

Hydrogen Storage by Reversible Hydrogenation of Liquid-phase Hydrogen Carriers

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STP 25

Overview

Timeline

- 2/04 – 9/08
- ~95% complete

Budget

- Total project \$6,121,242
 - DOE share \$4,346,082 (71%)
- FY07 funding \$1,025,000
- FY08 funding \$738,082

Interactions

- Current interactions: Auto OEM's, Argonne National Laboratory

Barriers

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

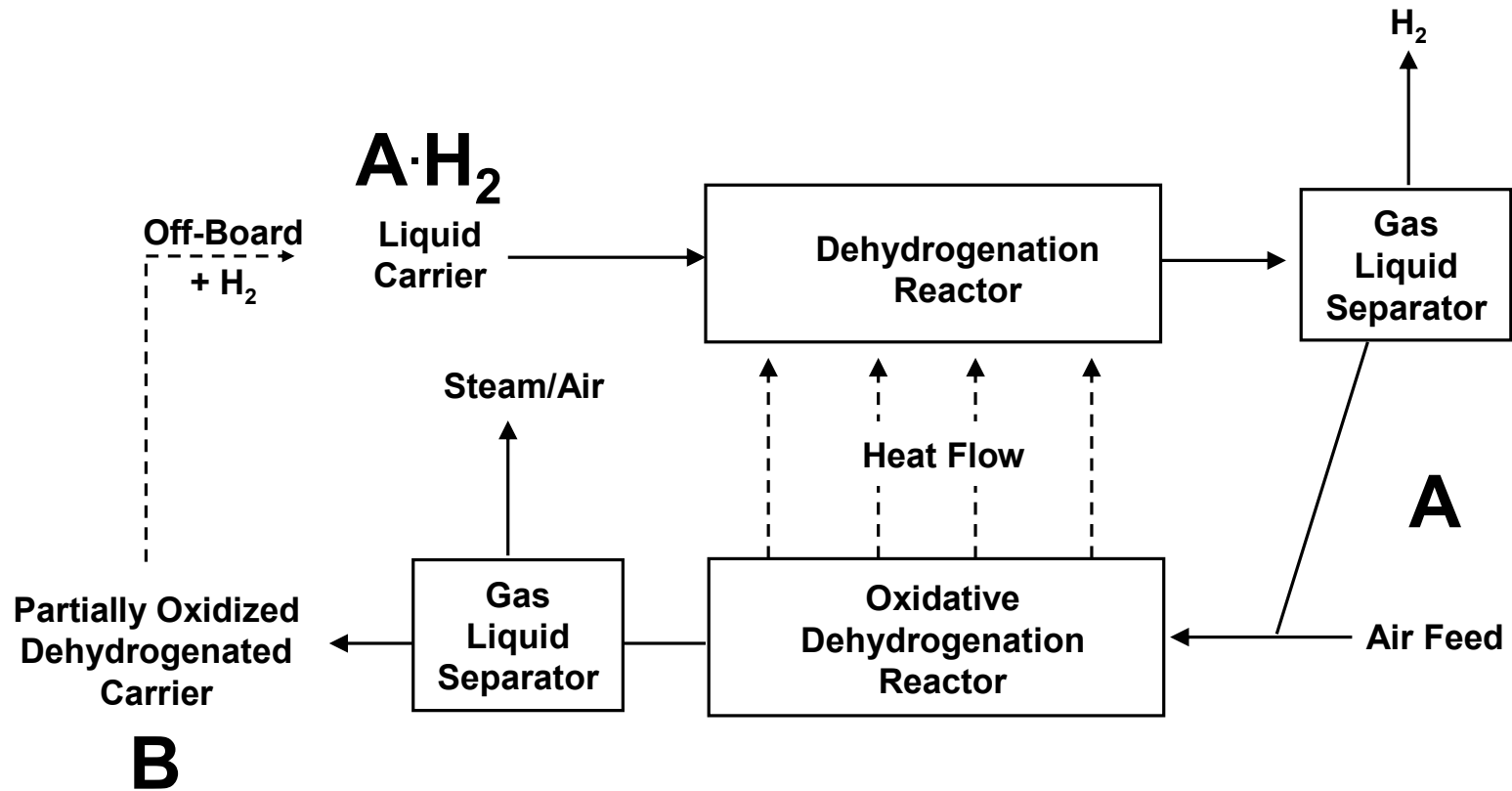
Objectives – H₂ Storage (2007-2008)

