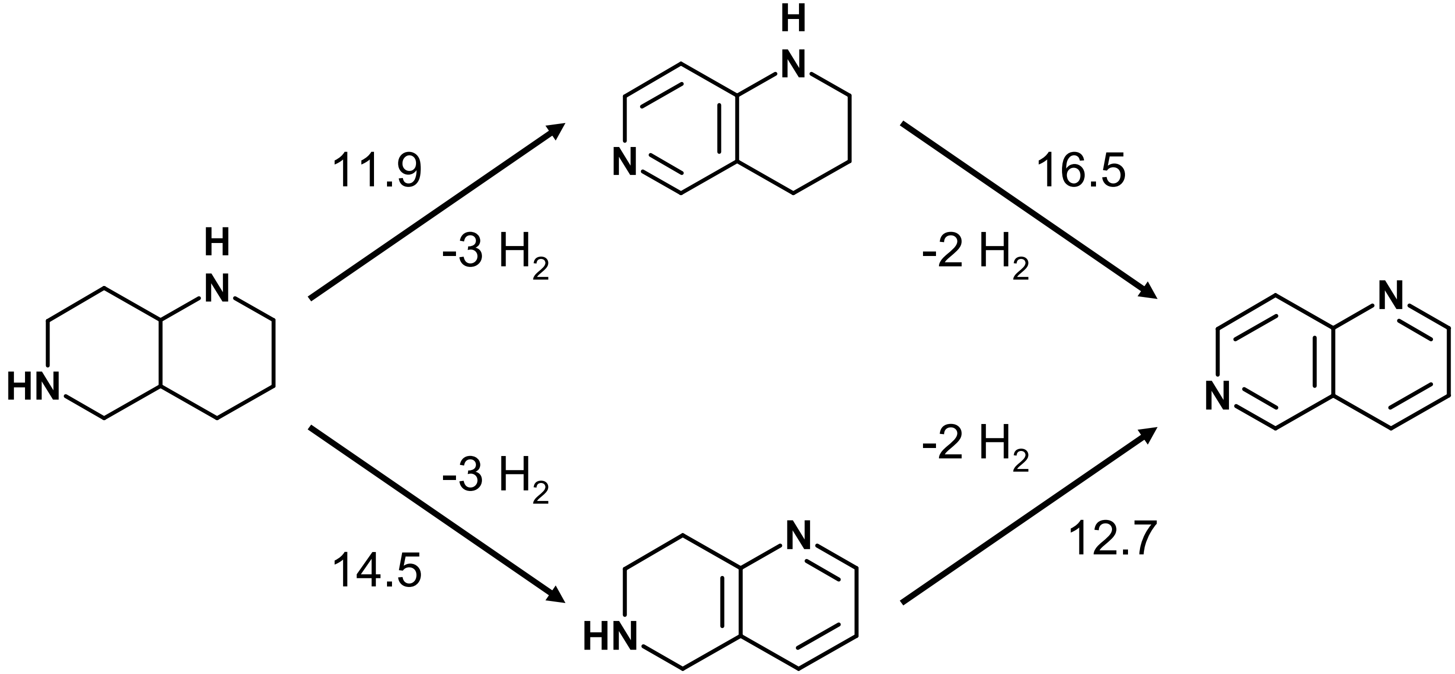
Comparison of Naphthyridine Isomers (Theoretical capacity 7.2 wt. % H_2)

				
	[1,5]	[1,6]	[1,7]	[2,6]
Calc. avg. ΔH (kcal/mol)	13.7	13.6	13.8	13.8
Melting point (^{o}C)	60-62	25-27	64-65	118-120

Large melting point differences between isomers.
Average heat of dehydrogenation similar, but....

