

IV.B.4 Development of a Practical Hydrogen Storage System Based on Liquid Organic Hydrogen Carriers and a Homogeneous Catalyst*

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*Congressionally directed project

(H) Balance-of-Plant (BOP) Components

(F) Thermal management

(R) Regeneration Processes

Technical Targets

1. Identification of a low-cost, LOC that, in the presence of low loading of a homogeneous pincer catalyst, will release >7 wt% H₂ at sufficiently high rates and low temperatures in a practical, onboard dehydrogenation reactor to meet the demands of an onboard fuel cell.
2. Identification of a LOC/pincer catalyst combination of sufficiently high hydrogen cycling capacity that rapidly dehydrogenates **without** also undergoing LOC degradation upon cycling.
3. Utilization of the advantages of the liquid hydrogen storage medium to eliminate thermal management problems associated with solid-state hydrogen absorbing materials.
4. Design of a space, mass and energy efficient tank and reactor system to house the LOC and facilitate hydrogen release that can be easily interfaced with a fuel cell.

Fiscal Year (FY) 2012 Objectives

The objective of this project is to optimize a hydrogen storage media based on a liquid organic carrier (LOC) for hydrogen and design a commercially viable hydrogen delivery system based on this LOC media. The project consists of two parts: Part 1 (conducted at Hawaii Hydrogen Carriers, LLC [HHC]) has the objective to develop an optimized catalyst/organic carrier combination; and Part 2 (conducted at General Motor Research Center) has the objective of designing of a space, mass and energy efficient tank and reactor system to house the carrier and release hydrogen.

Technical Barriers

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

- (A) System Weight and Volume
- (B) System Cost
- (C) Efficiency
- (E) Charging/Discharging Rates

FY 2012 Accomplishments

We have shown the homogeneous pincer catalysts to be effective for the rapid dehydrogenation of the 5-membered, nitrogen-containing ring of methylperhydroindole (MPHI), perhydro-indolizidine (PHI), and ethylperhydrocarbazole (EPHC). MPHI has been identified as the most promising candidate LOC among this group as it has the best combination of high performance and low cost. Additionally, our modeling studies have shown that the most effective heat transfer occurs in helical reactors which allow the design of a short, easy to package reactor which in turn reduces heat loss in the system. In consultation with other DOE contract holders (Oregon State University), we were able to significantly reduce both our engineering time and the mass and volume of the unit by use of micro-channel heat exchangers.



Introduction

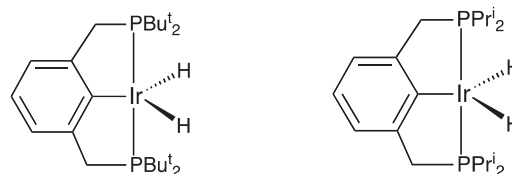
For decades, hydrogen has been targeted as the utopian fuel of the future on account of its abundance and environmental friendliness. However, a major difficulty

in the utilization of hydrogen as a fuel for vehicles is the problem of onboard storage because hydrogen is problematic to store at high density. While this is a major problem for vehicles, it is also a significant problem for portable power as it adds to both the cost and inconvenience of frequent delivery and change-over of hydrogen supply for all fuel cell applications. Thus a high density, high stability method for storing hydrogen is essential to the implementation of fuel cells in all but a few niche applications. Another major concern about hydrogen is putting an infrastructure in place. While this could be done for any form of hydrogen carrier, the barrier to implementing a LOC would be significantly lower than others because it is a similar type of chemical to the current distribution system. The tanks, piping and refinery systems used to make and deliver gasoline are appropriate for LOCs. In addition to the easy adaption to existing infrastructure, LOCs have many other enormous practical advantages. Cheap, abundant LOCs can reversibly release 7-8 wt% hydrogen. They can be economically manufactured in the massive quantities required to meet the anticipated demand and would eliminate the thermal management problems commonly associated with the systems based on solid-state hydrogen absorbing materials. The technology has the potential to exceed the performance of carbon-emitting technologies such as direct methanol fuel cell. We have recently discovered catalysts that enable this technology that has remained a tantalizing but impractical possibility for over the last 60 years. This project targets the development of a commercially viable LOC-based hydrogen storage and delivery system. The project consists of two parts: 1) development of an optimized catalyst/carrier combination; and 2) the design of a space, mass, energy efficient tank and reactor system to house the carrier and release the hydrogen.

