Hydrogen Storage in Fullerenes and in an Organic Hydride

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Abstract

While we have demonstrated the importance and usefulness of thermal management to the hydrogen storage in fullerenes, our recent effort has concentrated on materials improvement and physical model development. In this paper, we report the results of this effort as follows: (1) Liquid phase hydrogenation of fullerenes indicated that more than 6 wt% capacity can be obtained at 180 °C, 350-400 psi; (2) Dehydrogenation of fullerene hydrides below 225 °C was demonstrated using an Ir-based P-C-P pincer complex catalyst; (3) Cyclic hydrogenation and dehydrogenation tests of an organic hydride at 7 wt% capacity were conducted at 180-260 °C; and (4) Physical models developed for fullerenes were determined to be applicable to this organic hydride (with much smaller activation energies).

Introduction

The overall objective of our project is to investigate thermal management technologies for various hydrogen storage options. For a given option (e.g., the fullerene option) this is accomplished through (1) development of an understanding of the relevant storage mechanisms and (2) incorporation of the understanding into simulations that can be used to facilitate material enhancement and to optimize storage capabilities. As demonstrated in our previous heat generation/conduction simulations, the characteristics of a hydrogen storage device using fullerenes can be significantly controlled by the heating and cooling rates in the device (Murphy et al. 1997, Wang et al. 1996). This is because the thermal activation mechanisms involved
exhibit a very strong temperature dependence [see, for example, Eq. (1) below]. While we have demonstrated the importance and usefulness of thermal management to the hydrogen storage in fullerenes, our recent effort has concentrated on materials improvement and physical model development. This paper summarize the results of this effort.

Fullerenes such as C_{60} can absorb large amounts of hydrogen (e.g., 7.7 wt% of hydrogen in C_{60}H_{60}) if suitable pressure and temperature are applied. Previous experimental results obtained at Materials Research & Electrochemical (MER) Corporation demonstrated that greater than 6 wt% of hydrogen can be stored in C_{60} and C_{60}/C_{70} mixed fullerenes (Murphy et al. 1997, Wang et al. 1996). The absorbed hydrogen can be released if the fullerene hydrides are suitably heated. Both the hydrogenation and dehydrogenation processes can be reasonably characterized by thermal activation mechanisms. For example, the rate of hydrogen release from a fullerene hydride sample can be represented by the Arrhenius form

$$ Rate = A \frac{c}{c_{\text{max}}} e^{-\frac{E}{kT}} $$

(1)

where $c$ is the concentration of hydrogen in the fullerene, $c_{\text{max}}$ its maximum value, $E$ the activation energy, and $A$ the pre-exponential factor related to the attempt frequency of the hydrogen "atoms" to escape from the fullerene. $A$ has the same units as $Rate$ and the dimensionless factor $c/c_{\text{max}}$ represents the trend that at a given time, the hydrogen escape rate is proportional to the amount of hydrogen present in the sample. The activation energy for dehydrogenation (160 kJ/mole) was estimated to be approximately 60 kJ/mole greater than that for hydrogenation. The difference was interpreted as the heat of hydrogenation for fullerenes. This interpretation was found to be consistent with the results of subsequent combustion calorimetry measurements (Murphy et al. 1997).

Although fullerenes are capable of storing hydrogen, there remains the challenge of bringing the hydrogenation/dehydrogenation conditions (e.g., pressure and temperature used) to practical ranges. Material improvements were made by experimenting with various catalysts including Ni, Pt, Ru, and mechanically alloyed Mg and Ni powder. The idea was based on the expectation that the catalysts would lower the potential barrier in the thermal activation mechanisms so that the needed temperature (around 400 °C according to our earlier work) could be reduced. Tests conducted for fullerenes in the solid phase, however, showed only limited success. To make the catalysts function more effectively, we have been experimenting with methods of improving their contact with the fullerenes. One method tried was to use a solvent as a bridge between the catalysts and the dissolved fullerene molecules. The current status of our effort of using solvents to improve the hydrogenation and dehydrogenation of fullerenes is presented in this paper.