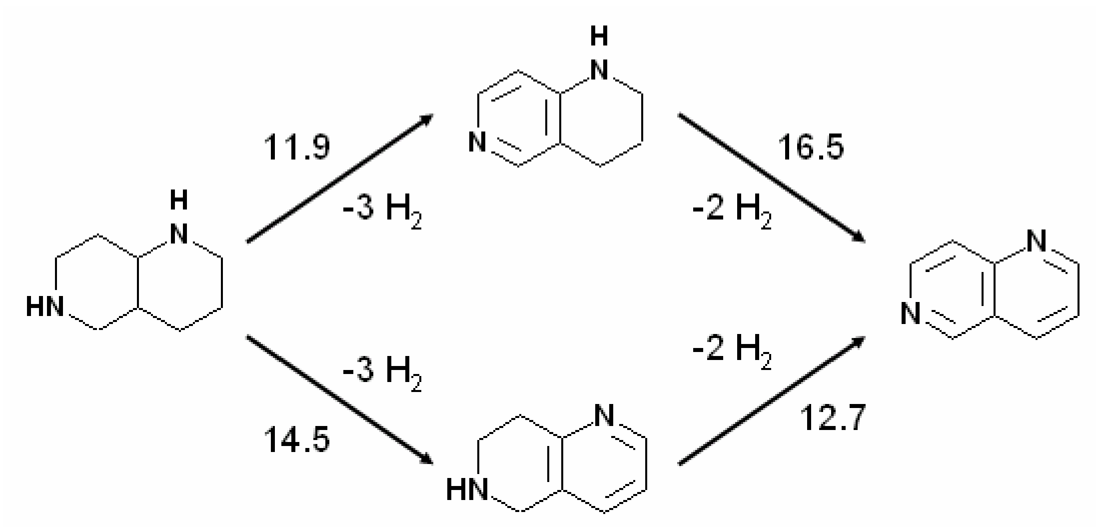
Energetics of stepwise heat of dehydrogenation

1,6-Naphthyridine, ΔH (kcal/mol)