- **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 H₂), enabling the catalytic dehydrogenation at unprecedented temperatures (<200°C).**

Objectives (cont.) – H₂ Storage (2007-2008)

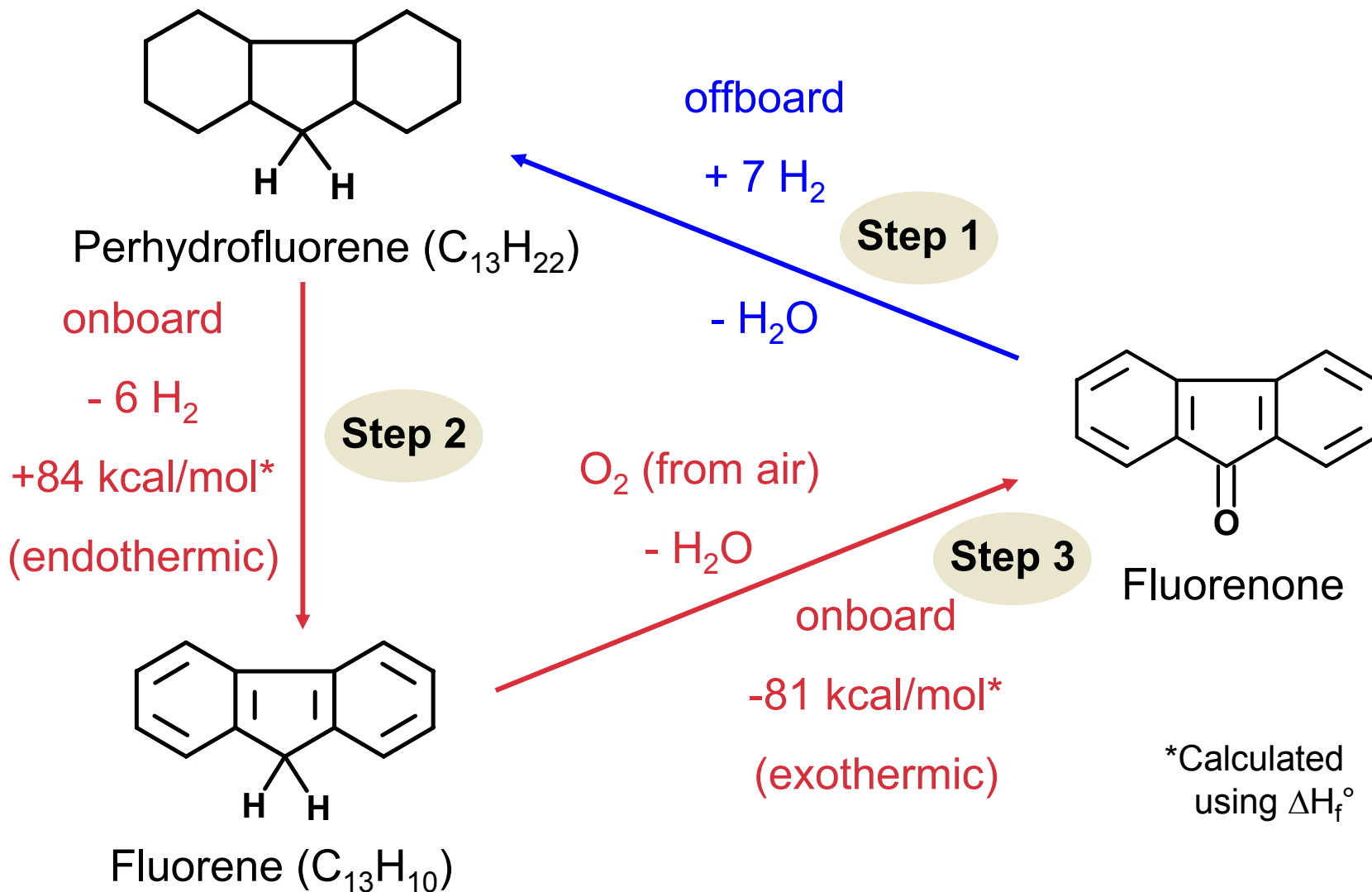
- **Multi-functional liquid carriers that enable autothermal dehydrogenation (primary project focus in 2007-2008)**
- **Low volatility (b.p. > 300°C), enabling the use of these liquids in simplified systems onboard vehicles and reducing exposure to vapors.**
- **Enhanced rates of catalytic dehydrogenation with wash coat catalysts.**

