

IV.B.2 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.
 - Discovery of multi-functional liquid carriers that enable the development of an autothermal hydrogen storage system (i.e., liquid carrier dehydrogenation with no external input of heat).
 - Demonstration of selective, reversible catalytic hydrogenation, dehydrogenation, and oxidation (autothermal carriers) and multiple cycles of use with no significant degradation of the materials.
 - Discovery of liquid carriers that have optimal heats of dehydrogenation (10-13 kcal/mole H₂), enabling the catalytic dehydrogenation at unprecedented temperatures (<200°C).

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

Technical Targets

Discovery and testing of off-board, regenerable liquid carriers for vehicles and stationary H₂ gas delivery with the following progress towards volumetric and gravimetric capacity targets:

TABLE 1. Hydrogen Storage Material Targets

Storage Parameter	Units	FY08 Material Targets	FY07 Materials	FY08 Materials
Specific Energy	wt% H ₂	6.5	7.0	6.3
Volumetric Energy Capacity	g H ₂ /l	60	67	58
Desorption Temperature	°C	Autothermal	275	235 (Autothermal)

Table 1 demonstrates progress towards the Fiscal Year 2008 material targets and FY 2007/2008 gravimetric and volumetric material performance. As detailed in the results section, a goal in FY 2008 was the discovery of an autothermal liquid carrier rather than a lower desorption temperature. 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

- Discovery and successful demonstration of an autothermal liquid carrier prototype that exhibits >99% conversion and selectivity for all three steps of the autothermal cycle featuring:
 - A two-step hydrogenation scheme which uses only gaseous hydrogen as a reagent and commercially available catalysts and results in >99% yield of a desired isomer of the perhydrogenated carrier.

- The highly selective gas-phase catalytic oxidation of the dehydrogenated carrier with uncompressed air to yield a single product.



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 some utilization 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 19 gallons of a liquid carrier, offering an attractive solution to both the hydrogen distribution and onboard storage challenges in a hydrogen economy.

Approach

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 testing and selective oxidation testing (for autothermal carriers) to verify high selectivity.

Results

Autothermal Hydrogen Storage Concept Development

We have been pursuing the concept of an autothermal dehydrogenation process wherein the heat required for the release of H₂ from the hydrogenated liquid carrier is supplied by an aerobic oxidative dehydrogenation step using the dehydrogenated carrier, thus not requiring an input of heat from an external source or heat derived from burning of the hydrogen (Figure 1). The temperature of the heat generated by

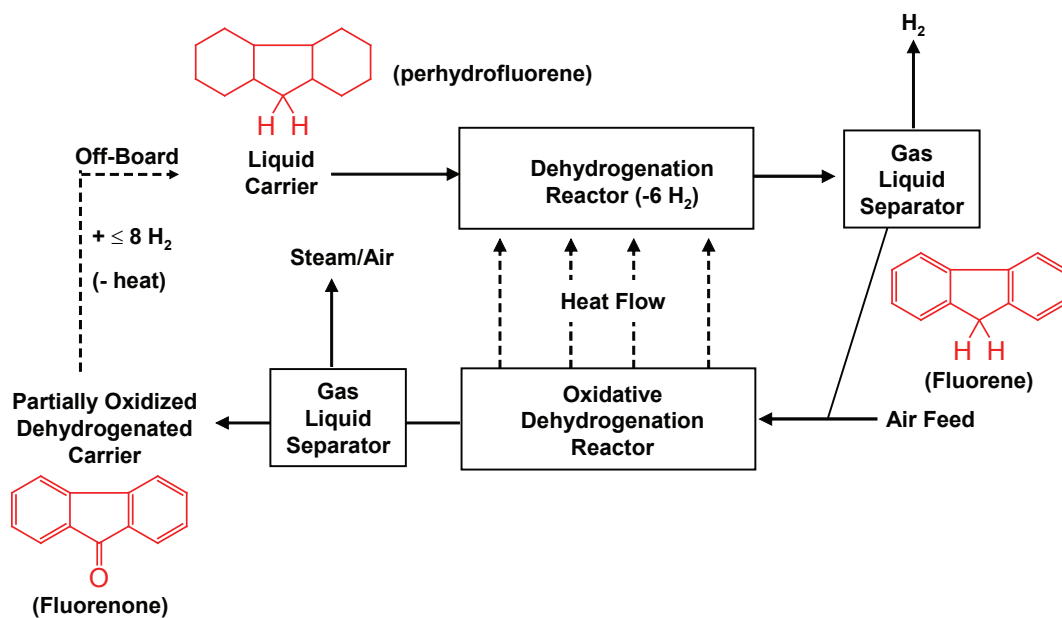


FIGURE 1. Autothermal Dehydrogenation Reactor System Schematic

oxidation should be made available at least slightly above the dehydrogenation temperature of the liquid carrier to provide heat transfer to the endothermic H_2 liberation step.