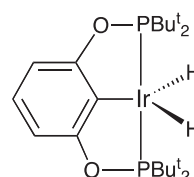
Although promising hydrogen cycling performances have been demonstrated, these previous LOC studies utilized very high loadings of heterogeneous and precious metal catalysts in order to achieve acceptable dehydrogenation kinetics at temperatures that are near the operating temperatures of proton exchange membrane (PEM) fuel cells ($\leq 150^\circ\text{C}$). The high cost of the massive quantities of precious metals precludes the commercialization of these systems.

In order to overcome the barrier to practicality that is imposed by the heterogeneous catalysts, we have developed alternative homogeneous catalysts. Homogeneous catalytic systems typically operate at significantly lower temperatures and show much greater product specificity than their heterogeneous counterparts. In 1997, we discovered that the “pincer” complex, $\text{IrH}_2\{2,6\text{-C}_6\text{H}_3\text{-CH}_2\text{P}(\text{Bu}^t)_2\}_2$ (**1**), catalyzes the dehydrogenation of cycloalkanes to arenes. This was the first report of a homogeneous catalyst for this reaction. The unique reactivity of this especially robust and active catalyst can be ascribed to the tridentate “PCP pincer” ligands which contain two coordinating, neutral phosphorus

centers as well as an anionic, coordinating carbon site. It has been found that the electronic environment of the catalytic metal center of the pincer complex is highly sensitive to minor changes in the PCP pincer ligand. Following our report that (**1**) catalyzes the dehydrogenation of aliphatic groups, the related PCP pincer complexes, $\text{IrH}_2\{2,6\text{-C}_6\text{H}_3\text{-CH}_2\text{PPri}_2\}_2$ (**2**) and $\text{IrH}_2\{\text{C}_6\text{H}_3\text{-2,6-(OPBu}^t)_2\}$ (**3**) were shown to



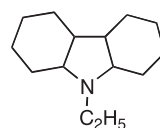
$\text{IrH}_2\{2,6\text{-C}_6\text{H}_3\text{-CH}_2\text{P}(\text{Bu}^t)_2\}_2$ (**1**) $\text{IrH}_2\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{PPri}_2\}_2$ (**2**)



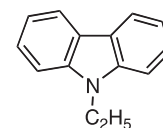
$\text{IrH}_2\{\text{C}_6\text{H}_3\text{-2,6-(OPBu}^t)_2\}_2$ (**3**)

have incremental improvement in catalytic efficiency. It is now well established that dihydro PCP pincer iridium complexes can selectively dehydrogenate aliphatic groups under much milder conditions than those required for the corresponding heterogeneous catalysts, such as platinum on alumina, without harm to other functional groups of an organic molecule.

More recently, we found **1** and the related complexes, **2**, and **3**, to be highly active catalysts for the dehydrogenation of amines, EPHC and other



N-ethylperhydroethylcarbazole (EPHC)



N-ethylcarbazole (EPHC)

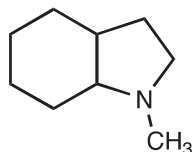
heterocyclic LOCs. We have recently synthesized the novel AsCAs pincer complex, $\text{IrH}_2\{\text{C}_6\text{H}_3\text{-2,6-(OAsBu}^t)_2\}$ (**4**), and found it to be a highly active dehydrogenation catalyst for LOCs. At 150°C , **4** catalyzes the dehydrogenation of EPHC at rates that are nearly double those achieved with **3**. Furthermore, it exhibited acceptable activity at 125°C , at temperatures at which the PCP catalysts are completely inactive.

