



Hawai'i Natural Energy Institute Research Highlights

Advanced Materials

Develop Reversible Liquid Hydrogen Carriers Containing Magnesium Boranes

OBJECTIVE AND SIGNIFICANCE: The objective of this project is to develop a commercially viable, two-way liquid hydrogen carrier (LOHCs) based on solutions of metal hydrides in heterocyclic LOHCs that have a greater energy efficiency and lower delivery costs than existing hydrogen carriers and conventional compressed H₂ gas transport technology. The successful development of the liquid hydrogen carriers would support acceptance and expansion of hydrogen and fuel cell technologies.

BACKGROUND: A substantial network of tanker trucks and pipelines to transport hydrogen at ambient temperature and pressure already exists. The LOHCs of interest in this work would be able to utilize this infrastructure. Both one-way carriers, which form benign products upon elimination of hydrogen that are released to the environment, and two-way LOHCs which can be cycled between their hydrogenated and dehydrogenated phases have been investigated. A recent comparative cost and energy consumption analysis of LOHCs performed at Argonne National Laboratory showed the one-way carrier, methanol to be the strongest candidate. However, it showed no overall cost advantage over tube trailer delivery of compressed hydrogen and pointed to the need to develop new hydrogen carriers.

Methylcyclohexane, the prototypical two-way LOHC has enthalpy of dehydrogenation of 69 kJ/mol H₂, which is a major drawback to its utilization in practical systems as its dehydrogenation is intrinsically energy extensive. It also has a relatively low volumetric available hydrogen density of 47 g/L which translates to a high cost of hydrogen transport.

Heterocyclic LOHCs have excellent thermodynamic properties but are challenged by low volumetric available hydrogen densities which impose an economic barrier to their application as practical hydrogen carriers. Our approach to overcoming this barrier is the addition of high density hydrogen storage materials, especially Mg(BH₄)₂, to the heterocyclic LOHC which can result in up to 19% increase of the available volumetric hydrogen density. The enhanced density, up to 100 g/L, is more than double that of methylcyclohexane.

In collaboration with UH's Department of Chemistry and the DOE-HyMARC Consortium (including

Pacific Northwest Laboratory and National Renewable Energy Laboratory), this project targets the generation of two-way LOHCs by charging selected heterocyclic LOHCs with borohydrides. The project aims to identify the best heterocycle/hydride/catalyst combination in terms of rate, cycling capacity, and product selectivity with goal of maximizing energy efficiency of hydrogen storage and delivery.

PROJECT STATUS/RESULTS: The initial studies were focused on synthesis and characterization of a variety of ionic liquid borohydride LOHCs materials, as well as, carbazole and pyridine-based borohydride LOHCs. Characterization of the synthesized materials was performed using nuclear magnetic resonance spectroscopy (NMR), infrared vibrational spectroscopy (FTIR) and thermogravimetric analyses (TGA-DSC). The vibrational spectroscopy confirmed the typical borohydride peaks in the 2200-2500 cm⁻¹ and 1100-1400 cm⁻¹ region whilst ¹¹B solution NMR spectroscopy directly confirmed the BH₄⁻ ion peaks, at -36 to 39 ppm region. The dehydrogenation of the materials was performed below 200°C. Attempts to re-hydrogenate the materials in Parr Inc. high pressure reactors vessels were unsuccessful in presents and absents of Ru and Pd based catalysts.

The next phase of the project was focused on preparation and (de)hydrogenation performance studies of N-heterocycle-magnesium borohydride (LOHC-Mg(BH₄)₂) solutions with and without catalyst. These studies are meant to allow the identification of the optimal N-heterocycle based LOHC-Mg(BH₄)₂ solutions/emulsions for development as hydrogen carriers. The N-heterocycles analyzed included (de)hydrogenated indole, methyl imidazole, 1,4-bipiperidine, morpholine, butyl-imidazole, N-methylindole, 1,2 dimethyl-imidazole, quinolone, and pyrrolidine.

The LOHC-Mg(BH₄)₂ screening reactions were performed in Parr mini-reactors at 180-200°C for up to 24 hours. Hydrogen evolution from the solutions was confirmed by the increase in pressure of the reactor vessels. Analyses of the dehydrogenated materials was performed utilizing ¹H and ¹¹B NMR. Products formation upon H₂ release from the LOHC-Mg(BH₄)₂ samples was confirmed by ¹¹B peaks at -23 to -31 ppm (cyclic B-N species) and -5 to -18 ppm

N-BH_x (borane species). The best dehydrogenated Mg(BH₄)₂-LOHC mixtures based on NMR results and H₂ release pressure were N-heterocycles solutions containing 1,4-bipiperidine, morpholine, and pyrrolidine. The 1:6 Mg(BH₄)₂/pyrrolidine emulsions were found to release the most hydrogen, at 49 to 52 g H₂ /L.