In addition to the development for the fullerene option, an organic hydride was found to have a good potential for hydrogen storage. For proprietary reasons, we represent the hydrogen storage process for this material in the following form:

$$ \text{OrgHydr1} + \text{Hydrogen} \rightarrow \text{OrgHydr2} $$

(2)
where OrgHyd1 and OrgHyd2 are abbreviations for organic hydride 1 and 2, respectively. Multi-cycle tests involving the hydrogenation and dehydrogenation of these organic hydrides showed that up to 7 wt% of hydrogen can be stored and released. Preliminary results for this hydrogen storage system are presented in this paper.

**Liquid-Phase Hydrogenation**

To perform hydrogenation of fullerenes in the liquid phase, a pressure-concentration-temperature vessel was designed at MER which allows dehydrogenation without moving the samples. A fullerene sample in a solvent (25 - 30 ml) plus catalyst was placed in the vessel, and the system was flushed with hydrogen and evacuated. Hydrogen gas was then introduced into the vessel at a specified starting pressure and the vessel heated to a pre-set temperature. After maintaining the temperature for a given duration, the hydrogen uptake by the sample in weight percent was determined from pressure changes recorded during the experiment. The temperature was measured by a thermocouple placed on the top of the reaction chamber.

The test results indicated that more than 6 wt% of hydrogen can be absorbed by fullerenes at 180 °C under 350-400 psi. No significant dehydrogenation occurred at this temperature, suggesting that the dehydrogenation temperature is higher than that for hydrogenation. This is qualitatively consistent with our conceptual model developed for the solid-phase hydrogenation/dehydrogenation of fullerenes: the activation energy for dehydrogenation is greater than that for hydrogenation (Murphy *et al.* 1997, Wang *et al.* 1996).

The experiment just described was performed to explore the feasibility of liquid-phase hydrogenation of fullerenes. The main conclusion from this experiment is that the presence of the solvent and catalyst enables the hydrogenation to take place at a much lower pressure and temperature in the liquid-phase than in the solid-phase. The solvent together with the catalyst can be considered as a "homogeneous catalyst."

The separation of the solvent from the fullerene hydride in a hydrogen storage device is believed to be relatively simple and should pose no problem in practice. A possible conceptual design of the storage device is to use the solvent during hydrogenation, and separate and store it away after the hydrogenation is completed.

In order to gain some kinetic information on the hydrogenation of fullerenes using a solvent and catalyst, a series of experiments was designed and performed as follows:

1. Hydrogenation of samples was carried out under a 500 psi (34 atm) hydrogen pressure at 100, 120, 150, 180, and 200 °C; and
2. For each temperature, the hydrogenation time of 30 min was used.

By keeping the hydrogenation time short, the amounts of hydrogen absorbed at different temperatures reveal kinetic information about the process. The hydrogen absorption results are listed in Table 1 and an Arrhenius plot of these data is shown in Fig. 1. As can be seen from the figure, two activation energies are identifiable: 4.3 and 22 kJ/mole at low (<3.5 wt % H2) and
high (>3.5 wt % H₂) hydrogen concentrations, respectively. These activation energies are much smaller than the earlier estimate for the solid-phase hydrogenation, 100 kJ/mole. The break in the Arrhenius plot shown in Fig. 1 implies that during the liquid-phase hydrogenation of fullerenes, two different processes control the reaction rate. The process with higher activation energy dominates only when the temperature becomes high enough.

### Table 1. Hydrogen absorbed in fullerene during 30 min of liquid-phase hydrogenation.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Hydrogen Absorbed (x in C₆₀Hₓ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>21.4</td>
</tr>
<tr>
<td>120</td>
<td>23.0</td>
</tr>
<tr>
<td>150</td>
<td>25.2</td>
</tr>
<tr>
<td>180</td>
<td>38.2</td>
</tr>
<tr>
<td>200</td>
<td>48.8</td>
</tr>
</tbody>
</table>