Approach

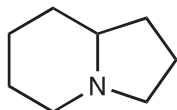
Clearly, our studies of the LOC/pincer catalyst systems have demonstrated the potential of these systems to serve as

the basis of a practical hydrogen storage system. However, further studies must be conducted to find the system and conditions that gives the best combination of high cycling capacity, rapid dehydrogenation kinetics, and lack of LOC degradation upon cycling. In order to accomplish this we will conduct the following four sub-tasks:

Task 1.1: Isothermal kinetic studies of the pincer complex catalyzed dehydrogenation of the candidate LOCs, perhydro-ethylcarbazole, perhydro-methylindole, PHI, and aminomethyl-cyclohexane (AMC).



perhydro-methylindole



perhydro-indolizidine

Task 1.2: In cases where incomplete dehydrogenation of the LOC is observed, studies of the dehydrogenation reaction in the presence of a hydrogen acceptor (transfer dehydrogenation) will be carried out to determine if the reaction is limited by kinetic or thermodynamic constraints.

Task 1.3: Studies to determine if the formation of unwanted side products that arise in some LOC systems can be controlled by the addition of additive.

Task 1.4: Cycling studies to determination if LOC/catalyst combinations that have acceptable dehydrogenation kinetics and capacity will undergo cycling without degradation of LOC and/or catalyst.

Additionally, the practical advance of LOC systems awaits the design of a deployable reactor to house the LOC and facilitate the hydrogen release that can be easily interfaced with a fuel cell. This task consists of the following four sub-tasks:

Task 2.1 Model Development: The first part is to devise a notional model of the entire system. In part 2, one or more reactor model(s) are developed in detail using COMSOL. As the model or models are completed, they will be validated in part 3 to be certain the fluid mechanics, heat transfer, and reaction proceed as would be expected based on the standard engineering concepts. Part 4 will entail a basic estimate of the cost of the system.

Task 2.2 Function Evaluation: Our experience indicates that the system function and cost is often fixed by the full flow condition. To ensure efficient use of resources, we will evaluate this functionality first. Once the reactor “runs” at the full flow condition it will be evaluated at idle. Once these extremes have been evaluated, the mid-speed/mid-load condition will be evaluated and finally transient performance will be evaluated.

Task 2.3 System Optimization: This sub-task is centered on improving both the engineering and the storage materials.

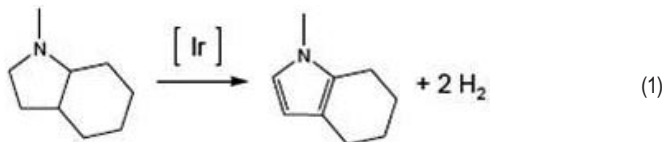
Based on what we have learned about the system function, we will look for both reactor and balance of plant aspects where cost effective change is possible. It may also be possible to: further improve the design; reduce reactor and BOP size; or improve operation conditions.

Task 2.4 Final Simulations: This subtask is analogous to sub-task 2.2. Steady-state and transient simulations will both be done with multiple reactions paths so that both efficiency and selectivity can be evaluated. At the conclusion of the simulations the data will be evaluated, and documented.

Results

Task 1.1 Isothermal Kinetic Studies: The unsaturated, candidate LOCs, methylindole, indolizidine, and ethylcarbazole were obtained from commercial sources. The saturated, perhydro LOCs were prepared through hydrogenation of the commercially obtained materials with the appropriate metal (Ru or Pd) on carbon at high temperature (120-150°C) and high pressure (69 bar). The PCP pincer catalysts were prepared using standard Schlenk techniques using the methods reported in the literature. Catalysts were then checked for activity under well-established protocols, specifically for the conversion of cyclooctane to cyclooctene with a hydrogen acceptor molecule, tert-butylethylene. The high purity of the perhydro-LOCs and pincer complexes was established by comparison to literature reports by the appropriate technique (gas chromatograph-mass spectrometry, ^1H , ^{13}C , and ^{31}P nuclear magnetic resonance) and found acceptable. Once the LOCs and pincer catalysts were in hand, isothermal studies were carried out in order to elucidate any discrepancies in the literature. We found that heating to 180°C (rather than 150°C as previously reported) was required to achieve practical levels of dehydrogenation of N-EPHC within a 24 hour period.

