IV.D.3 Chemical Hydride Rate Modeling, Validation, and System Demonstration

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Fiscal Year (FY) 2012 Objectives

- Investigate reaction characteristics of various fluid-phase ammonia-borane (AB)-ionic liquid (IL) compositions
- Identify and quantify hydrogen impurities and develop novel impurity mitigation strategies
- Design, build, and demonstrate a subscale prototype dehydrogenation reactor using chemical hydrides (technology area lead)
- Develop an onboard fluid-phase chemical hydrogen storage system; system designer

FY 2012 Accomplishments

- Designed and built novel fluid-phase chemical hydrogen reactors
- Identified reactor operating limits for various fluid-phase chemical hydrogen storage media
- Quantified impurities generated from fluid-phase AB compositions
- Developed boundary conditions of borazine adsorption unit to meet engineering center of excellence targets

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Introduction

Hydrogen storage systems based on chemical hydrides require a chemical reactor to release the hydrogen from the storage media, which is a fundamental difference from the other modes of hydrogen storage, adsorbents and metal hydrides. This hydrogen-release reactor is crucial to the performance of the overall storage system, especially in meeting the DOE targets for hydrogen generation rate, transient operation, and startup times. The reactor must be designed to achieve these targets while meeting the constraints of the overall system volume and weight targets.

LANL will also address the unique requirements of onboard automotive hydrogen storage systems. For example, these systems require fast startup, operation over a wide dynamic range (10:1 turndown or greater), and fast transient response to meet the demands of a drive cycle. The LANL team will develop novel reactor designs and operation strategies to meet these transient demands. In addition, the shelf life and stability of the hydrogen storage media is crucial for an automotive system, especially pertaining to safety and cost. Starting with the kinetics models, the LANL team will develop mathematical models for the aging characteristics of candidate hydrogen storage media (for example, complex metal hydrides or chemical hydrides) subjected to a range of environmental factors. These models can be incorporated into system-level models of performance and cost and also used for the development of accelerated aging protocols necessary for later testing.

Results

Reaction Characteristics of Fluid-Phase AB Compositions

Experiments were performed to determine the reaction characteristics of fluid-phase IL compositions as a function of IL (e.g., EmimCl, Tebmp MS, EmimAC, BmimCl, etc.). The reaction characteristics of interest are the reaction selectivity, chemical compatibility and total mass loss. The collected data allow for determining the maximum reactor operating temperature that will maximize the selectivity of the dehydrogenation reaction. Shown in Figure 1 are two examples of AB/IL compositions that demonstrate differing reaction selectivities. The fluid-phase composition of AB/EmimAc (Figure 1a) demonstrated a chemical incompatibility with ammonia borane for temperatures greater than 100°C.

The total mass loss for the AB/EmimAc composition is well above of what the maximum that can be expected for the dehydrogenation of AB reaction (~15.2 wt%). The total mass loss for this composition was greater than 60 wt%. The additional mass loss is attributed to the chemical incompatibility of EmimAc with AB (confirmed via gas phase Fourier transform infrared). The mass loss curve also suggests that the dehydrogenation kinetics of AB is comparable to the kinetics of AB reacting with EmimAc. The convoluted kinetics results in a system that cannot be controlled through reactor temperature or space-time. In contrast, the composition of AB/IoliLyte (Figure 1b) shows two clearly distinct kinetics regions. The first event occurring from 75–150°C is the dehydrogenation of AB. The second event is the side reaction of AB and iolilyte and occurs at a temperature greater than 180°C. The width of the temperature plateau between the two events is a measure of the flexibility in the reactor operating temperature. In short, the maximum operating temperature for the AB/Iolilyte composition would be around 170°C in order to isolate the dehydrogenation reaction from the unwanted side reaction.

Chemical Compatibility of AB/IL with Bladder Tank Material

Preliminary investigations are under way to investigate the chemical compatibilities of various 20 wt% AB fluid-phase compositions (solutions and slurries). No physical degradation of the bladder material has been observed after three months of room temperature soaking.

