DEVELOPMENT OF A REVERSIBLE HYDROGEN STORAGE MATERIAL FROM METAL DOPED SODIUM ALUMINUM HYDRIDE

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Introduction

Chemical and metal hydrides have been investigated as materials of predilection for hydrogen storage;[1-6] efforts have also explored the use of activated carbon and carbon nanotubes. Chemical hydrides, such as $NaAlH_4$ and $LiAlH_4$, are promising materials in this regard because of their high concentration of useful hydrogen (5.6 and 7.9 wt%, respectively), which is typically much higher than most metal hydrides (0.5–2.0 wt %) and carbon materials (0.5-1.0 %). Also, the costs and the hydrogen dissociation energies of these materials are sufficiently small to warrant further investigation.

At standard conditions, the dehydrogenation of $NaAlH_4$ is thermodynamically favorable, but it is kinetically slow and takes place at temperatures well above 200°C in a two-step process involving the following reactions:[1-4]

$$3NaAlH_4 \rightarrow Na_3AlH_6 + 2Al + 3H_2 \quad (1)$$

$$Na_3AlH_6 \rightarrow 3NaH + Al + 3/2H_2 \quad (2)$$

Bogdanovic and Schwickardi[1] found that the hydrogen dissociation temperature in $NaAlH_4$ could be lowered by about 50°C when catalyzed with at least 2 mol% of titanium, consequently improving the kinetics and the conditions for reversibility. Zidan and other investigators[3-5] discovered later that a further lowering of the dehydrogenation temperature was highly dependent on the doping and homogenization procedures. Zidan et al.[3-4] also found that zirconium when mixed with titanium improved the dehydrogenation reversibility of $NaAlH_4$ over Ti alone.

The present study is an update of the on-going effort to lower the hydrogen desorption temperature of catalyzed $NaAlH_4$. In this regard, the search for new and better catalysts, other than the traditional Ti and Zr catalysts, is underway. The effect of two new metals, Fe and Va, as well as combinations of these with Ti and Zr on the hydrogen desorption kinetics is shown. Note that the samples utilized in this study were doped manually only using a mortar and pestle in tetrahydrofuran; nevertheless, it was assumed that the relative effect of a catalyst or combination of catalysts was not going to be affected. Thermogravimetric measurements were carried out on both catalyzed and uncatalyzed $NaAlH_4$ to determine the initial dehydrogenation temperature and the temperature at which the maximum rate of dehydrogenation occurs.

Experimental

$Ti(Bu^nO)_4$ (Aldrich, 97%), $Zr(PrO)_4$ (Aldrich, 70%), $Fe(EtO)_3$ (Gelest) and Bis(cyclopentadienyl)Va (Aldrich) were used as precursors for the catalysts. Each of these precursors was diluted into 100 mM solutions using THF (Aldrich, 99.9%) as a solvent. The $NaAlH_4$ (Fluka) was purchased as a 1.0 M solution in THF; the THF was completely removed by drying at 55 °C overnight. The dried $NaAlH_4$ was mixed with a predetermined amount of catalyst solution to produce a doped sample in the desired concentration. Samples containing a single catalyst or a combination of them with concentrations varying from 0.25 to 8 mol% were all prepared in this manner. The THF evaporated while the $NaAlH_4$ and the catalyst were mixed manually for about 30 minutes using a mortar and pestle, or until the samples were completely dry. The above procedures were carried out in a N_2–laden glove box free of oxygen and moisture.

A DSC7 Perkin-Elmer thermogravimetric analyzer (TGA) was used for to determine the hydrogen desorption kinetics at atmospheric pressure. This instrument was located in another glove box under nitrogen atmosphere to prevent any exposure of the samples to air and moisture. Samples were heated to 300°C at a ramping rate of 5°C/min under 1 atm of He, using an initial 15 minute delay to ensure an environment of pure He. Approximately 10 mg of sample was used in the TGA analyses.

Results and Discussion

Figure 1 shows the TGA results for a series of single and multiple metal catalyzed $NaAlH_4$. Note that since all the samples were evaluated as prepared, weight losses larger than the maximum expected for $NaAlH_4$ were observed; however, this was only a consequence of the organic precursors still being present in the samples. Except for the pure Fe and Va catalysts, all the samples exhibited an initiation of the weight loss at about 150°C. The pure Fe and Va catalysts exhibited initial weight losses at approximately 180°C. Table 1 summarizes the effect of the catalyst and its concentration on the initial dehydrogenation temperature. In general, the samples containing Ti exhibited the best behavior. However, it was particularly interesting to observe the synergistic behavior with the Fe-Ti mixed catalyst system, which performed better than either Fe or Ti alone; it also performed better than the Zr-Ti mixed catalyst system that has been studied previously,[3-4] despite the fact that the sample catalyzed only with Zr performed better than the sample catalyzed only with Fe. It is also observed that post-washing with THF and drying after preparation of the sample did not cause any significant effect on the desorption behavior of the sample.