A promising autothermal liquid carrier prototype, *cis,cis*-perhydrofluorene, was identified and we have successfully demonstrated each step of an autothermal cycle with >98% conversion and >99% selectivity. In a similar fashion to the non-autothermal liquid carriers discovered in previous work conducted in this project, high conversion is necessary to maximize the gravimetric and volumetric hydrogen capacity of the carriers. High selectivity is also required to ensure high hydrogen purity and acceptable economics for the distribution and storage of hydrogen using liquid carriers. The three steps of the autothermal cycle (shown in Figure 2) are the hydrogenation of dehydrogenated, oxidized carrier, the dehydrogenation to provide hydrogen to the fuel cell/internal combustion engine, and the selective oxidation of the carrier to provide the heat required for the endothermic dehydrogenation. For the fluorene-based autothermal hydrogen storage system, calculated thermodynamics reveal that the required heat input of 84 kcal/mole carrier to liberate 6 moles of hydrogen from each carrier molecule (6.7 wt% hydrogen based on the weight of perhydrofluorene) is nearly offset by 81 kcal of heat generated per mole carrier from the selective oxidation of fluorene to fluorenone.

A critical step in an autothermal cycle is demonstrating the ability to convert the oxidized compound(s) back to the perhydrogenated form using conventional hydrogenation conditions and only gaseous hydrogen as the reductant (i.e., avoiding the need for expensive steps such as electrolysis or the use of more reducing chemical reagents such as hydride compounds). Furthermore, our dehydrogenation testing revealed that the lowest dehydrogenation temperatures are achieved with a specific isomer of perhydrofluorene, *cis,cis*-perhydrofluorene, which has the lowest heat of

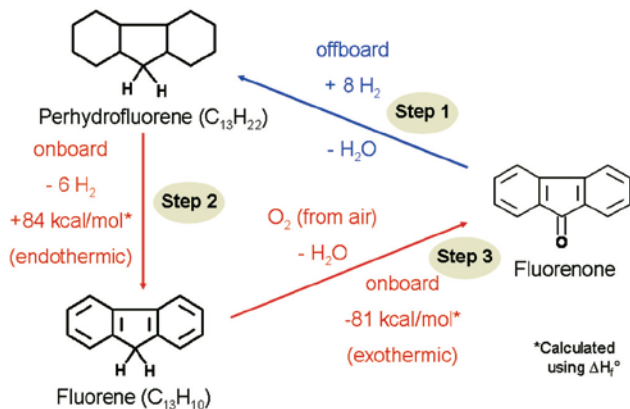


FIGURE 2. Illustration of the Three Steps and Thermodynamics of an Autothermal Hydrogen Storage Cycle with Fluorene

hydrogenation of the possible isomers. This conformer is ~ 1.5 kcal/mole H_2 less stable than *trans,trans*-perhydrofluorene and the use of *cis,cis*-perhydrofluorene allows us to dehydrogenate at significantly lower temperatures than what would be required for dehydrogenating the more stable isomer. In our initial hydrogenation testing, we found that a number of catalysts (e.g., supported platinum and rhodium) were able to fully convert fluorenone to perhydrofluorene in one step, however, these catalysts yielded a mixture of perhydrofluorene isomers including the undesired *trans,trans* isomer.

A number of catalysts and hydrogenation conditions were evaluated for the partial hydrogenation of fluorenone to fluorene, avoiding complete hydrogenation to produce a mixture of perhydrofluorene isomers. This was necessary to investigate the feasibility of a 2-step hydrogenation sequence that will convert fluorenone to fluorene and subsequently selectively convert fluorene to *cis,cis*-perhydrofluorene. The hydrogenation of fluorenone to fluorene can be conducted with high selectivity using palladium on silica at moderate temperatures and hydrogen pressures (e.g. $70^\circ C$ and 8 bar H_2). In a second step, the fluorene is hydrogenated using a supported ruthenium catalyst, remarkably yielding >99% *cis,cis*-perhydrofluorene at $160^\circ C$ and 60 bar H_2 pressure. Dehydrogenation of *cis,cis*-perhydrofluorene under 1 bar H_2 pressure at $230^\circ C$ using a Pt/Al_2O_3 catalyst results in 99% conversion to fluorene with >99% selectivity (Figure 3).