Borazine Adsorption Unit

The Hydrogen Storage Engineering Center of Excellence has imposed a mass and volume target on the automotive-scale borazine adsorption unit. The mass and volume design constraints are 4 kg and 3.6 L. The adsorption unit must be able to achieve an 1,800 mile replacement interval. The design constraints allow the required borazine adsorption capacity, the monolayer coverage and the adsorbent surface area to meet the mass target. Shown in Figure 2 are the required adsorbent masses for a borazine adsorption unit as a function of borazine impurity production (kg borazine/kg AB), adsorbent surface area, and borazine coverage. A surface coverage of one monolayer is equivalent to the entire surface area being covered and a 0.25 monolayer is indicative of one fourth of the surface being covered. The general trend is, the higher the surface coverage the lower the mass and volume of the adsorption unit. Physical adsorbents tend to be equilibrium limited and require large volume and mass. Currently, in order to meet the mass target of the borazine adsorption unit, surface areas greater than 2,000 m^2/g and surface coverages greater than one monolayer are required.

Novel Fluid-Phase Reactor Designs

We have developed a novel helical reactor design that is expected to promote gas-liquid separation and prevent liquid slugging from occurring. Eliminating liquid slugging will result in a more efficient and compact reactor. Shown in Figure 3 is one example of our novel reactors. Additional reactors have been designed and built, but are not shown. The reactors will be validated in the coming FY.

Summary

- Successfully designed and built novel fluid-phase reactors (currently being evaluated)

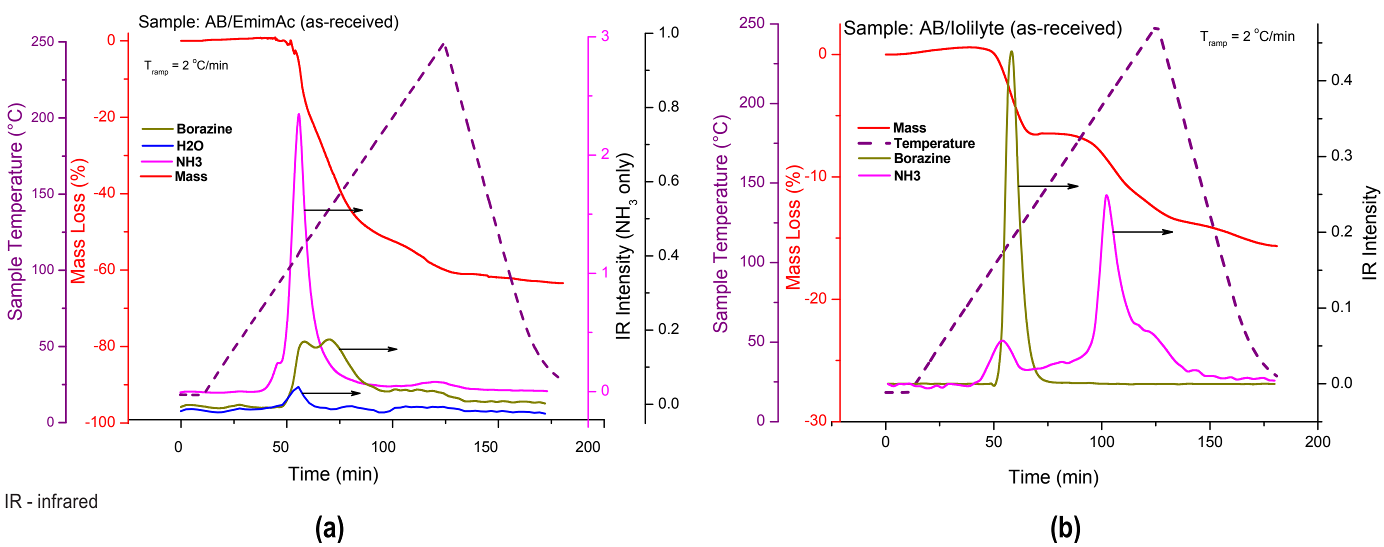
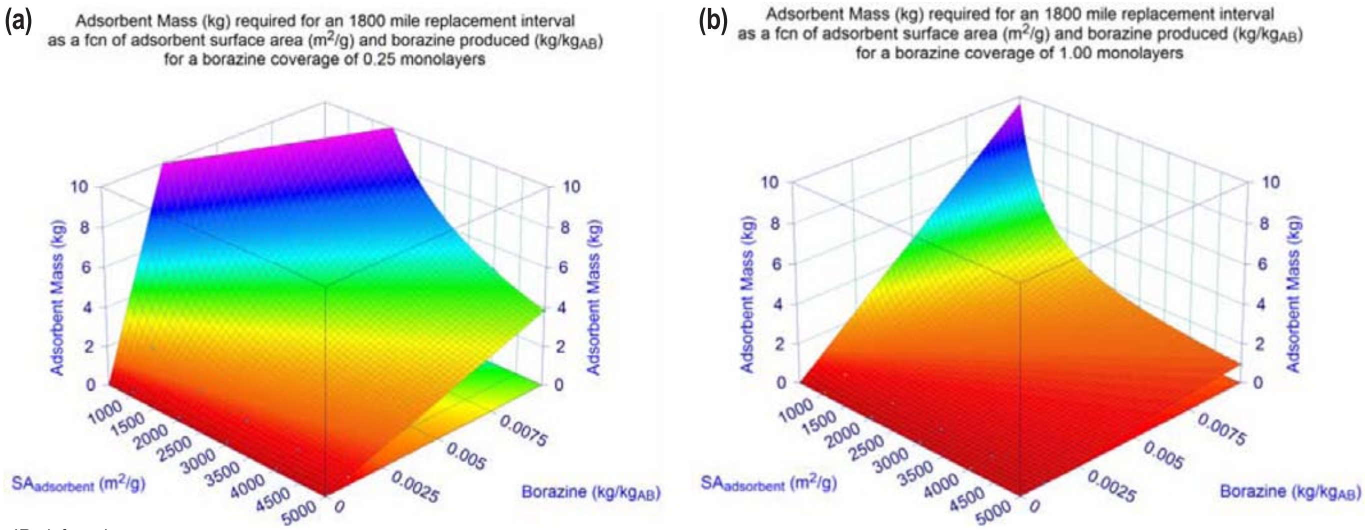