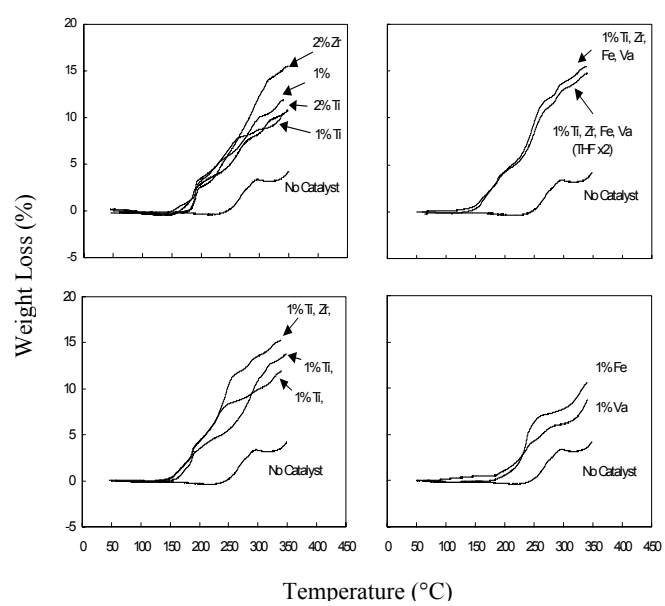

Figure 1. Thermogravimetric analyses of $NaAlH_4$ doped with varying amounts of single and multiple metal catalysts.

Figure 2 shows the differential TGA results for the same series of single and multiple metal catalyzed $NaAlH_4$. With the exemption of the samples containing Fe and Va alone, all the samples had a maximum rate of weight loss at about 180 °C, which coincided with the melting point of the chemical hydride. Samples containing pure Fe and Va catalysts had maximum weight losses at approximately 220°C. In contrast, the uncatalyzed $NaAlH_4$ exhibited maximum weight losses at temperatures between 250 and 270°C. The valleys observed at the higher temperatures for these samples were believed to be mainly due to the decomposition and/or desorption of the organic precursors.

These preliminary results were quite exciting in that they demonstrated very clearly the positive effect of doping $NaAlH_4$ with a transition metal. However, they tend to generate more questions than answers. Why does the $NaAlH_4$ doped with single and mixed metal catalysts appear to reach a threshold dehydrogenation temperature of around 140 to 150 ^{o}C, essentially independent of the type of metal? What is the role of the metal dopant? Is it a surface catalytic mechanism or is it a mechanism that alters the molecular framework of the $NaAlH_4$? Will reversibility, i.e., hydrogenation, be as insensitive to the metal catalyst as dehydrogenation? Answers to these questions are currently being sought with more experimentation.

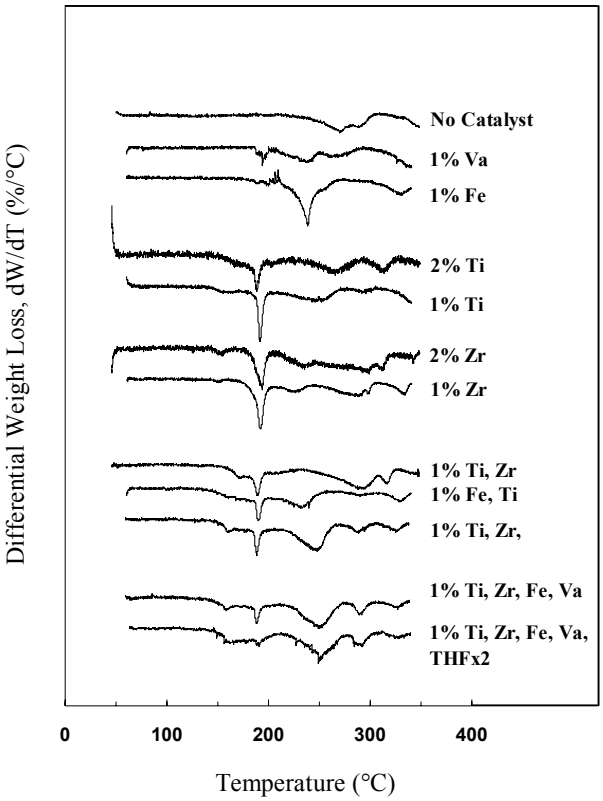

Figure 2. Differential thermogravimetric analyses of $NaAlH_4$ doped with varying amounts of single and multiple metal catalysts.

Conclusions

In an ongoing effort to reduce the kinetic limitations of the dehydrogenation of sodium aluminum hydrides ($NaAlH_4$) the addition of different transition metal catalysts (Ti, Zr, Fe and Va) in various concentrations and combinations have been investigated using thermogravimetric analysis (TGA). The TGA results revealed that Ti and Zr doped systems had their effective hydrogen desorption temperature lowered by approximately 85°C, while systems with only Fe or Va had their effective desorption temperature lowered by about 55°C. The systems with the lowest desorption temperature (in order of performance) were Ti-Fe, Ti-Zr-Fe and Ti in 1-1, 1-1-1 and 1 mol%, respectively; although with only slight differences among them. Overall, these results continue to prove that doping $NaAlH_4$ with transition metals improves the dehydrogenation kinetics.

Additional studies are under way to determine the effect of those catalysts on the hydrogenation conditions of $NaAlH_4$. The study is also aimed at determining the effect of high energy balling milling on the performance of the catalyzed samples investigated here. This overall effort will involve optimizing the conditions (temperature and pressure) needed for cycling, thereby making a more viable reversible hydrogen storage material for transportation applications.

Table 1. Effect of the Catalyst and Its Concentration on the Initial Dehydrogenation Temperature of $NaAlH_4$

Catalyst	Initial Dehydro-genation T (°C)	Catalyst	Initial Dehydro-genation T (°C)
No Catalyst	240	1% Va	189
2% Zr	152	1% Ti, Zr, Fe, Va	150
1% Zr	152	1% Ti, Zr, Fe, Va (THF x 2)	152
2% Ti	155	1% Ti, Zr, Fe	145
1% Ti	149	1% Ti, Zr	158
1% Fe	180	1% Ti, Fe	142

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