IV.B.1 Hydrogen Storage by Reversible Hydrogenation of Liquid-Phase Hydrogen Carriers

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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°C).
- Multi-functional liquid carriers that enable autothermal dehydrogenation.
- Low volatility (boiling point >300°C), enabling the use of these liquids in simplified systems on-board vehicles and reducing exposure to vapors.
- Enhanced rates of catalytic dehydrogenation with wash coat catalysts.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) System Weight and Volume
(C) Efficiency
(E) Charging/Discharging Rates
(R) Regeneration Processes

Technical Targets

An off-board, regenerable liquid carrier for vehicles and stationary H_2 gas delivery with the following progress towards volumetric and gravimetric capacity targets:

TABLE 1. Hydrogen Storage Material Targets

Storage Parameter	Units	FY 2007 Material Targets	FY 2006 Materials	FY 2007 Materials
Specific Energy	wt% H_2	5.5/7	6.8	7.0
Volumetric Energy Capacity	g H_2/l		60	67
Desorption Temperature	°C	120/200	225	275

Table 1 demonstrates progress towards the FY 2007 material gravimetric target and FY 2006/FY 2007 gravimetric and volumetric material performance. Estimates of system-level hydrogen capacity (2010 storage system targets) can only be completed when several tasks (dehydrogenation reactor engineering and on-board system modeling) in an associated DOE hydrogen delivery project can be completed and potential 'credits' regarding conformability and waste heat utilization are evaluated.

Accomplishments

- Development of new liquid carriers with >7 wt% theoretical capacity and demonstration of high selectivity for hydrogenation and dehydrogenation.
- Introduction of a new autothermal hydrogen storage concept with organic liquid carriers. Initial demonstration of high selectivity for catalytic exothermic oxidation of carrier prototypes.
- Development of wash-coated catalysts with high activity approaching slurry catalysts.

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Introduction

This project is dedicated to the discovery of liquid-phase hydrogen storage materials (liquid carriers) that can be reversibly hydrogenated, allowing the storage of hydrogen in a safe, easily transportable form. The liquid carriers can be hydrogenated at large central or regional sites, in locations where inexpensive hydrogen is available, allowing for high overall energy efficiency through recovery and use of the heat generated by the exothermic hydrogenation. Alternatively, autothermal hydrogen carriers could provide both hydrogen and the thermal energy needed to liberate the hydrogen from the carrier. With potential use of at least part of the existing liquid fuels infrastructure, the hydrogenated liquid carrier could be provided to distribution sites where the liquid would be dispensed to hydrogen-powered vehicles. With a reasonable gravimetric hydrogen capacity (7 wt%) and density (1 g/cc), 5 kilograms of hydrogen would be contained in only 18.9 gallons of a liquid carrier, offering an attractive solution to both the hydrogen distribution and on-board storage challenges in a hydrogen economy.

Approach

The liquid-phase hydrogen carriers that are under development in this project must ideally demonstrate characteristics such as dehydrogenation thermodynamics allowing for low-temperature operation, stability over many cycles of hydrogenation and dehydrogenation, and low volatility. The dehydrogenation catalysts that are undergoing development should display high activity at low temperatures, high selectivity towards dehydrogenation, and long lifetime. Our high-throughput catalyst testing, designed to identify new catalyst compositions, is performed with slurry catalysts in small stirred tank reactors. However, the dehydrogenation catalyst must be utilized in a stationary form in end-use application on-board vehicles; research towards translating the effectiveness of slurry catalysts to surface-supported catalysts is therefore necessary. Autothermal hydrogen carriers under development that provide both hydrogen and the thermal energy needed to liberate the hydrogen from the carrier must demonstrate stability over many cycles of hydrogenation, dehydrogenation, and selective oxidation.

