

IV.B.3 Design and Development of New Carbon-based Sorbent Systems for an Effective Containment of Hydrogen

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Objectives

- Development of liquid-phase hydrogen storage materials with capacities of greater than 7 wt% and >60 g H₂/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.
 - Optimal heat of dehydrogenation (10-13 kcal/mole H₂), enabling the catalytic dehydrogenation at unprecedented temperatures ($<200^{\circ}\text{C}$).
 - Low volatility (boiling point $>300^{\circ}\text{C}$), enabling the use of these liquids in simplified systems onboard vehicles and reducing exposure to vapors.
 - Acceptable cost for the liquid carrier and the hydrogenation process.

Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies

Program Multi-Year Research, Development and Demonstration Plan:

- (A) Cost
- (B) Weight and Volume
- (C) Efficiency
- (E) Refueling Time
- (R) Regeneration Processes

Technical Targets

An off-board, regenerable liquid carrier for vehicles and stationary H₂ gas delivery with the following progress towards volumetric and gravimetric capacity targets (Table 1).

TABLE 1. Hydrogen Storage Material Targets

Storage Parameter	Units	FY 2006 Material Target	FY 2005 Materials	FY 2006 Materials
Specific Energy	Wt% H ₂	7	5.7	7.2
Volumetric Energy Capacity	g H ₂ /l		54	69
Desorption Temperature	$^{\circ}\text{C}$	200	180-200	200-225

Table 1 demonstrates progress towards the FY 2006 material gravimetric target and FY 2005/FY 2006 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

- Demonstrated reversible hydrogen capacity of >7 wt% and >65 g H₂/l with new liquid carrier prototypes.
- Identified energetic conformers that significantly lower dehydrogenation temperatures for perhydro-N-ethylcarbazole to 100-120 $^{\circ}\text{C}$ for a portion of the stored hydrogen. This strategy could be used for a large number of potential liquid carriers.
- Designed and tested dehydrogenation catalysts with precious-metal loading decreased by a factor of 10

relative to commercial catalysts, while also showing superior activity relative to the commercial catalysts.

- Discovered a new class of liquid carriers with oxygen heteroatoms.

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. Potentially using 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.

Approach

The liquid-phase hydrogen carriers that are being developed in this project must demonstrate characteristics including: 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.

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) hydrogenation of carrier candidates to establish viability based upon selective hydrogenation, and 5) dehydrogenation testing to verify high selectivity and to screen known dehydrogenation catalysts in a preliminary catalyst optimization.

Results

The previous year results showing the highly selective and reversible hydrogenation of N-ethylcarbazole (5.7 wt% H₂) have been improved by the use of more energetic conformational isomers (conformers) of perhydro-N-ethylcarbazole to lower the dehydrogenation temperature. The hydrogenation of molecules that have multiple fused rings may in some cases yield more than one product of the same overall chemical composition. There may be found structural isomers or conformers of the product molecule that differ only in the relative disposition of the molecule's carbon-hydrogen bonds or of other atoms or groups of atoms in the molecule. The conformers will each have different energies (standard heats of formation, ΔH_f°), the thermodynamically most stable conformer having the lowest ΔH_f° . In practice, the formation of conformers will depend on the conditions at which the catalytic hydrogenation of the pi-conjugated substrate is carried out; lower hydrogenation reaction temperatures favor formation of the least stable (i.e., more energetic) conformer molecules. Conversely, a hydrogenation of the pi-conjugated substrate at higher temperatures results in an equilibrium (i.e., a lower energy distribution of conformers). The formation of such non-equilibrium conformers provides a means of desirably lowering the hydrogenation enthalpy, ΔH , of the pi-conjugated, unsaturated molecule, by making its hydrogenation product less stable, thus enabling the dehydrogenation process to occur at a lower temperature. In some cases, depending on the catalytic dehydrogenation mechanism, there may also be the additional advantage of a kinetically more facile dehydrogenation of the more energetic non-equilibrium conformers.