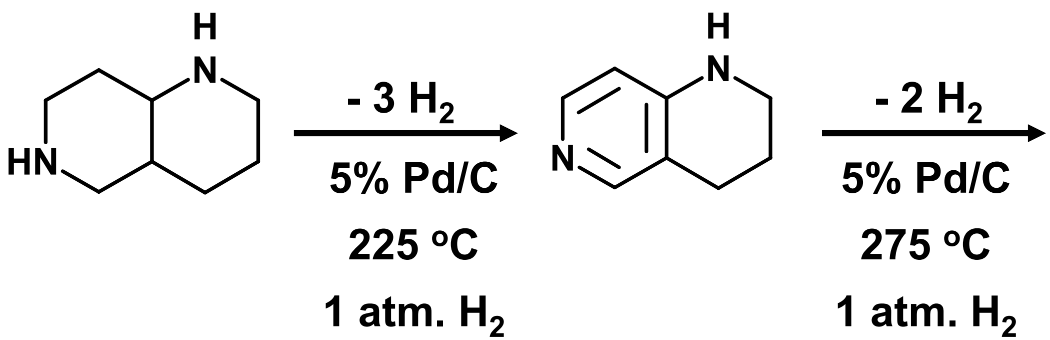


Large differences in heats within possible reaction pathways for this isomer

Dehydrogenation of 1,6-Naphthyridine



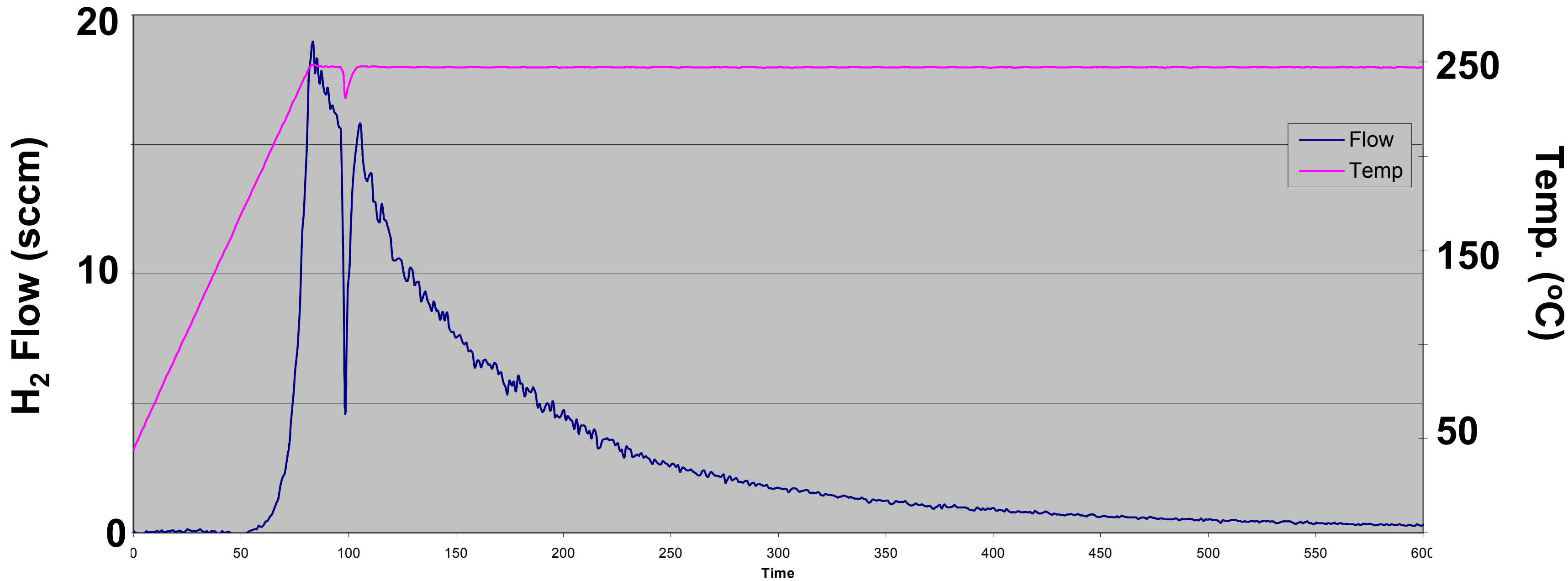
Calculation

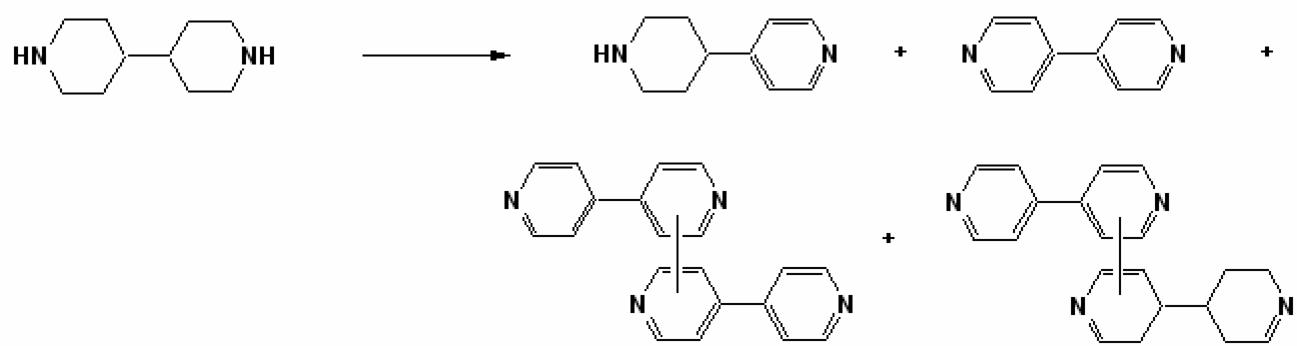


Experiment

- >7 wt. % hydrogen evolution, but reaction pathway goes through non-preferred intermediate (high temperature for second step)
- This carrier is not optimal for complete endothermic dehydrogenation, but may be suitable for autothermal dehydrogenation

