Thermal Stability of Organic Microporous Polymers Packed with Hydrogen Storage Materials

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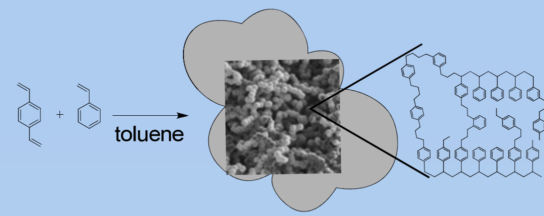
Motivation: This work attempts to reduce the hazards associated with on-board vehicle storage of hydrogen. Currently, complex metal hydrides, like sodium alanate ($NaAlH_4$), are investigated as reversible materials for hydrogen storage. However, concerns over a “breach-in-tank” event require methods to mitigate such hazards.

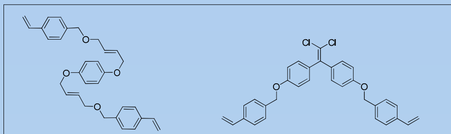
Background: Hydrogen has been proposed as an alternative to gasoline for fueling vehicle transportation. In order to realize this concept, a safe and reliable method for storing hydrogen on-board vehicles must be developed as outlined by the U.S. Department of Energy.[1] Compressed hydrogen, cryogenic hydrogen tanks, physisorbed hydrogen, and chemical/metal hydrides have all been investigated.

General Approach: One avenue is to encapsulate pyrophoric materials in a fire-suppressant polymer[2] foam while providing a rigid, yet low density framework to immobilize particles within a storage tank. Prior IP at Sandia developed a process for immobilizing particulate materials in a packed bed.[3] Sandia also developed synthetic methods for making microporous polymer foams with high surface area and low density.[4] Can these two concepts be combined to make microporous organic materials packed with complex metal hydrides?



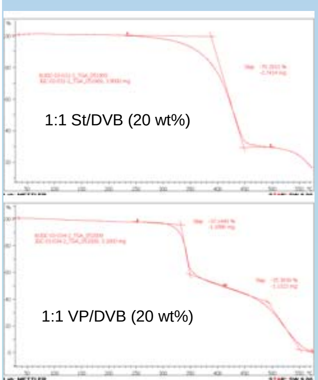
Strategy

- Identify low-density polymer foams that are chemically inert to metal hydrides and contain fire-suppressant properties.
- Develop methods to incorporate metal hydrides into polymer foam either pre- or post-polymerization.
- Incorporate active sites on polymer surface for catalysis or to modulate reactivity.
- Determine thermal stability of polymer foams and composite materials, and characterize reactivity properties.



Char-Forming Cross-Linkers

Synthesis: Composite materials are made by mixing 5 – 20 wt% monomer in toluene with an equal wt% metal hydride. Polymerization is initiated with azobisisobutyronitrile (AIBN) at 60 ºC for 18h. Excess solvent is removed leaving a hard puck-like material. Foams are similarly made but with no metal hydride. Monomers selected include divinyl benzene, styrene, and vinyl pyridine.



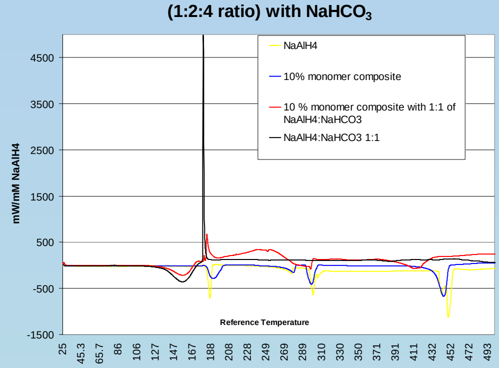
1:1 St/DVB (20 wt%)

1:1 VP/DVB (20 wt%)

Characterization

- Thermal gravimetric analysis (TGA) in air and argon showed no significant difference in char with vinyl pyridine.
- Differential Scanning Calorimetry (DSC) of 10 and 20 wt% composite materials revealed no deleterious effects of encapsulation.
- Preliminary experiments investigating the reaction of composite material with NaHCO3 indicate that the exothermic reaction occurs at a slower rate than free materials.
- Scanning electron microscopy images of 20 wt% composite containing $NaAlH_4$ reveal blossoms of polymer coating inorganic particles.

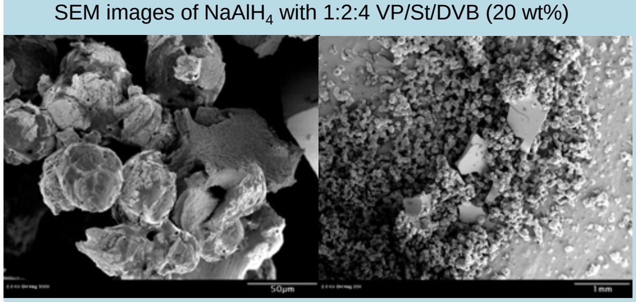
$NaAlH_4$ Composite with 10 wt% VP/St/DVB (1:2:4 ratio) with $NaHCO_3$



$$2NaHCO_3 \xrightarrow[\Delta]{} Na_2CO_3 + H_2O + CO_2$$

$$NaAlH_4 + H_2O + CO_2 + Na_2CO_3 \longrightarrow \text{Exothermic RXN}$$

SEM images of $NaAlH_4$ with 1:2:4 VP/St/DVB (20 wt%)



Conclusions and Outlook

- Successfully polymerized vinyl aryl monomers in the presence of metal hydrides.
- Composite materials containing 10 – 20 wt% polymer were characterized via TGA, DSC, and SEM.
- Thermal stability of polymer foam is higher than desorption temperature of hydrogen from metal hydride.
- While metal hydrides can be solvated with pyridine, an unknown reaction occurred when vinyl pyridine was co-polymerized with metal hydride.
- Diffusion of melted sodium alanate is slowed by encapsulation suggesting mitigation strategy might be useful to inhibit diffusion of other contaminates (e.g. water).

References:
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2. J. L. Jurs, and J. M. Tour, 2003, "Novel Flame Retardant Polyarylethers: Synthesis and Testing," *Polymer*, 44(13), pp. 3709-3714.
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4. T. J. Shepodd, D. L. Miller, and R. Lagasse, 1996, "Organic Microporous Materials and Their Interactions with Different Gases," SAND9608240 Sandia National Laboratories, Albuquerque.

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