

DEVELOPMENT OF HYDROGEN CYCLING CATALYSTS FOR SODIUM ALUMINUM HYDRIDE: A HYDROGEN STORAGE MATERIAL WITH PRACTICAL SPACE APPLICATIONS.

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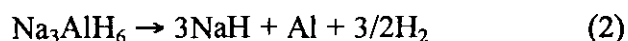
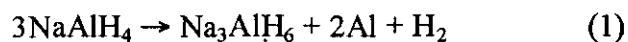
ABSTRACT

The following describes the experimental methods and results obtained from catalytically enhancing the hydrogen desorption kinetics of the hydrogen storage material, sodium aluminum hydride. Development of a practical hydrogen storage material alleviates the thermal and volumetric constraints imposed by utilizing liquid or gaseous hydrogen. Moreover, hydrogen energy is the prime choice of the NASA space program. Transition metal catalysts are delivered to the sodium aluminum hydride in an attempt to produce interactions which reduce the energy activation barrier required for hydrogen desorption. A practical hydrogen storage material should release hydrogen at pressures greater than one atmosphere and at temperatures below 100 °C.

INTRODUCTION

My project explores the effects of particular transition metal dopants on the dehydrogenation and rehydrogenation of NaAlH₄. Original transition metal catalysts experimented with include vanadium, iron, and nickel. The bulk of the first semester was spent purifying the NaAlH₄, and replicating experiments to ensure reproducibility. The second semester included altering the host, NaAlH₄, by mechanical alloying with selective compounds. These compounds were then characterized by infrared spectroscopy (IR) and their desorption kinetics measured. However, a snag occurred when our mechanical alloying machine broke down. The remainder of the semester was spent doping the NaAlH₄ and measuring desorption kinetics.

Hydrogen cycling catalysts are particular compounds or elements added to a reaction mixture to lower the energy required to achieve the desired results. Cycling in this case implies reversible regeneration of the host. Transition metal catalysts were added to lower the temperature required to release hydrogen from pure sodium aluminum hydride, NaAlH₄, according to the following reactions.



Moreover, the catalysts reduce the hydrogen pressure and time required to make the NaAlH₄ reform via absorption of hydrogen.

Sodium aluminum hydride was chosen as a hydrogen storage host because it contains a very high weight percent of usable hydrogen, 5.6%. Despite its high hydrogen content, NaAlH_4 has generally been precluded as an acceptable hydrogen storage material in earlier studies. Although reactions 1 and 2 are favorable, they are extremely slow and reversibility occurs only under severe conditions; high temperatures and pressures (Zidan et.al, 1999). In a groundbreaking study, however, selective titanium catalysts were shown to markedly improve NaAlH_4 's desorption kinetics while reversibility was attained at more moderate conditions (Zidan et.al, 1999). More recently, Ti-Zr dopants and novel doping procedures were found to further reduce the temperature at which hydrogen is released from NaAlH_4 (Zidan et.al, 1999).

How does the development of a practical hydrogen storage material relate to the goals of NASA?

Hydrogen is an inexpensive and abundant high energy fuel source presently employed by NASA for space shuttle propulsion. The high energy content and natural abundance of hydrogen suggest its applicability to space exploration vehicles such as the National Aero-Space Plane. The fact that hydrogen burns with oxygen to produce water further enhances its appeal as a fuel source on a space station. Furthermore, hydrogen-oxygen fuel systems are attractive because of their high performance, nontoxic, noncorrosive nature and their compatibility with other subsystems such as the main propulsion, power generation, and environmental control and life support systems. "Integrating subsystems that use hydrogen, oxygen, and water could lead to a simpler and more operationally efficient vehicle" (Reed and Schneider, 1991). Unfortunately, gaseous and liquid hydrogen storage is impractical due to volumetric constraints. The Space Shuttle's large fuel tanks are a necessary drawback resulting from hydrogen's low density (Hardy and Whalen, 1992). Moreover, liquid hydrogen storage requires extremely low temperatures; the hydrogen arcjet program was discontinued because of long term hydrogen storage problems related to boil off (Curran et. al, 1991). Hydrogen storage in a solid compound alleviates these volumetric and thermal considerations.