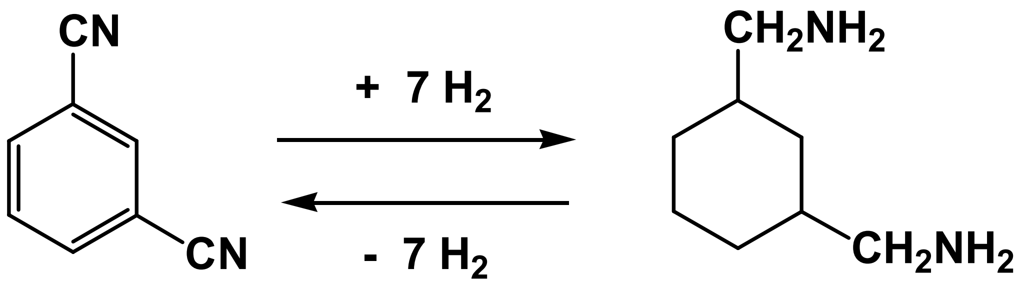
4,4’-Bipiperidine Dehydrogenation



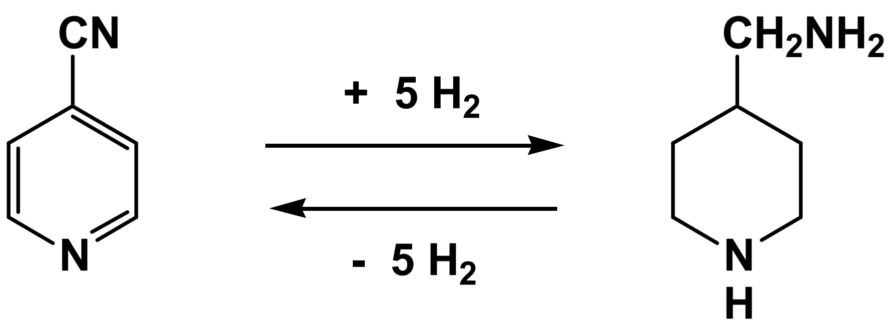


- High conversion of 4,4’-Bipiperidine with ~5 wt. % H_2 evolved; significant amount of dimer formation

Potential hydrogen carriers with >7 wt. % H_2



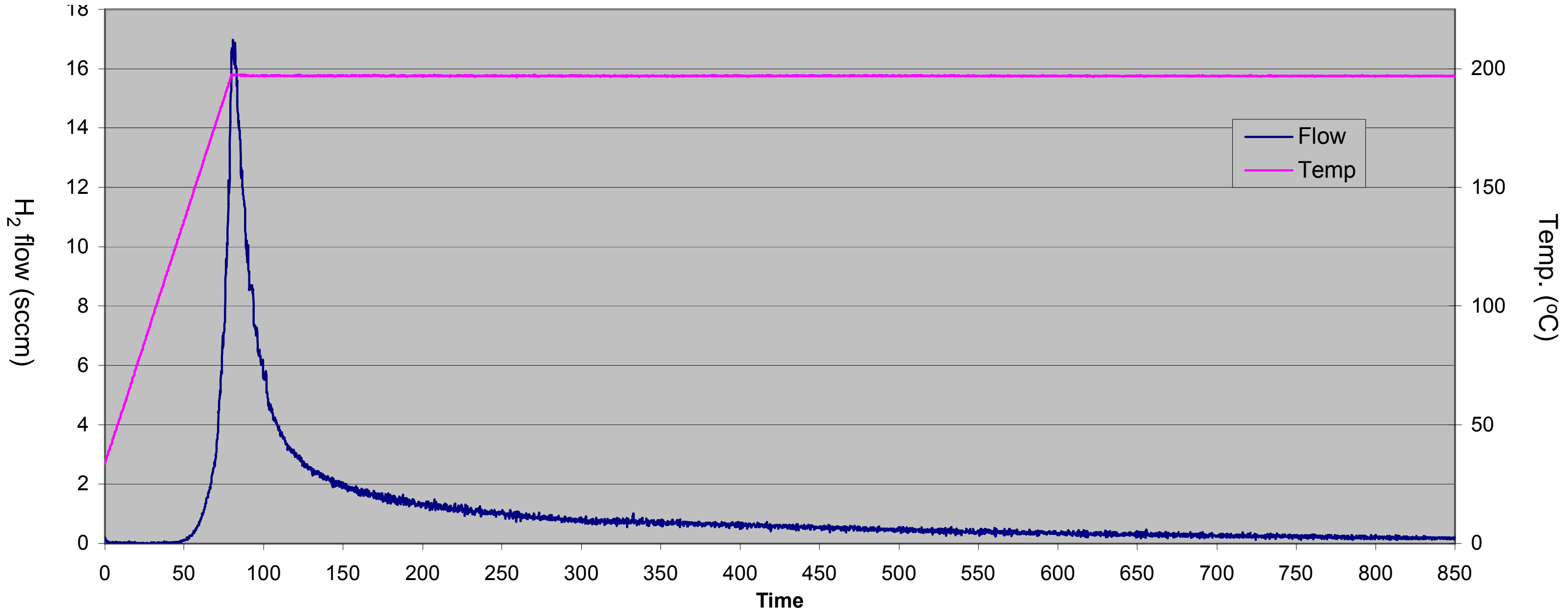
- 9.87 wt. % H_2
- Avg. ΔH = ca. 16.7 kcal/mol H_2