Autothermal Dehydrogenation Reactor System Schematic

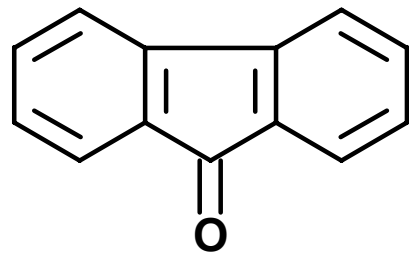


Endothermic dehydrogenation of the carrier thermally coupled to an exothermic selective oxidation of the dehydrogenated carrier \rightarrow no external heat input requirement

Autothermal Cycle Development Using Fluorene – Energetics



Step 1: Regeneration of oxidized carrier (fluorenone) back to perhydrofluorene

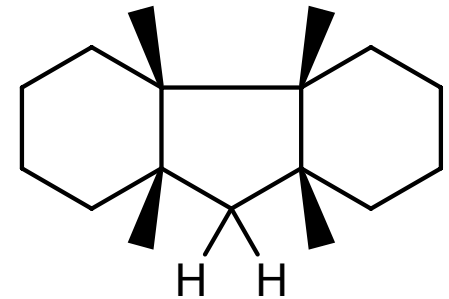


Fluorenone

Solid m.p. 83°C

b.p. ~350°C

- 1) Pd/SiO₂ catalyst, 70°C, 8 bar H₂
 - 2) Ru/Al₂O₃ Catalyst, 160°C, 60 bar H₂
- >99% conversion and selectivity**



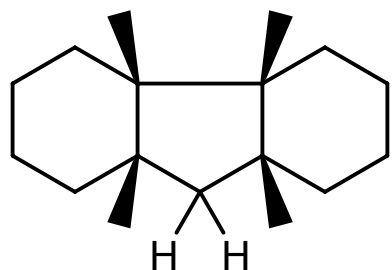
+ H₂O

>99% *cis,cis* conformer

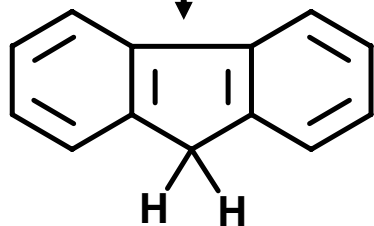
Liquid b.p. 253°C

Other catalysts (e.g., Pd, Rh) are equally selective, but yield mixtures with other conformers that have higher dehydrogenation temperatures.