METHODS

All reactions and operations were performed under nitrogen in a glove box or using standard Schlenk techniques with oxygen and water free solvents. Sodium aluminum hydride is obtained as a crude gray powder from Aldrich Chemical and purified by extraction of pure NaAlH_4 in THF followed by recrystallization from THF/pentane. Pure white NaAlH_4 is recovered. Samples of pure NaAlH_4 are doped with two mole percent of catalyst via a homogenization method developed by the Jensen research group. The catalyst is ground into the NaAlH_4 using a mortar and pestle; a color change indicates the presence of a new species. Infrared spectroscopy is utilized to characterize the doped complex. Hydrogen desorption kinetics were measured using a thermovolumetric analyzer. In essence, the sample (ca. 0.5 g) is loaded into the chamber of a stainless steel, high pressure reaction apparatus equipped with a programmable temperature controller unit. The temperature is increased at a rate of 2 °C per minute from room temperature to 280 °C. The system's varying temperature and pressure were recorded using a high precision 16-bit National Instruments data acquisition system. The data was analyzed by plotting the weight percent of hydrogen evolved as a function of time.

RESULTS

All samples were cycled three times during the kinetic experiments. The Zr-Ti doped NaAlH_4 is the standard to which other samples will be compared. For the standard, hydrogen desorption commences at approximately 100 °C initially, and the first reaction corresponding to equation 1 reaches completion evolving ca. 3.5 wt. % H_2 by 150 °C; at which point, the reaction corresponding to equation 2 commences. A total of ca. 5 wt. % H_2 is released by ca. 220 °C. A plot of psi/time as a function of temperature shows that the maximum desorption rate is reached at just under 150 °C for the first reaction and just over 200 °C for the second reaction. The second and third cycle reveal that desorption occurs at ca. 80 °C and maximums are reached at ca. 130 and 180 °C, respectively; though total hydrogen desorption fall off to ca. 3.3 wt. %.

Vanadium doped NaAlH_4 began releasing H_2 at ca. 120 °C, and the second reaction corresponding to equation 2 started at ca. 180 °C. Desorption maxima occurred at ca. 150 and 210 °C. The second cycle revealed higher H_2 desorption temperatures. Nickel doped NaAlH_4 began dehydrogenation at ca. 160 °C, and H_2 desorption maxima occurred at ca. 210 and 240 °C respectively. The second and third cycles revealed no significant improvement in dehydrogenation kinetics. Iron doped NaAlH_4 began evolving at ca. 150 °C; desorption maxima were at ca. 170 and 220 °C. The second and third cycles showed higher desorption temperatures. Sodium aluminum hydride doped with both V and Zr evolved H_2 at ca. 120 °C with maxima at 160 and 210 °C, respectively. The second cycle showed a marked decrease of H_2 evolution from ca. 5 to 2 wt. %.

DISCUSSION

The data obtained from the dehydrogenation of Ti-Zr doped NaAlH_4 were easily reproduced. The second and third cycles continuously gave the lower dehydrogenation numbers. Vanadium was tried because it is located adjacent to Ti on the periodic table and similar results were expected. Vanadium doped data mirror Ti doped NaAlH_4 (Jensen et. al, 1999) but breakdown occurs upon continuous cycling. Also, V-Zr doped NaAlH_4 does not release H_2 at temperatures as low as its Ti-Zr counterpart, and again cycling results in breakdown. The V source used was the V^{3+} , $\text{V}(\text{OPr}')_3$. Nickel(II) 2-ethylheptanoate was the Ni source used to catalyze the dehydrogenation of NaAlH_4 . While it does catalyze the reaction, it does not work as well as Ti and Zr. Iron(III) acetylacetonate was the iron source. The iron catalyst works better than the Ni but not as good as V. The source of the transition metal catalyst is significant. A desirable source delivers the metal catalyst to the host during homogenization, then volatilizes leaving only the metal with the host. Furthermore, each oxidation state of a metal acts as a novel species. For instance, Fe (II) has produced different results than the Fe (III) used in this project.

CONCLUSIONS

The search for a practical hydrogen storage material involves exhaustive experimentation. My project merely tested the catalytic effects of four metal dopants. Experiments to alter the host itself were cut short by equipment failure, though this direction may prove more fruitful in the future. The Ni (II) and Fe (III) catalysts did not dramatically improve the dehydrogenation kinetics of NaAlH₄. Vanadium (III) seemed more favorable but broke down upon repeated cycling. Moreover, when combined with Zr, no improvement was noted. Further research is necessary to create a viable hydrogen storage material which will provide the NASA Space program with an alternative, portable energy source making space exploration more facile.

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