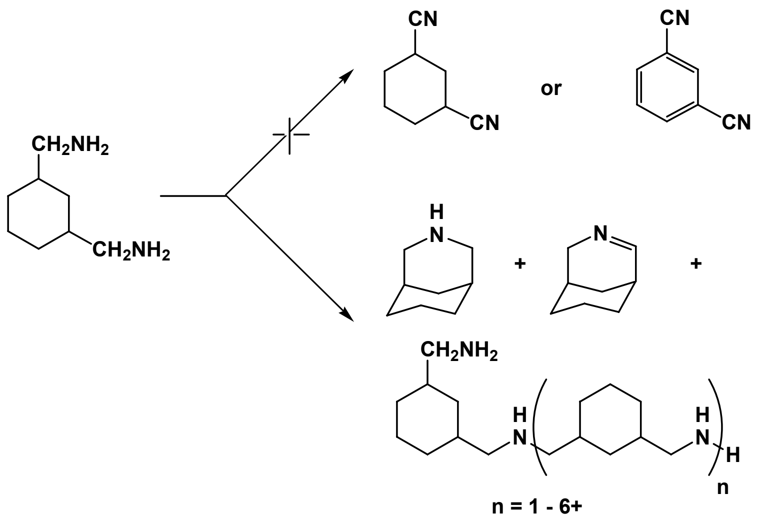


- 8.77 wt. % H_2
- Avg. ΔH = ca. 16.0 kcal/mol H_2

- Hydrogenation of nitriles can be achieved with high selectivity using “base modified” catalysts
- Dehydrogenation will require higher temperatures than other liquid carriers (ΔH above preferred 10-13 kcal/mol range)

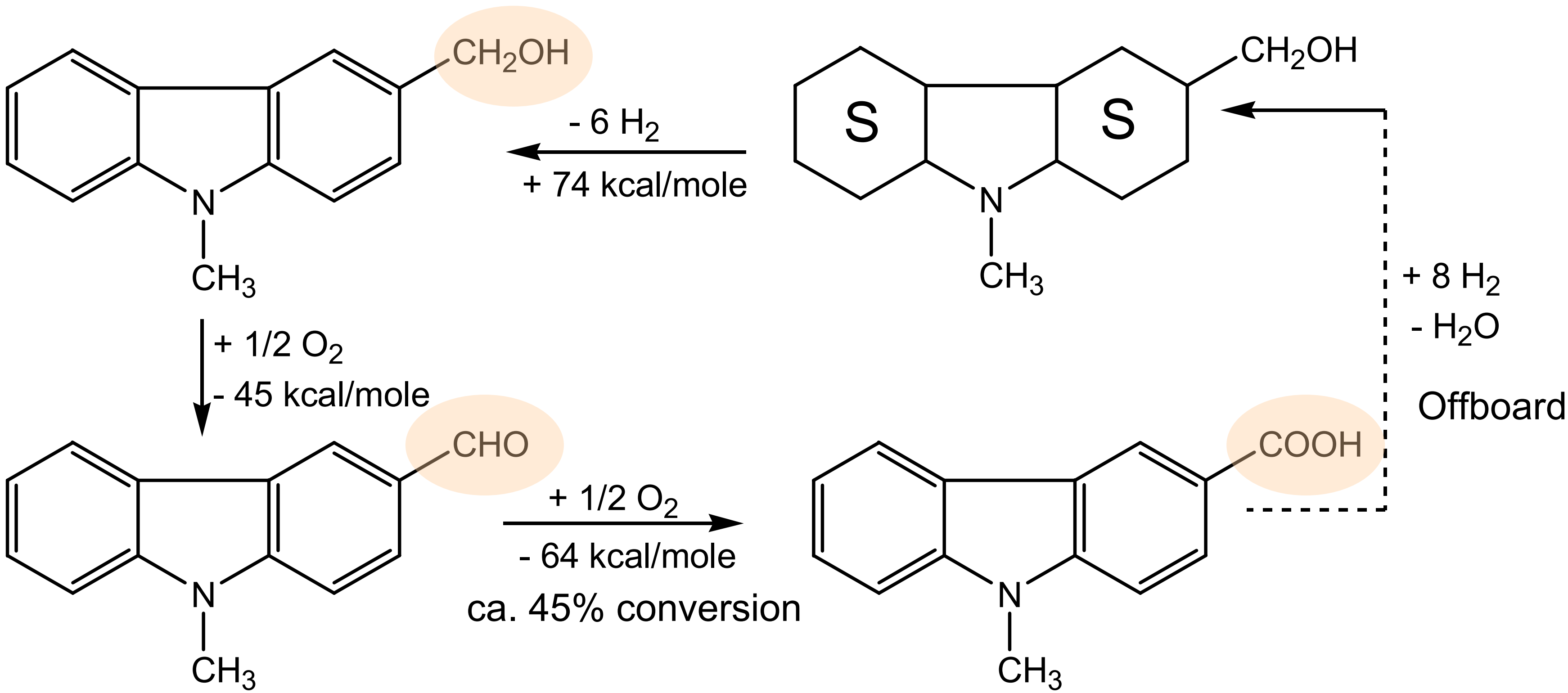
Dehydrogenation of 1,3-bis(methylamino)cyclohexane