FIGURE 1. Dehydrogenation of fluid-phase AB/IL compositions (a) AB/EmimAc (b) AB/IoliLyte (temperature ramp rate = 2°C/min)



IR - infrared

FIGURE 2. Adsorbent mass as a function of adsorbent surface area and borazine production for an 1,800 mile replacement frequency for (a) 0.25 monolayer surface coverage and (b) 1.00 monolayer surface coverage

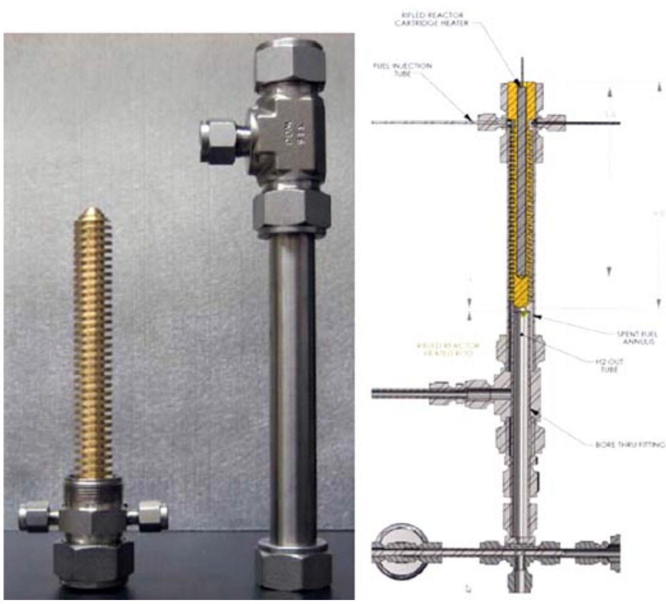


FIGURE 3. Novel reactor design for handling fluid-phase chemical hydrogen storage media

- Identified reactor operating limits of a number of fluid-phase AB/IL compositions that maximize hydrogen selectivities
- Quantified gas phase impurities produced from a number of AB/IL compositions
- Developed and designed automotive scale fluid-phase chemical hydrogen storage system
- Identified the boundary conditions of the required borazine adsorption unit

Future Directions

Borazine Adsorbents

- Develop and optimize the most promising borazine adsorbent

Reactor Design and Testing

- Quantify and compare performances of novel reactors

Shelf-Life Studies

- Continue shelf-life studies on viable chemical hydrogen storage media

Subscale Component Design and Validation

- Gas-liquid separator
- Reactor
- Hydrogen purification train

FY 2012 Publications and Presentations

1. "Overview of LANL's Engineering Research Efforts for Chemical Hydrogen Storage" WHEC 2012, Toronto CA, *Invited Speaker.*

2. "Chemical Hydride Rate Modeling, Validation, and System Demonstration" 2012 Annual Merit Review, Washington, D.C., May 2012.