Once the benchmarking of the EPHC “standard” LOC was completed, we initiated the isothermal kinetic studies of the $\text{IrH}_2\{\text{C}_6\text{H}_3\text{-2,6-(OPBu}^t\text{)}_2\}$ catalyzed dehydrogenation of MPHI in the 150-200°C temperature range. As seen below in equation 1, it was observed that only the 5-membered, nitrogen-containing ring undergoes rapid dehydrogenation and the 6-membered ring does not undergoes appreciable dehydrogenation at relevant rates.



An activation energy of 133 kJ/mol and frequency factor of $9.457 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ were derived from an Arrhenius plot of the kinetic data. Although we determined an activation energy of 111 kJ/mol and a frequency factor of $1.26 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ for EPHC, it should be noted that only

limited data can be obtained for EPHC as the rate of the catalytic dehydrogenation is prohibitively slow below 180°C and the pincer catalyst undergoes thermal decomposition at significant rates above 200°C.

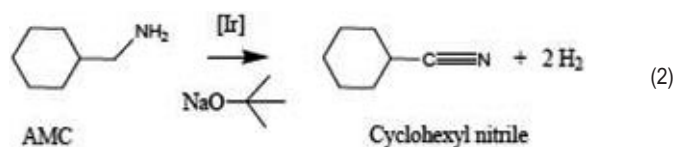
Our studies of the dehydrogenation of AMC at temperatures up to 200°C showed that while the dehydrogenation of the methylamino group to nitrile (as seen in equation 2) occurs at relevant rates, the dehydrogenation of the saturated 6-membered ring does not. Thus AMC has been eliminated as a potential LOC.

We have also found that at temperatures up to 200°C, only the 5-membered ring of PHI undergoes rapid dehydrogenation while the 6-membered ring does not undergoes dehydrogenation at relevant rates. In view of the much higher cost (>50x) PHI and similarity of its dehydrogenation behavior to MPHI, we have eliminated PHI as a candidate LOC.

Higher rates of dehydrogenation of EPHC were not observed in preliminary studies in which the phosphorous pincer complex was replaced by the arsenic pincer complex, $\text{IrH}_2\{\text{C}_6\text{H}_3\text{-2,6-(OAsBu}^t_2)_2\}$. Thus the combination of the EPHC and arsenic pincer complex have been ruled out for further cycling studies.

Task 1.2 Differentiation of Thermodynamic vs. Kinetic Limitations: Work on this task has not been initiated.

Task 1.3 Additive Intervention of Side Reactions: As seen in equation 2, we have found that



addition of hindered base (sodium tert-butoxide) inhibits the unwanted imine condensation side reaction during the dehydrogenation of AMC. However, it was found that the level of dehydrogenation was only 33% and not 95-97% as reported in the literature.

Task 1.4 Cycling Studies: We found that ruthenium, one of the cheapest metals that was screened, is an effective catalyst for the hydrogenation of carbazole-related compounds. However, it was also discovered that ruthenium is not an effective catalyst for the hydrogenation of similar indole compounds but instead catalyzes a previously unknown carbon-carbon bond cleavage reaction.

Task 2.1 Model Development: Four notional models of the entire system have been devised and developed in detail using COMSOL and validated in terms of the fluid mechanics, heat transfer, and reaction progress. Our studies show that the more effective heat transfer in helical reactors allows the design of a short, easy to package reactor which in turn reduces heat loss in the system. Basic estimate of

the system cost have been carried out and show that the reactor could be constructed from parts currently in standard production and thus insures price reasonableness of the reactor.