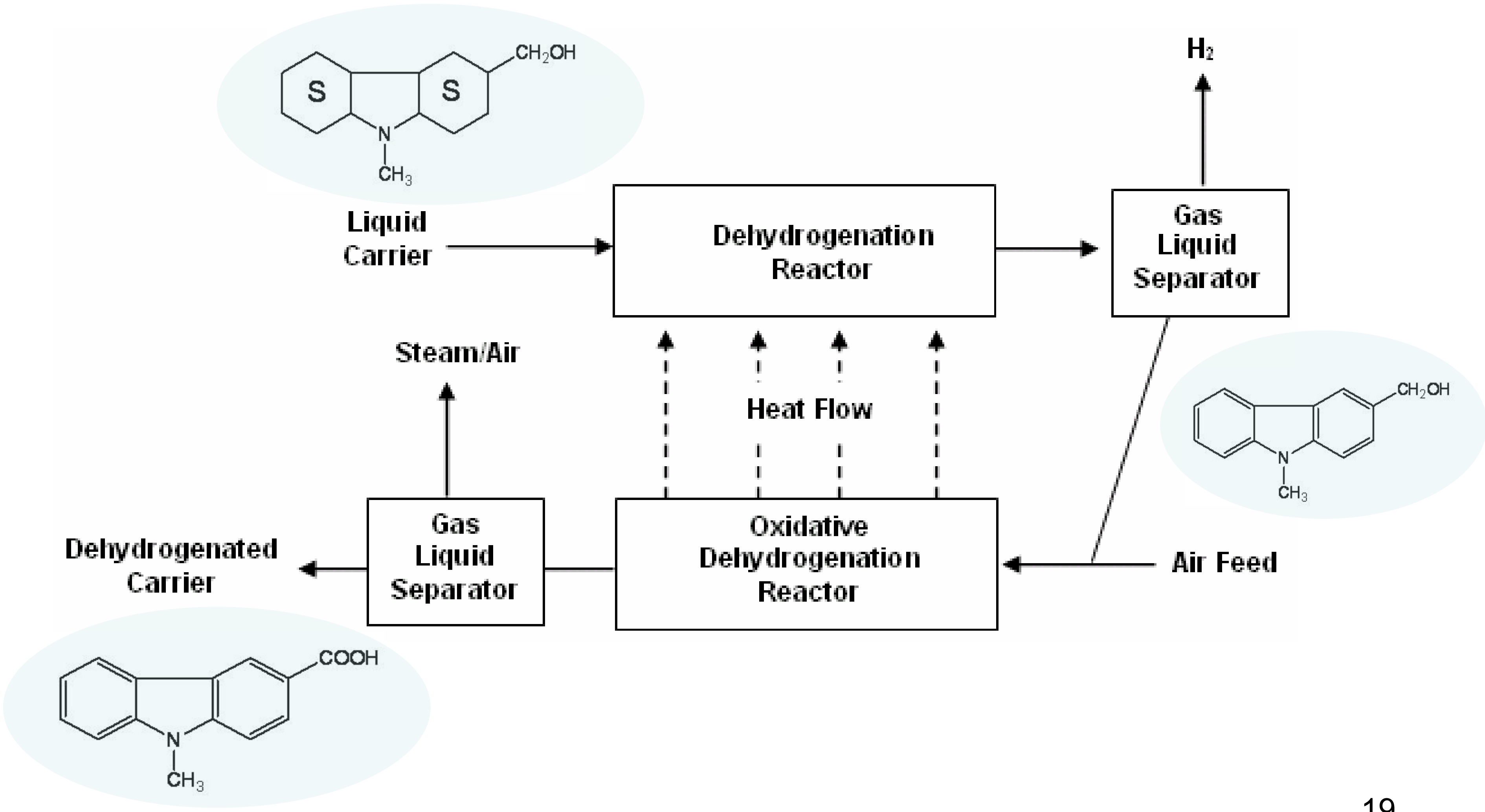
- **ca. 3 wt. % H_2 evolved under catalytic dehydrogenation conditions**
- **Undesired coupling of imine (CH=NH) intermediates leads to cyclization and formation of oligomers**
- **Other isomers may be less prone to oligomerization and/or cyclization**