*aUnder a hydrogen pressure of 500 psi (34 atm)*

A possible interpretation of the break in the Arrhenius plot is given below: After C₆₀ molecules absorbing some hydrogen with the lower activation energy (4.3 kJ/mole), C₆₀Hₓ molecules become insoluble and precipitate as solid particles. The inner part of a precipitated particle can absorb additional hydrogen only when hydrogen "atoms" reach them by diffusion under concentration gradient. If this interpretation is correct, then the higher activation energy of 22 kJ/mole may be associated with the diffusion of hydrogen atoms among the C₆₀Hₓ molecules. Further experiments are needed to verify this interpretation. No similar break in the Arrhenius plot has been observed in the solid-phase hydrogenation experiments. This may be due to the fact that the activation energy for hydrogenation in that case is much higher (100 kJ/mole) and, at the hydrogenation temperatures, diffusion is too fast to be a controlling factor for hydrogenation.

### Dehydrogenation Experiment using Iridium-Based Catalyst

Gupta et al. (1996, 1997) recently reported that a number of alkanes and cycloalkanes can be successfully dehydrogenated using Ir-based complexes. The process is believed to proceed through an initial oxidative addition of the alkane C-H bond to the metal, followed by further liberation of molecular hydrogen. Through a cooperation with Professor Craig Jensen, an Ir-based compound (dihydro irridium bisphosphine complex) was purchased from the University of Hawaii and used in preliminary experiments on the dehydrogenation of fullerene hydrides. To avoid contamination by moisture, 375 mg of fullerene hydride (containing about 4.5 wt% of hydrogen) was mixed with 125 mg of Ir-based P-C-P pincer catalyst in a glovebox. The mixture,
together with 5 g of naphthalene, was placed in a dehydrogenation chamber. The chamber was closed, removed from the glovebox, connected to the experimental setup, wrapped with heating tapes, and insulated. After evacuation of the lines, the system was heated, and the pressure and temperature in the chamber monitored for the duration of the experiment. The recorded pressure and temperature as functions of time are plotted in Fig. 2.

At the end of the heating period, the system was allowed to cool down to the room temperature overnight and the final pressure reading at room temperature then taken. The overall pressure versus temperature graph is shown in Fig. 3. Also plotted in the figure is the vapor pressure of naphthalene as a function of temperature obtained by curve fitting experimental dat (Boublik et al. 1984). As indicated in the figure, the activation energy for naphthalene evaporation is estimated (from an Arrhenius plot) to be about 50 kJ/mole.

At temperatures above 170 °C, the total pressure shown in Fig. 3 is less than the vapor pressure of naphthalene alone. We believe this was because that some of the lines connected to the chamber were at a lower temperature than that measured in the chamber and condensation at those places probably reduced the naphthalene vapor pressure in the system. In any case, from the initial and final pressures (at room temperature), it was estimated that about 23% of the total hydrogen stored in the fullerene became hydrogen gas in the chamber at the end.

The dehydrogenation result described above is preliminary and additional experiments need to be performed when more catalyst becomes available. Nevertheless, this result is very encouraging and has important implications. As mentioned earlier, our previous solid phase dehydrogenation of fullerenes required a temperature of approximately 400 °C. A dehydrogenation temperature near 225 °C (as can be seen from Fig. 3) suggests a substantial reduction of the activation energy for dehydrogenation. This result and the small activation energies for hydrogenation reported in the liquid phase hydrogenation section (see Fig. 1) demonstrate the possibility that, when a suitable catalyst is used in the presence of a solvent, the potential barrier in the thermal activation mechanisms can be significantly reduced.

**Hydrogen Storage in an Organic Hydride**

As described by Eq. (2), hydrogen may be absorbed by one organic hydride to form another organic hydride. If the process is reversible, the system may be used for hydrogen storage applications. The organic hydride system reported here is capable of storing more than 7 wt% of hydrogen with a gravimetric capacity of more than 60 kg/m³. Multi-cycle tests have been performed on the system. The following is a report of our preliminary results.