Task 2.2 Function Evaluation: The basic function of four reactor types have been investigated. We found the reactor length in steady-state operation to have a profound impact of kinetics. In consultation with other DOE contract holders (Oregon State University), we were able to significantly reduce both our engineering time and the mass and volume of the unit by use of micro-channel heat exchangers.

Task 2.3 System Optimization: We have begun to introduce several designs to this step. We are presently carrying out exact reactor simulations and working on BOP issues.

Task 2.4 Final Simulations: Work on this task has not yet been initiated.

Conclusions

Our isothermal kinetic studies have shown the pincer catalysts to be effective for the rapid dehydrogenation of only the 5-membered, nitrogen-containing ring of MPHI, PHI, and EPHC. EPHC has been down-selected as the LOC for use in our system since significantly higher rates of catalysis were observed for the dehydrogenation of MPHI and PHI. In view of the much higher cost (>50x) PHI and similarity of its dehydrogenation behavior to MPHI, we have also eliminated PHI as a candidate LOC. Our studies of the dehydrogenation of AMC have shown that while the dehydrogenation of the methylamino group to nitrile occurs at relevant rates, the dehydrogenation of the saturated 6-membered ring does not. Thus AMC has also been eliminated as a potential LOC. Higher rates of dehydrogenation of EPHC were not observed in preliminary studies of the arsenic pincer complex, $\text{IrH}_2\{\text{C}_6\text{H}_3\text{-2,6-(OAsBu}^t_2)_2\}$. Thus the arsenic pincer complex has been ruled out for further cycling studies.

Four notional models of the entire system have been devised and developed in detail using COMSOL. Our studies show that the most effective heat transfer occurs in helical reactors that allow the design of a short, easy to package reactor which in turn reduces heat loss in the system. Basic estimate of the cost system have been carried out and show that the reactor could be constructed from part currently in standard production and thus insures price reasonableness of the reactor. Reduction of enthalpy and conservation of waste heat from both the reactor and other sources on the vehicle are key to a high hydrogen capacity system. In consultation with other DOE contract holders (Oregon State University), we were able to significantly reduce both our engineering time and the mass and volume of the unit by use of micro-channel heat exchangers.

Future Directions

LOC Screening and Evaluation: We plan to continue the isothermal kinetic studies of the PCP pincer complex catalyzed dehydrogenation of LOCs. Our studies of MPHI and EPHC have shown that the “outer rings” (the 6-member rings that do not containing the nitrogen atom) undergo very little dehydrogenation. We will determine whether this phenomenon is due to kinetic or thermodynamic constraints using the Task 2 procedure. However, in view of the low levels of dehydrogenation that has been found to occur in the outer rings, we have decided to screen perhydro-indolizidine and other candidate LOCs that have two 5-membered ring systems and appropriate physical properties. We also plan to carry out cycling studies on methylperhydro-indole and/or a better performing alternative LOC.

Reactor Design: We plan to finish the down-selection of reactor design using calculations of dynamic performance to select the best option. We will also carry out a trade-off analysis of hydrogen-hydrocarbon separator options. Finally, we will determine the properties required to meet different DOE targets.

FY 2012 Presentations

1. “Development of Processes for the Reversible Dehydrogenation of High Capacity Hydrogen Carriers at Practical Conditions”; Craig M. Jensen, Godwin Severa, Marina Chong, Zhouhui Wang, Ewa Rönnebro, Tom Autrey, and Ahbi Kamkamkar, 1st Low Carbon Earth Summit 2011, Forum 7 Clean and Sustainable Energy, Complex Hydrides; Dalian, October 24–26 2011.
2. “Development of Liquid Organic Hydrogen Carriers”, Daniel Brayton and Craig M. Jensen, Materials Challenges in Alternative & Renewable Energy 2012, Clearwater, Florida, February 26–29, 2012.