The experimental project operates via a systematic approach in which successful liquid carrier candidates have been identified through a process that involves: 1) rational selection based upon our experience with structure/property relationships, 2) computational modeling to establish heat of hydrogenation for carrier candidates using reliable high-level models, 3) obtaining high-purity compounds for laboratory testing from commercial sources or in-house organic synthesis, 4) catalytic hydrogenation of carrier candidates to establish viability based upon selective hydrogenation, and 5) catalytic dehydrogenation/selective oxidation testing to verify high selectivity and to screen known dehydrogenation catalysts in a preliminary catalyst optimization.

Results

Organic Liquid Carrier Discovery and Testing

Our new liquid carrier development includes primarily two types of new liquid carriers: 1) higher temperature, high capacity carriers, and 2) lower temperature, moderate capacity carriers. A lower ΔH potentially enables substantial conversion at lower temperatures than N-ethylcarbazole and closer to proton exchange membrane fuel cell waste heat temperatures (desirable ΔH range is 10-13 kcal/mol H_2).

We have identified a family of carrier prototypes, with low enthalpies of hydrogenation, based upon β-carboline (Figure 1). The average heat of hydrogenation of β-carboline is 10.4 kcal/mol H_2 (cf. N-ethylcarbazole average $\Delta H = 11.3$ kcal/mol H_2). The synthesis of perhydro-N-ethyl-β-carboline was completed starting from commercially available tetrahydro-β-carboline. Upon dehydrogenation testing using palladium on carbon catalyst, clean dehydrogenation was observed (no byproducts), but only partial conversion – limiting the available hydrogen storage capacity. In addition, the temperatures required for dehydrogenation were higher than predicted by calculated dehydrogenation energetics. Our conclusion is that the catalyst activity is limiting at lower temperatures (<150°C). Devising more active catalysts will be necessary for exploiting the potential of perhydro-N-ethyl-β-carboline dehydrogenation at these temperatures.

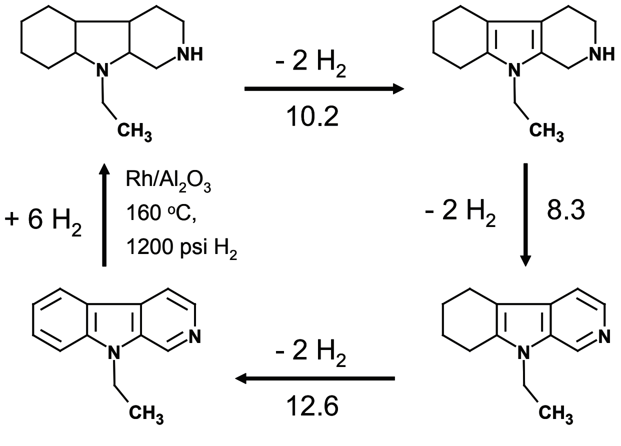


FIGURE 1. Calculated Energetics of Stepwise Heat of Dehydrogenation (kcal/mol H_2) of Perhydro-N-Ethyl-β-Carboline

The calculation of an average heat of hydrogenation of a potential hydrogen storage candidate is a valuable technique that has been used successfully as the first step in our liquid carrier discovery effort. However, the energetics of stepwise dehydrogenation are critical in evaluating potential carriers. With certain molecules, a number of isomers are possible and each isomer has different stepwise heats of dehydrogenation which, depending on the molecule symmetry, results in multiple possible pathways for stepwise dehydrogenation. An example of a potential carrier with a number of isomers is naphthyridine (7.2 wt% H_2 theoretical capacity). The 1,6 isomer of this molecule has two different potential dehydrogenation pathways with large differences in heats for the intermediate steps (Figure 2). Experimental testing must be performed to determine the operational pathway for catalytic dehydrogenation. A sample of perhydro-1,6-naphthyridine was synthesized for dehydrogenation testing. The results showed 7 wt% hydrogen evolution, but we found that the reaction pathway presumably goes through the non-preferred intermediate (Figure 2, top) due to the very high temperature (ca. 275°C) that was necessary for complete dehydrogenation.