The re-hydrogenation of the best N-heterocycles was performed at 180°C for up to 72 hours. The catalysts utilized in the re-hydrogenation reactions of the heterocycles-Mg(BH₄)₂ were Ru/C and Ru/Al₂O₃ at 5-10 wt%. However, none of the dehydrogenation products were discovered to undergo rehydrogenation back to the starting materials under hydrogen pressure of 80-120 bars.

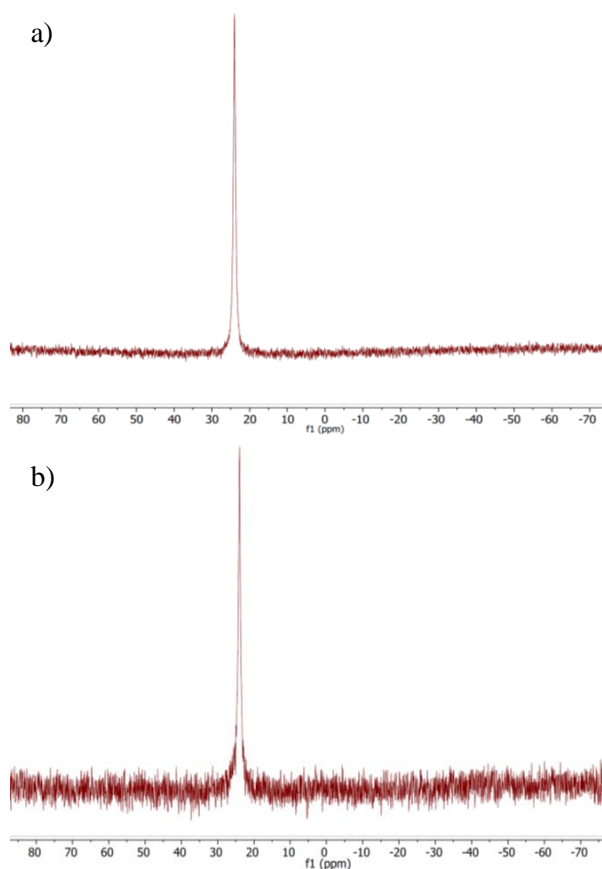


Figure 1. ¹¹B NMR of Pyrrolidine + 6 Mg(BH₄)₂ mixture (a) dehydrogenated at 180°C for 24 hours followed by (b) re-hydrogenation at 180°C for 72 hours.

The dehydrogenation of the Mg(BH₄)₂/pyrrolidine emulsions was discovered to form trispyrrolidinoborane, B{N(CH₂CH₂)₃}₃ complex with a peak at -23 ppm (Figure 1a). As seen in the NMR spectra (Figure 1b), there is no evidence of the reformation of the Mg(BH₄)₂ after re-hydrogenation of the product. The Mg(BH₄)₂ normally occurs as a peak with a chemical shift at ~ -41 ppm in ¹¹B NMR spectra. The re-hydrogenation back to Mg(BH₄)₂ or boranes is hindered by the challenge of adding hydrogen across the highly stabilized B-N bonds of the trispyrrolidinoborane.

Our future work will continue to explore the discovery of new LOHC-Mg(BH₄)₂ type systems which can be rehydrogenated using catalysts. However, in light of the challenges of re-hydrogenation of the LOHC-Mg(BH₄)₂ solutions/emulsions to borohydrides or boranes that we have studied to date, we will be exploring new alternative routes generated through this project such as the reversible (de)hydrogenation of the heterocyclic rings of trispyrrolidinoborane, (TPB) to give trispyranoborane, (TPyB) (Figure 2).

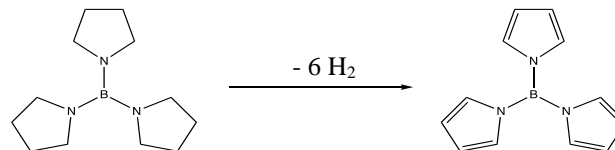


Figure 2. Dehydrogenation of trispyrrolidinoborane to trispyranoborane.

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