Figure 4 shows the hydrogenation result under 8-10 atm (120-150 psi) of hydrogen pressure at 180 °C. During the experiment, the hydrogen flow rate was controlled in order to slow down the reaction. Hence, kinetic information cannot be reliably extracted from this result. However, compared to the results listed in Table 1, the hydrogenation pressure and temperature for this organic hydride system are even lower than those needed for the liquid phase hydrogenation of fullerenes.
The stored hydrogen can be released by heating the organic hydride samples. The release rate depends on the catalyst used. A set of dehydrogenation curves at various temperatures is shown in Fig. 5. For this set of experimental results, the total amount of hydrogen stored in each sample before dehydrogenation was 28.9 liters. As can be seen from the slopes of the curves, the hydrogen release rate increases with temperature, a trend which is consistent with the thermal activation mechanisms.

An Arrhenius plot was obtained (Fig. 6) using the release rates estimated near t=100 min. The activation energy for dehydrogenation was estimated to be about 84 kJ/mole. This value is much smaller than the corresponding value for fullerene hydrides which was estimated to be 160 kJ/mole. Overall, the hydrogen storage mechanisms in the organic hydrides and in the fullerene hydrides discussed in this paper are very similar. A schematic comparison of the thermal activation mechanisms for the two systems is provided in Fig. 7. The question mark in the figure indicates that a corresponding estimate of the activation for hydrogenation is not yet available for the organic hydrides.

**Summary of Current Status**

From the results reported above, the current status of our project is summarized as follows:

- Liquid phase hydrogenation of fullerenes showed that more than 6 wt% of hydrogen can be absorbed by fullerenes at 180 °C under a pressure of 350-400 psi;
- Dehydrogenation of fullerene hydrides below 225 °C using an Ir-based P-C-P pincer complex catalyst has been demonstrated;
- Evidence that the activation energies for hydrogen storage in fullerenes can be significantly lowered has been accumulated;
- Multi-cycle test involving the hydrogenation/dehydrogenation of an organic hydride at 7 wt% capacity has been demonstrated at 180-260 °C; and
- The results of data analysis indicated that the physical models developed for fullerenes are also applicable to the organic hydride (with much smaller activation energies).

**Plans for Future Work**

Future work will address both fullerene and other carbon-based hydrogen storage options. A substantial portion of the methodology developed and the experience gained for hydrogen storage in fullerenes is applicable to this wider family of materials. Future work is planned as follows:

- Continue to experiment with various catalysts to improve the hydrogen storage performance of fullerenes;
- Continue to experiment with liquid phase hydrogenation/dehydrogenation of fullerenes including the use of liquid catalysts with low vapor pressures;
- Expand the database for the organic hydride hydrogenation/dehydrogenation option;
- Interpret all new information, refine current models, determine the most attractive carbon-based options, and perform thermal management simulations as needed;
- Continue to cooperate with others (such as Univ. of Hawaii and NIST) to improve and/or characterize material properties; and
- Participate in the Annex 12 International Energy Agency cooperative project.

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References


Figure Captions

Fig. 1. Arrhenius plot using the liquid-phase hydrogenation data listed in Table 1.

Fig. 2. Pressure and temperature graphs for the dehydrogenation of a fullerene hydride sample in naphthalene.

Fig. 3. Dehydrogenation curve of a fullerene hydride sample in naphthalene.

Fig. 4. Hydrogenation curve of OrgHydr1 at 180 °C under 8-10 atm.

Fig. 5. Dehydrogenation of OrgHydr2 at various temperatures.

Fig. 6. Arrhenius plot for the dehydrogenation or OrgHydr2 showing the activation energy.

Fig. 7. Comparison of conceptual models for hydrogen storage in OrgHyd1 (solid line) and fullerenes (dashed line).
Ir-based catalyst

Temperature (°C) or Pressure (10⁻¹ psi)

Time (min)

T

P
$E_a = 84 \text{ kJ/mole}$

$\text{OrgHydr2} \rightarrow \text{OrgHydr1} + \text{Hydrogen}$
absorption

\[ \text{H}_2 \rightarrow 100 \text{ kJ/mole} \]

? 

\[ \text{H}_2 \rightarrow 60 \text{ kJ/mole} \]

\[ 84 \text{ kJ/mole} \rightarrow 2 \text{ H} \]

\[ 160 \text{ kJ/mole} \rightarrow 2 \text{ H} \]

desorption