A potential class of hydrogen carriers with >7 wt% H_2 are aromatic molecules with nitrile groups (carbon-nitrogen triple bond). The hydrogenation of nitriles is well known in the chemical literature and can be achieved with high selectivity using "base modified" catalysts. The thermodynamics of nitrile hydrogenation have been calculated for a number of examples and suggest that the dehydrogenation will require higher temperatures than other liquid carriers (ΔH above preferred 10-13 kcal/mol range). Our preliminary experimental testing of fully saturated aromatic nitriles was performed with dehydrogenation of 1,3-bis(methylamino)cyclohexane (9.9 wt% H_2 theoretical capacity). The results suggest that only ca 3 wt% H_2 evolved under catalytic dehydrogenation conditions. The selectivity of hydrogenation was very poor and undesired coupling of imine (CH=NH) intermediates was likely, leading to cyclization byproducts and and formation of oligomers. While the testing of 1,3-bis(methylamino)cyclohexane was unsuccessful, other molecules are under investigation which may be less prone to oligomerization and/or cyclization.

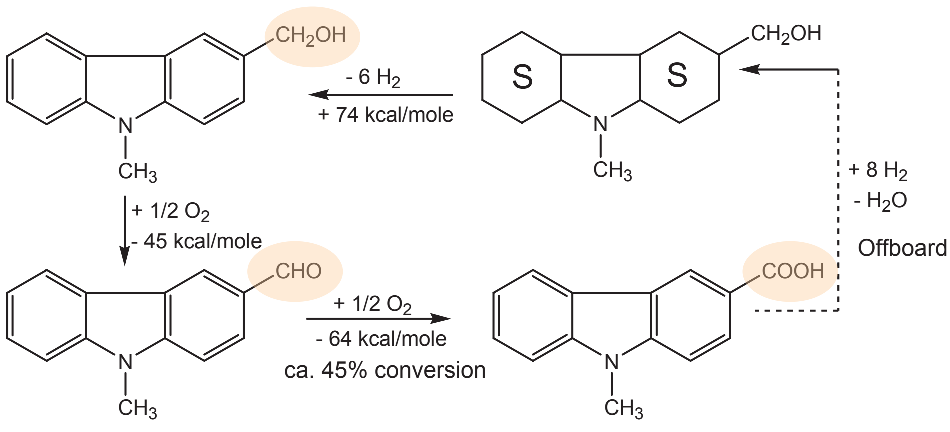


FIGURE 3. Illustration of the Complete Autothermal Dehydrogenation Cycle of Perhydro-3-Hydroxymethyl-N-Methylcarbazole Showing Calculated Reaction Energies for the Individual Steps

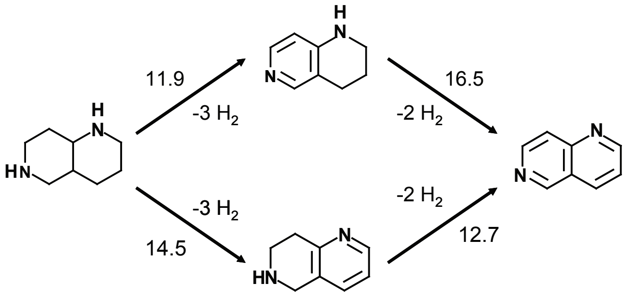


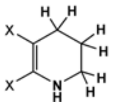
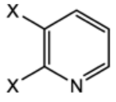
FIGURE 2. Calculated Energetics of Stepwise Heat of Dehydrogenation (kcal/mol H_2) of Perhydro-1,6-Naphthyridine for Two Possible Reaction Pathways