The final step of the autothermal cycle is the selective oxidation of the dehydrogenated carrier to provide heat for the process. To ensure simplicity of the hydrogen liberation process and safety, it is imperative that the oxidation be conducted using air and not pure oxygen or oxygen-enriched air. It is also important that this aerobic oxidation is chemically selective to yield only desired oxidation products that can be rehydrogenated. Overoxidation which breaks carbon-carbon bonds in the carrier molecule or formation of CO_2 will result in low hydrogen purity and

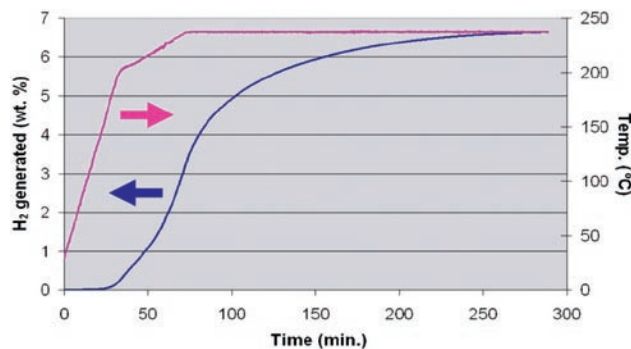


FIGURE 3. Plot of hydrogen generation from the dehydrogenation of *cis,cis*-perhydrofluorene under 1 bar H_2 pressure using a Pt/Al_2O_3 catalyst.

costly purification and liquid replenishment during the rehydrogenation step.

There is a great deal of literature on the catalytic selective oxidation of hydrocarbons and these reports provided several known catalyst systems for testing in our autothermal hydrogen storage approach. It is well known that gold-based catalysts are active for the selective oxidation of alcohols and hydrocarbons [1], therefore, we first tested a gold-palladium (Au-Pd) bimetallic catalyst for the oxidation of fluorene. Oxidation of fluorene to fluorenone using Au-Pd/SiO₂/TiO₂ proceeds with >99% conversion and high selectivity to fluorenone in the liquid phase at low temperatures (<225°C). While the aerobic oxidation of fluorene at 245°C using the Au-Pd catalyst yielded primarily the desired fluorenone product, other lower yield products were formed. These byproducts include a dimer of fluorene (likely connected at the position in the molecule where oxidation takes place) and various hydroxylated and ether-bridged dimer compounds. From a thermodynamic viewpoint, the presence of more highly oxidized products might be perceived as a positive result since the greater degree of oxidation in forming these compounds could generate extra heat necessary to offset the endothermic dehydrogenation. However, the various byproducts were not fully converted back to perhydrofluorene upon hydrogenation and we were unable to find a catalytic system and hydrogenation conditions that provided the necessary >99% selectivity for conversion of the mixture of oxidized products to *cis,cis*-perhydrofluorene.

An alternate approach was developed which involved a new catalyst and the oxidation of fluorene in the gas phase rather than the liquid phase. Following literature reports [2,3], we have recently shown that a mixed metal oxide composed of V:Fe:Cs (approximate atomic ratio of 1:1.4:0.6) is an effective catalyst for the gas-phase conversion of fluorene to fluorenone with air at 350°C. In our experiments, the material in the product collection zone of the test reactor consisted of fluorenone at >99% purity. Gel permeation chromatography and mass spectroscopy (MS) were used to confirm that no high molecular weight compounds were formed in the oxidation. The catalyst Au-Pd/SiO₂/TiO₂, which previously showed activity for oxidizing fluorene in the liquid phase, was not as active in the vapor phase. The mixed metal oxide composed of V:Fe:Cs is also active for the highly exothermic oxidative dehydrogenation of perhydrofluorene to a mixture of fluorene, fluorenone and partially hydrogenated fluorene. This may be useful for providing excess heat for an autothermal hydrogen storage system during startup.

New Liquid Carrier Development: Low Temperature Dehydrogenation

Our new non-autothermal liquid carrier development primarily includes 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 H₂).

We have identified a family of carrier prototypes, with low enthalpies of hydrogenation, based upon β -carboline. The average heat of hydrogenation of β -carboline is 10.4 kcal/mol H₂ (cf. N-ethylcarbazole average $\Delta H = 11.3$ kcal/mol H₂). Perhydro-N-ethyl- β -carboline is liquid carrier prototype with moderate hydrogen capacity and thermodynamics suitable for low temperature dehydrogenation. Several synthetic strategies for the synthesis of this compound from commercially available tetrahydro- β -carboline were evaluated. The direct alkylation of tetrahydro- β -carboline results in a mixture of products from alkylation at both nitrogen atoms. In an alternative route, tetrahydro- β -carboline is dehydrogenated to β -carboline prior to alkylation and hydrogenation. Attempts to hydrogenate N-ethyl- β -carboline resulted in a very unexpected mixture of methylated derivatives of perhydro-N-ethyl- β -carboline. A hypothesis for the unexpected methylation, involving traces of water in the reaction solvent, was proposed. In order to test this hypothesis, the direct hydrogenation of tetrahydro- β -carboline in rigorously anhydrous solvent was found to proceed with high selectivity and moderate conversion. Subsequent attempts to increase conversion by increasing the catalyst loading and reaction time resulted in decreased selectivity.