We verified that less stable conformers (prepared by hydrogenating N-ethylcarbazole at 120°C) will release hydrogen at lower temperatures relative to the more stable conformers (prepared by hydrogenating at 170°C). In Figure 1, mixture A of hydrogenated N-ethylcarbazole

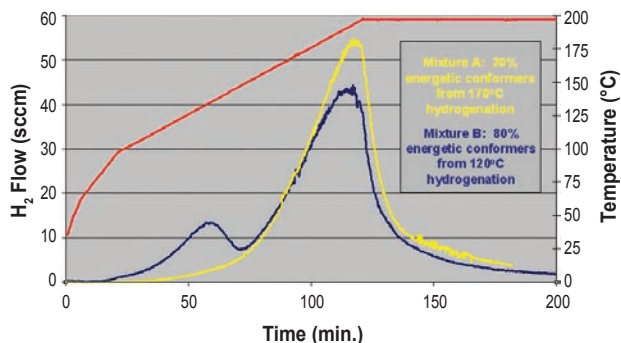


FIGURE 1. Overlay Plot of Dehydrogenation of Two Samples of Perhydro-N-ethylcarbazole Demonstrating Differences between Conformer Mixtures

contains a low percentage (20% overall) of two less stable perhydro-N-ethylcarbazole conformers, and this mixture shows lower hydrogen release at the more desirable low temperatures of dehydrogenation. Mixture B of hydrogenated N-ethylcarbazole contains a high percentage (80% overall) of two less stable perhydro-N-ethylcarbazole conformers, and this mixture shows higher hydrogen release at the more desirable low temperatures of dehydrogenation. During the temperature ramp from 100 to 200°C (indicated by the red line), mixture A shows a peak in the hydrogen flow in the low temperature range of ca. 100-140°C, which was not observed for mixture B.

To enable dehydrogenation of liquid carriers at very low temperatures, it is necessary to have a dehydrogenation catalyst that is active and that demonstrates acceptable rates at these low temperatures. We have continued the development of novel dehydrogenation catalysts and have demonstrated that the amount of precious metal loading can be reduced significantly while maintaining activity at temperatures <200°C. In a comparison of two platinum-based catalysts for the dehydrogenation of perhydro-N-ethylcarbazole, we were able to reduce the platinum loading by a factor of 10 relative to a commercial 5% platinum on alumina catalyst, while demonstrating higher activity, as shown by the faster rates of dehydrogenation relative to the commercial catalyst in Figure 2. As shown in the dehydrogenation of less stable conformers of perhydro-N-ethylcarbazole in Figure 1, these dehydrogenation catalysts demonstrate some activity at temperatures as low as 100°C.

In an effort to increase the hydrogen capacity of the liquid carriers, we have developed and tested a number of new, higher capacity liquid carriers during the past year of the hydrogen storage project. We have

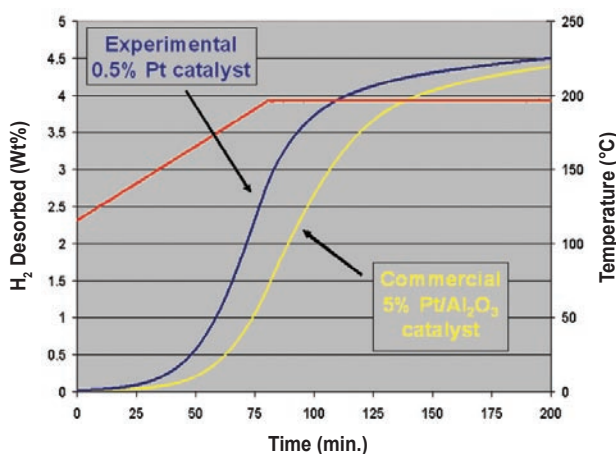


FIGURE 2. Overlay Plot of Dehydrogenation of Perhydro-N-ethylcarbazole with Two Platinum-On-Alumina Catalysts Showing Development of Highly Active Dehydrogenation Catalysts

increased the capacity of alkylated carbazole carriers by demonstrating that N-methylcarbazole (6.2 wt% H₂ and 59 g H₂/l) can be reversibly hydrogenated in the same manner as N-ethylcarbazole (5.7 wt% H₂). Figure 3 shows the dehydrogenation of perhydro-N-methylcarbazole by ramping the temperature to 200°C and holding at this temperature.

However, in order to achieve >7 wt% H₂ capacity, every carbon and/or nitrogen atom in the liquid carrier molecules must be utilized during the hydrogenation (unlike the nitrogen atom and alkyl groups in the alkylated carbazoles). We have developed a new class of liquid carrier prototypes based upon nitrogen-substituted aromatic molecules in which the hydrogen capacity is >7 wt% H₂ and typically >65 g H₂/l (depending on liquid density). An example of this class of liquid carriers is 4,7-phenanthroline. Figure 4 shows that perhydro-4,7-phenanthroline can be dehydrogenated at temperatures <225°C. Due to thermodynamic limitations with this particular molecule, a reversible capacity of >7 wt% is only achieved slowly at 225°C. However, we are