A New Concept: Autothermal Hydrogen Storage with Organic Liquid Carriers

Unlike the other types of liquid carriers under investigation within this project that require an external input of thermal energy (e.g. from power source waste heat or burning hydrogen), autothermal hydrogen carriers could provide both hydrogen and the thermal energy needed to liberate the hydrogen from the liquid carrier. This concept requires a highly selective catalytic oxidation step, using air, which is exothermic and well heat-integrated with endothermic dehydrogenation. An example of a molecule that could undergo autothermal dehydrogenation is perhydro-3-hydroxymethyl-N-methylcarbazole (Figure 3). This carrier has a theoretical hydrogen capacity 5.4 wt% H_2 (material basis) with no external input of heat. The endothermic dehydrogenation of the fully saturated alcohol can yield 6 moles of hydrogen per mole of carrier with input of 74 kcal/mol carrier. The necessary heat for dehydrogenation could be derived from a selective oxidation of the alcohol functional group to a mixture of the aldehyde and carboxylic acid functionalized carbazole (Figure 3). Only partial conversion to the fully oxidized product (carboxylic acid) is necessary for autothermal operation. Hydrogenation of the mixture of the aldehyde- and carboxylic acid-functionalized carbazole mixture back to the fully saturated perhydro-3-hydroxymethyl-N-methylcarbazole could be accomplished with hydrogen under known catalytic conditions. While the complete cycle requires three different steps, highly selective catalytic chemistry is known in the literature for all of these steps for similar substrates.

The oxidation of alcohols to aldehydes and/or carboxylic acids is only one example of the potential selectively oxidizable functional groups for liquid carriers. Table 2 shows a number of functional group oxidations and the calorific value per formula weight (FW) of the functional group.

TABLE 2. Functional Groups with Potential for Exothermic Selective Oxidation

Class of Selectively Oxidizable Functional Group	Functional Group in a Representative Molecule	Oxidative Dehydro-Genation Product	Calorific Value per FW of Functional Group (kcal/gram)
Primary Alcohols	Ar-$\mathbf{CH_2OH}$ Ar-$\mathbf{CH_2OH}$ 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	R-$\mathbf{CH_2NH_2}$	R-C≡N	2.79
Cyclic secondary Amines			0.53
N-Methyl Tertiary Amines	RR′N-**CH3**	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(S**O2**)R′	1.10

In laboratory testing, we have demonstrated very high selectivity for two of the selective oxidations shown in Table 2. In a non-optimized experimental example, perhydro-4,7-phenanthrolene was partially dehydrogenated to tetrahydro-4,7-phenanthrolene via endothermic dehydrogenation. The tetrahydro-4,7-phenanthrolene was then subsequently oxidized with 1 atm air to the fully aromatic 4,7-phenanthrolene, with generation of two moles of water per mole of 4,7-phenanthrolene. The 4,7-phenanthrolene can be converted back to perhydro-4,7-phenanthrolene using hydrogen under standard hydrogenation conditions.

An additional non-optimized experimental example is found in the selective oxidation of 1-(carbazolyl)-2-hydroxypropane to the corresponding ketone under 1 atm air at 190°C. Using a ruthenium catalyst, very high selectivity (>99%) observed for oxidation of this alcohol to the ketone. In order to prove oxidative dehydrogenation vs. endothermic dehydrogenation (to form hydrogen), water in the effuent of the air stream was captured in a cold bath and the quantity measured to confirm the correct stiochiometry (one mole of water per mole of 1-(carbazolyl)-2-hydroxypropane).

Dehydrogenation Catalyst Development

The development of wash-coated catalysts with high activity was accomplished in FY 2007. Our high-throughput catalyst testing, designed to identify new catalyst compositions, is performed with slurry catalysts in small stirred tank reactors. However, the dehydrogenation catalyst must be utilized in a stationary form in end-use application onboard vehicles. One simple example of a stationary form for catalysts is to place large pellets of the catalyst in a packed bed. Previously reported testing of dehydrogenation catalysts in pelletized form (e.g. in a packed bed reactor) showed that the effectiveness is limited by mass transfer limitations. The measured effectiveness factor (% of available active metal catalyst) was only 0.08. Thin catalyst coatings (10-20 μm) on a surface should improve the effectiveness of the catalyst. In chemical processing, thin coatings (wash coats) are catalysts used in practical reactors (e.g. microreactors and monoliths).