Autothermal H_2 storage: a new concept for organic liquid H_2 carriers

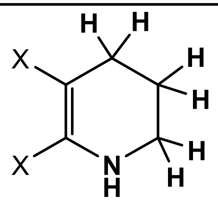
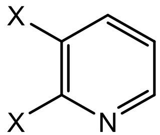


- 5.4 wt.% H_2 (material basis) with no external input of heat
- Only partial conversion to the fully oxidized product is necessary for autothermal operation
- Highly selective catalytic chemistry is known for all of these steps

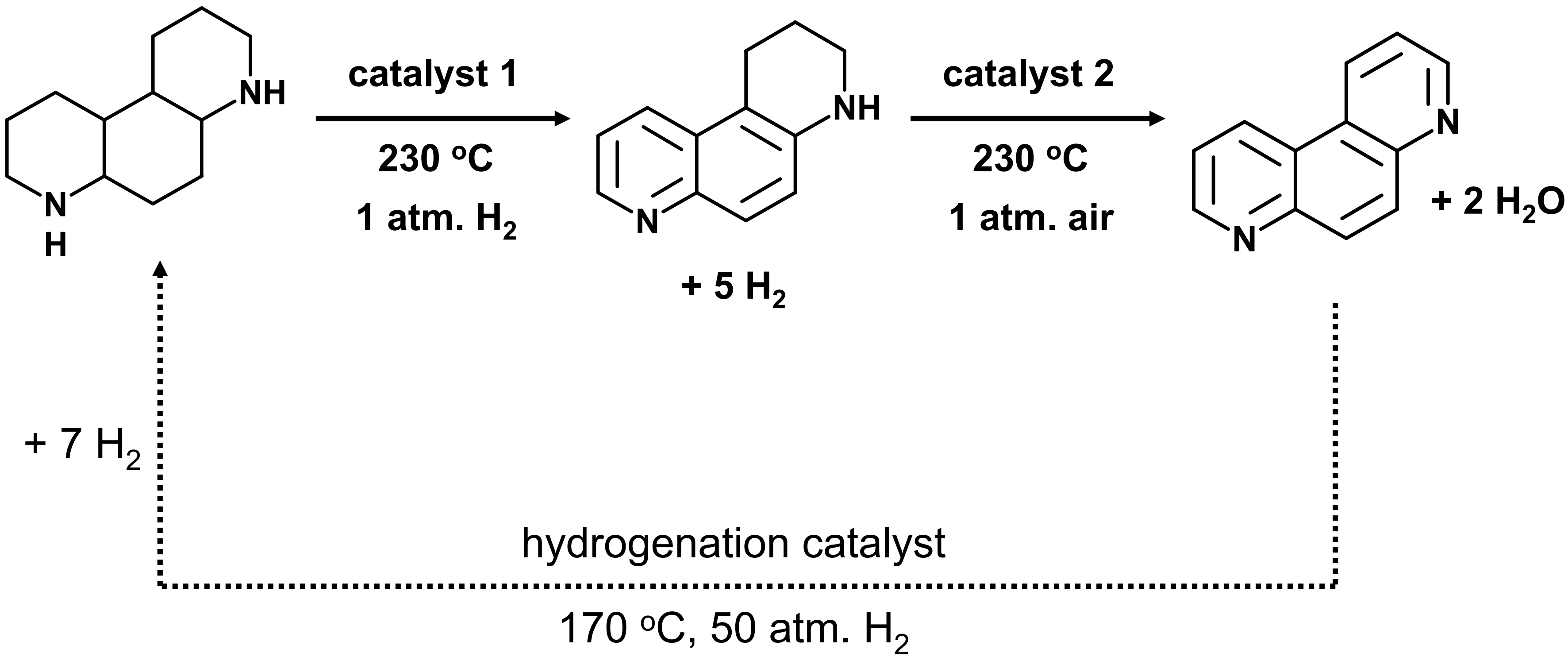
Autothermal H_2 storage: a new concept for organic liquid H_2 carriers