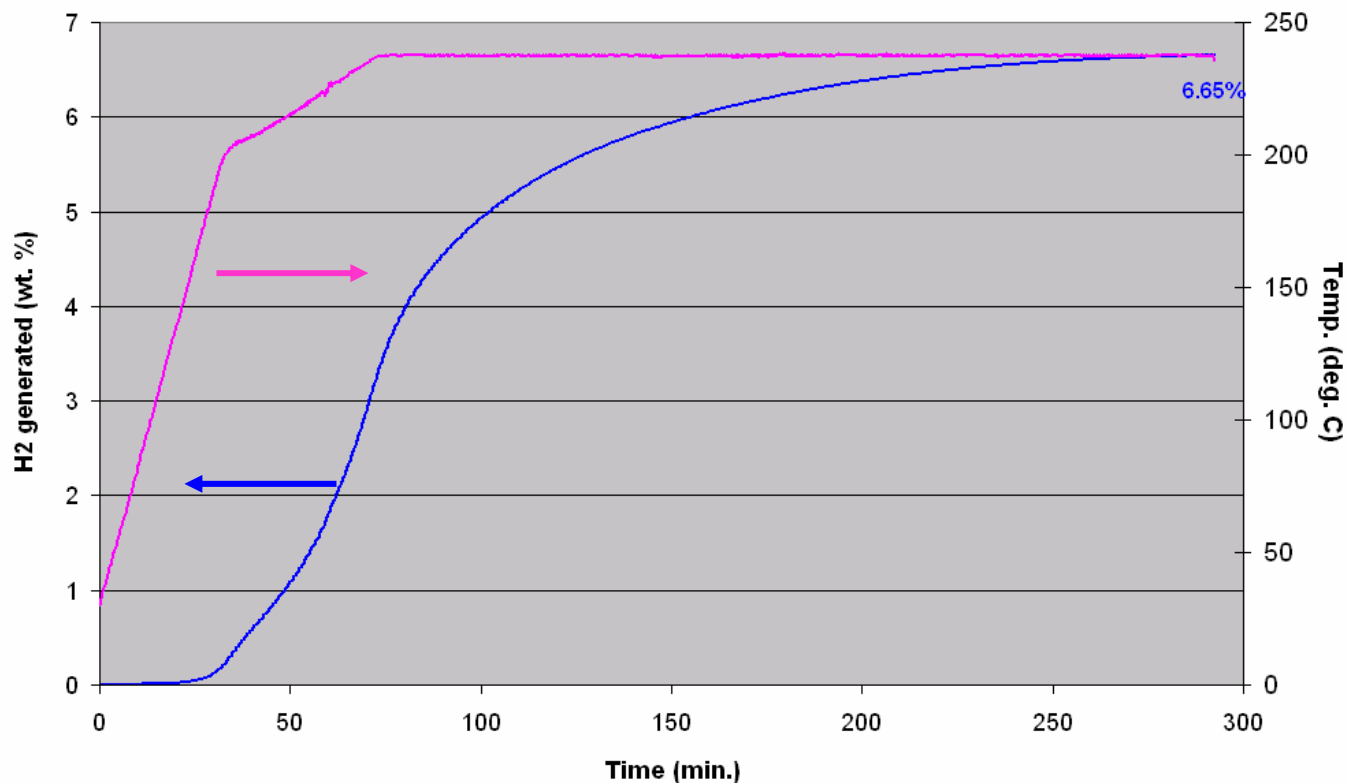
Step 2: Dehydrogenation of *cis,cis*-perhydrofluorene to fluorene (endothermic)