Our catalyst testing protocols use slurry reactors to measure intrinsic catalyst activity, data that is employed for modeling reaction kinetics. There are various reactor options for evaluating catalyst activity for wash-coated monoliths. In FY 2007, we began the use of a circulating flow reactor to measure wash coat catalyst activity on monoliths. In order to compare the two types of catalysts, the kinetics model for the slurry catalyst was used to relate the intrinsic activity of the slurry catalyst to a wash-coated catalyst on a monolith (Figure 4). The data shows that the activity of the monolith at low conversion is close to the slurry catalyst; a high effectiveness factor was demonstrated (8X higher than packed bed reactor).

Conclusions and Future Directions

Our efforts in FY 2007 have resulted in the development of new liquid carriers with >7 wt% capacity at high temperatures, potential low-temperature carriers with thermodynamics for hydrogen release at temperatures <120°C, initial demonstration of an

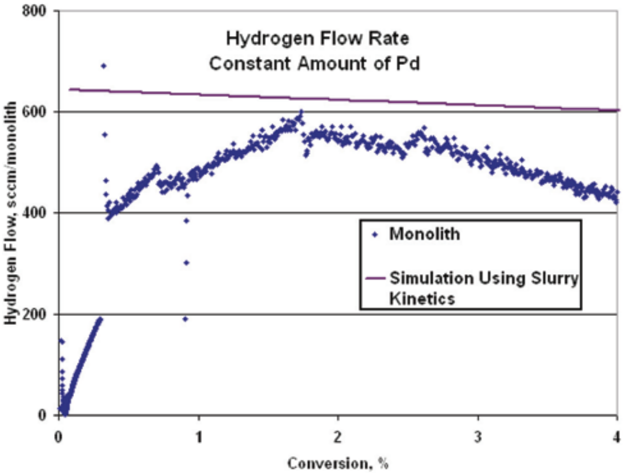


FIGURE 4. Plot of hydrogen flow vs. conversion for dehydrogenation of perhydro-N-ethylcarbazole in a circulating flow reactor with a palladium containing monolith. The overlay shows the simulated conversion from the kinetics modeling of dehydrogenation data with a palladium on alumina slurry catalyst.

autothermal hydrogen storage concept, and improved catalyst activity for wash-coated catalysts.

Future work includes the development of new, improved liquid carriers with either high capacity (7-9 wt%; e.g. using hydrogenated nitriles) at higher temperatures or substantial dehydrogenation conversion <120°C (e.g. using carbolines). To enable high dehydrogenation conversion <120°C, we need to demonstrate higher catalyst activity at these very low temperatures. To enable improved liquid carriers with high capacity (7-9 wt%; e.g. using hydrogenated nitriles), an increase in the selectivity for amine to nitrile dehydrogenation is necessary (perhaps via the use of "activated" nitriles).

Additional work is planned to complete the demonstration of autothermal dehydrogenation concept, including investigation of multiple functional group transformations (e.g. alcohol to ketone, alcohol to carboxylic acid) and additional improvement of surface-supported catalysts with the goal of higher dehydrogenation rates.

Special Recognitions & Awards/Patents Issued

1. U.S. 7,101,530, Hydrogen Storage By Reversible Hydrogenation of Pi-conjugated Substrates.

FY 2007 Publications/Presentations

1. "Integrated Hydrogen Storage and Delivery Using Organic Liquid-Phase Carriers", MH2006 Conference.

2. "Hydrogen Storage: From Carbon Nanotubes to H_2-Reversible Liquid Carriers", SAE Hydrogen Storage Challenges for Mobility Symposium, December 7, 2006.

3. "Hydrogen Storage by Reversible Hydrogenation of Liquid-phase Hydrogen Carriers", International Energy Agency Task 22 Workshop, January 2007.