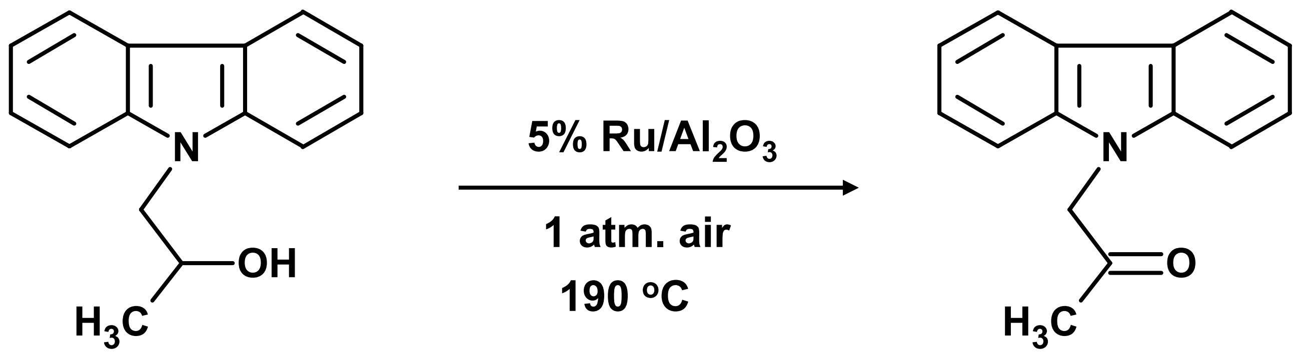
Selectively oxidizable functional groups for liquid carriers

Class of Selectively Oxidizable Functional Group	**Functional** Group in a Representative Molecule	Oxidative Dehydrogenation Product	Calorific Value per FW of Functional Group (kcal/gram)
Primary alcohols	a. Ar-$\mathbf{CH_2OH}$ b. Ar-$\mathbf{CH_2OH}$ c. R-$\mathbf{CH_2OH}$	Ar-CHO Ar-COOH R-CHO	1.37 3.33 1.34
Secondary alcohols	R-**CH(OH)-R’** Ar-**CH-OH-R**	RR’C=O Ar-CO-R	1.48 1.69
Primary amines	$\mathbf{R\text{-}CH_2NH_2}$	R−C≡N	2.79
Cyclic secondary amines			0.53
N-Methyl tertiary amines	RR’N-$\mathbf{CH_3}$	RR’CH(O)	6.53
Sulfides to Sulfoxides	R-**S**-R’	R−**S**(=O)−R'	0.84
Sulfoxides to Sulfones	R-**S(O)**-R’	R(SO_2)R’	1.10

Experimental example (non-optimized): Catalytic dehydrogenation and selective oxidation of 4,7-phenanthrolene



Experimental example (non-optimized): Catalytic dehydrogenation and selective oxidation of 1-(Carbazolyl)-2-Hydroxypropane



- Very high selectivity (>99%) observed for oxidation of alcohol to ketone

Future Work

- Development of new, improved liquid carriers
  - High dehydrogenation conversion <120 ^oC (eg. using carbolines)
    - Need: Better catalyst activity at very low temperatures
  - Complete amine → nitrile dehydrogenation studies
    - Increase selectivity for amine → nitrile dehydrogenation (eg. activated nitriles)
- Complete demonstration of autothermal dehydrogenation concept
  - Investigate multiple functional group transformations
    - alcohol → ketone
    - alcohol → carboxylic acid
- Additional improvement of surface-supported catalysts
  - Higher dehydrogenation rates
  - Characterization of hydrogen quality

- We seek input from DOE AMR reviewers and the FreedomCAR tech. team on the potential value of the autothermal dehydrogenation concept

Project 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. Multiple concepts to provide heat to liberate hydrogen onboard vehicle.
- Technical Accomplishments: Development of new liquid carriers with >7 wt. % capacity, Initial demonstration of autothermal hydrogen storage concept
- Future Research: Demonstrate complete autothermal dehydrogenation cycle with sufficient selectivity, rates. Complete testing of carriers with >7 wt. % capacity or dehydrogenation <120 ^{o}C.