5% Pt/Al₂O₃
1 bar H₂,
235°C



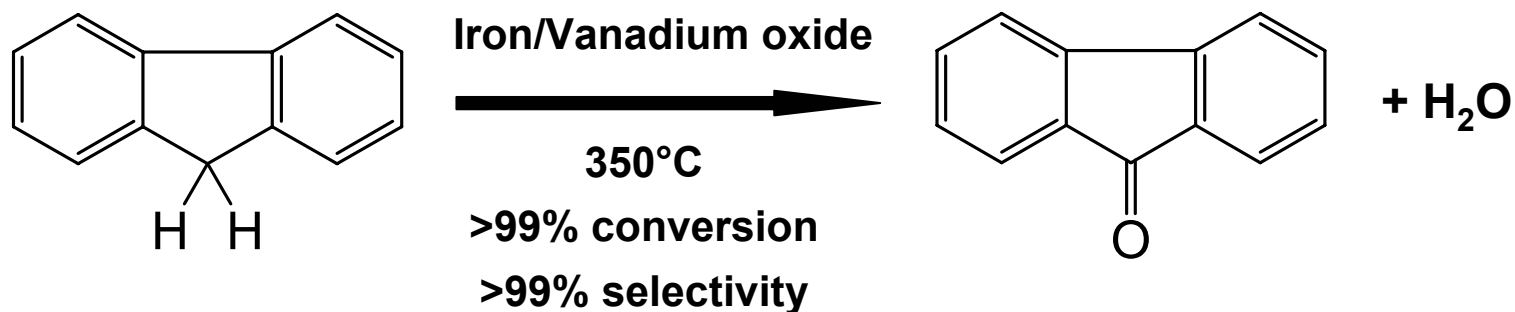
+ 6 H₂ (6.7 wt. %)



>99% conversion and selectivity at 235°C

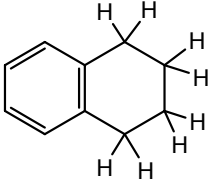
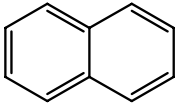
Not possible with a “natural” e.g., *cis, trans* mixture of conformers.

Step 3: Selective oxidation (exothermic) of fluorene to fluorenone

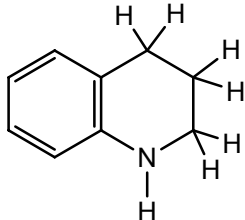
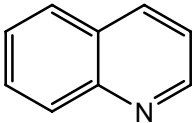
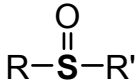


- Gas phase oxidation
- Very high selectivity and conversion

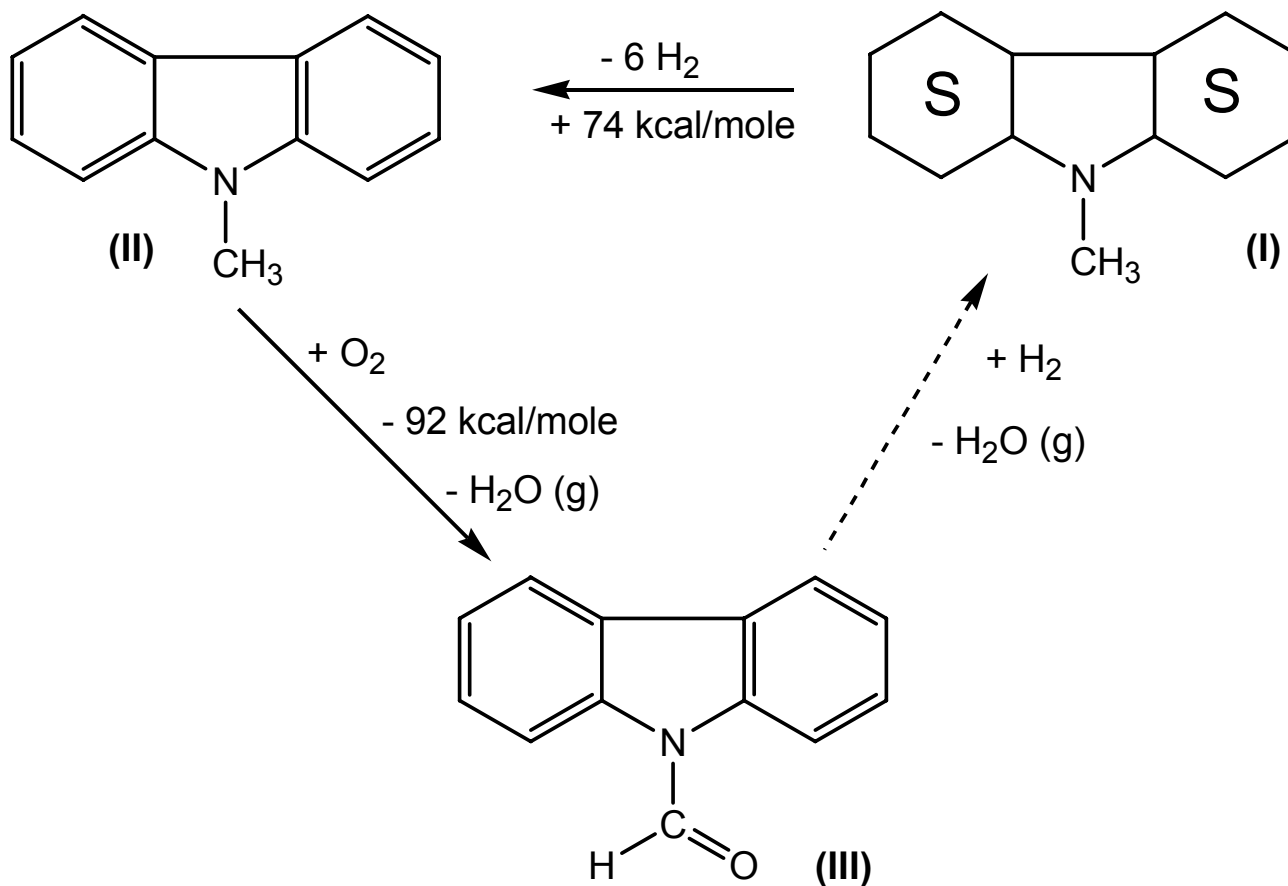
Selectively oxidizable functional groups for liquid carriers (I)