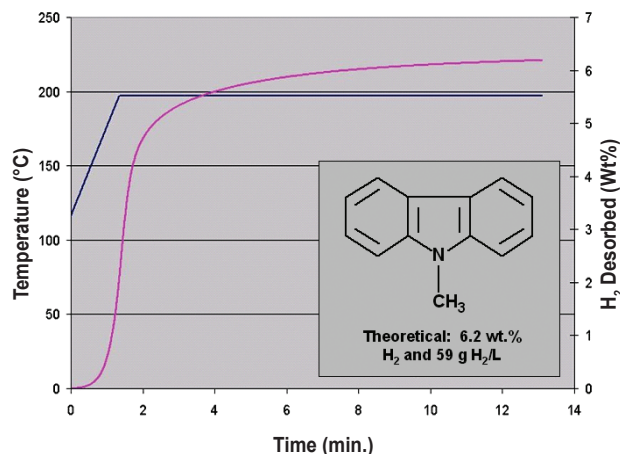


FIGURE 3. Plot of Perhydro-N-methylcarbazole Dehydrogenation

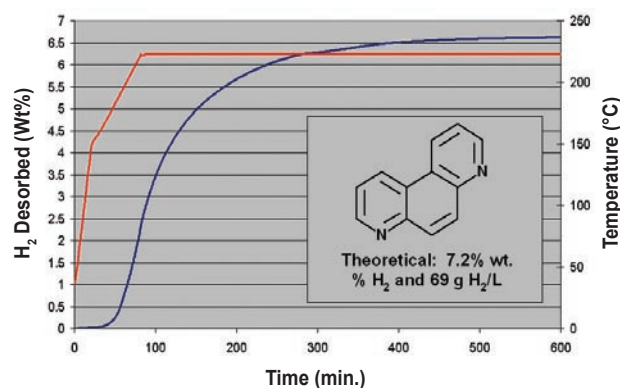


FIGURE 4. Plot of Perhydrophenanthroline Dehydrogenation

currently developing other similar liquid carrier prototypes based upon nitrogen-substituted aromatic molecules that have more suitable thermodynamics for low-temperature dehydrogenation while maintaining >7 wt% H₂ capacity.

We have also developed a separate class of liquid carrier prototypes that include oxygen heteroatoms instead of nitrogen. An example of this new class is perhydrodibenzofuran, containing only carbon, oxygen, and hydrogen (C₁₂H₂₀O) and a theoretical hydrogen capacity of 6.6 wt% H₂ and 69 g H₂/l. It is worth noting that we have been able to hydrogenate a large variety of liquid carrier candidates (nitrogen-containing, oxygen-containing, containing six-membered rings, containing five- and six-membered rings) with excellent (>99%) selectivity in many cases.

Conclusions and Future Directions

- Keep focus on fundamentals, e.g., energetic conformer identification and utilization.
- New carrier discovery:
 - Focus on current prototype carriers with 7+ wt% capacity.
 - Investigate new classes of carriers with higher chemical unsaturation (triple bonds) that can yield >1 H per atom and >8 wt% theoretical capacity.
- Maintain attention to correct thermodynamics for low-temperature dehydrogenation
- New dehydrogenation catalysts:
 - This discovery effort may benefit from combinatorial approach and possible participation by a partner (subcontractor).
- Select carriers for lifetime testing and scale up late in FY 2007.

Special Recognitions & Awards/Patents Issued

1. 2006 DOE Hydrogen Program R&D Award (presented at 2006 DOE Hydrogen Program Annual Merit Review).
2. Highest merit review score out of 18 hydrogen storage projects from the 2005 DOE Hydrogen Program Annual Merit Review.

FY 2006 Publications/Presentations

1. “Integrated Hydrogen Storage and Delivery using Organic Liquid Carriers,” Materials Science and Technology Conference, 9/05, Invited Presentation.
2. “Hydrogen Storage and Delivery in a Liquid Carrier Infrastructure,” Materials Research Society Spring Meeting, 4/06, Invited Presentation.
3. “Hydrogen Storage by Reversible Hydrogenation of Liquid-phase Hydrogen Carriers,” International Energy Agency Hydrogen Storage Workshop, 5/06.
4. “Hydrogen Storage by Reversible Hydrogenation of Liquid-phase Hydrogen Carriers,” 2006 DOE Hydrogen Program Annual Merit Review, 5/06.
5. “An Integrated Hydrogen Storage and Delivery Approach Using Liquid-phase Carriers,” World Hydrogen Energy Conference, 6/06 (presentation and publication).
6. “Hydrogen Storage by Reversible Hydrogenation of Liquid-phase Hydrogen Carriers,” FreedomCAR Technical Team review, 6/06.