The hydrogenation of commercially-available tetrahydro- β -carboline (160°C, 1,250 psig, 15 hours, 20 wt% catalyst) provided high (92%) conversion with good selectivity: 79% perhydro- β -carboline; 18% partially reduced intermediates, and <2% byproducts. To determine the catalyst loading required to balance conversion and selectivity, analogous reactions were done with 10 wt%, 5 wt% and 2.5 wt% catalyst loadings. With the lowest catalyst loading, quantitative conversion and high selectivity to perhydro- β -carboline were obtained. Furthermore, primary amine-containing byproducts which might interfere with subsequent dehydrogenation were not detected. A pair of large-scale reactions was performed to provide enough perhydrocarboline for at least two dehydrogenation tests. Initial dehydrogenation studies of the perhydrocarboline were conducted using 4 grams of neat perhydrocarboline and 250 mg of Pt/C catalyst. Upon a slow temperature ramp from 100°C to 150°C, no detectable hydrogen

evolution was observed. Increasing the temperature to 170°C resulted in a very small hydrogen flow (ca. 2 sccm). No heating was attempted at temperatures above 170°C and the perhydrocarboline was recovered from the reaction for additional dehydrogenation attempts under different conditions.

New Liquid Carrier Development: High Capacity Carrier Prototypes

A potential class of hydrogen carriers with >7 wt% H₂ 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).

Evaluation of a number of new aromatic nitrile liquid carrier prototypes was completed in FY 2007. A careful computational study of the stepwise dehydrogenation thermodynamics of saturated, cyclic aminomethyl compounds suggests that prototypes that include ring systems which can dehydrogenate at moderate temperatures have the most suitable overall thermodynamics. Unsaturation of the ring system before dehydrogenation of the aminomethyl group provides a more stabilized imine intermediate following aminomethyl dehydrogenation. Based on this criterion, 3-aminomethylindole derivatives were identified as promising liquid carrier prototypes. Preparation of 3-aminomethylindole by lithium aluminum hydride reduction of 3-cyanoindole was attempted following a literature procedure. Although conversion was complete, selectivity was poor (<60%), and isolation of the product was complicated by the extreme air and base sensitivity. As an alternative, 1-methyl-3-aminomethylindole was proposed as a more tractable substrate. Preparation of the immediate precursor, N-methyl-3-cyanoindole, in high purity was accomplished using an improvement on a literature procedure. Hydrogenation of the nitrile group to the primary amine was readily accomplished with high conversion and selectivity (both >98%). Upon dehydrogenation testing, N-methyl-3-methylindole was the major product observed by gas chromatography/MS (85%); lesser quantities of 3-methylindole (7%) and N-methyl-3-cyanoindole (6%) were also formed. Furthermore, MS showed the presence of dimeric and trimeric species. This is the first time that an aminomethyl compound has been dehydrogenated, at least in part, to the corresponding nitrile. However, owing to the low selectivity and multiplicity of side reactions, no further work is being done with this system.

Conclusions and Future Directions

- An autothermal hydrogen storage cycle is possible using perhydrofluorene with:
 - ~95% conversion on dehydrogenation (net 6.3 wt% material capacity with no external input of heat).
 - 100% conversion during selective oxidation.
- We have demonstrated all three steps of an autothermal hydrogen storage cycle with >99% selectivity:
 - Hydrogenation of fluorenone to *cis,cis*-perhydrofluorene.
 - Dehydrogenation of *cis,cis*-perhydrofluorene to fluorine.
 - Selective oxidation of fluorene to fluorenone.
- Several prototypes of new non-autothermal liquid carriers that were designed to exhibit either very low temperature dehydrogenation or very high hydrogen capacity did not demonstrate the required high conversion and selectivity.

Special Recognitions & Awards/Patents Issued

1. U.S. 7,351,395, “Hydrogen Storage By Reversible Hydrogenation of Pi-conjugated Substrates”, issued 4/08.
2. U.S. Patent Appl. “Autothermal Hydrogen Storage and Delivery Systems”, filed 4/08.

FY 2008 Publications/Presentations

1. September 2007: “An Integrated Hydrogen Storage and Delivery Approach Using Organic Liquid-phase Carriers”, MS&T 2007, Detroit, MI.
2. February 2008: “An Integrated Hydrogen Storage and Delivery Approach Using Organic Liquid-phase Carriers”, Materials Innovations in an Emerging Hydrogen Economy conference, Cocoa Beach, FL.

References

1. G. J. Hutchings, *Chem. Commun.*, 1148-1164 (2008).
2. F. Majunke *et al.* in *New Frontiers in Catalysis* (ed. L. Guzzi, *et al.*); Proceedings of the 10th International Congress on Catalysis, 19-24 July 1992, Budapest, Hungary, pp. 707-717.
3. T. Tsukasa, *et al.*, EP 779264 A1.