Class of Selectively Oxidizable Functional Group	Functional Group in a Representative Molecule	Oxidative Dehydrogenation Product	Calorific Value per FW of Functional Group (kcal/gram)
Activated hydrocarbon groups	a. Ar-CH ₃	Ar-CH ₂ OH	2.4
	b. Ar-CH ₃	Ar-CH(O)	5.2
	c. Ar-CH ₃	Ar-COOH	9.3
	d. Ar-CH ₂ -Ar	$\text{Ar}-\overset{\text{O}}{\parallel}{\text{C}}-\text{Ar}$	5.9
	e. 		1.1
Primary alcohols	a. Ar-CH ₂ OH	Ar-CHO	1.4
	b. Ar-CH ₂ OH	Ar-COOH	3.3
	c. R-CH ₂ OH	R-CH(O)	1.3
Secondary alcohols	R-CH(OH)-R'	RR'C=O	1.5
	Ar-CH-OH-R	ArRC=O	1.7

Selectively oxidizable functional groups for liquid carriers (II)

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 amines	$\text{CH}_3\text{-CH}_2\text{NH}_2$	$\text{R-C}\equiv\text{N}$	2.8
Cyclic secondary amines			0.5
N-Methyl tertiary amines	$(\text{CH}_3)_2\text{N-CH}_3$	$(\text{CH}_3)_2\text{N-CH(O)}$	6.5
Sulfides to Sulfoxides	$\text{R-S-R}'$ ($\text{R,R}'=\text{CH}_3$)		0.8
Sulfoxides to Sulfones	$\text{R-S(O)-R}'$ ($\text{R,R}'=\text{CH}_3$)	$\text{R(SO}_2\text{)R}'$	1.1

Potential Autothermal Cycle using N-methylcarbazole



Excess heat available from oxidation of methyl group to aldehyde

Summary

- An autothermal hydrogen storage cycle is possible using perhydrofluorene with:
 - ~95% conversion on dehydrogenation (net 6.3 wt. %)
 - 100% conversion during selective oxidation
- We have demonstrated all three steps of an autothermal hydrogen storage cycle with >99% selectivity.
 - Hydrogenation of fluorenone to perhydrofluorene
 - Dehydrogenation of perhydrofluorene to fluorene
 - Selective oxidation of fluorene to fluorenone
- A range of functional groups is available for exothermic selective oxidation reactions in designing new carriers.