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Investigation of Hydrogen Storage in Fullerene Hydrides

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Introduction

Hydrogen is a convenient, safe, versatile fuel source that easily converts to a desired form of energy without releasing harmful emissions [1]. One of the major applications of hydrogen as a fuel source is for the fuel cell-based energy sources, both for military and commercial use due to recent developmental advances in fuel cell technology. Currently, there are four major approaches to hydrogen storage. They include physical storage via compression or liquefaction, chemical storage in hydrogen carriers (e.g. methanol, ammonia), metal hydrides and gas-on-solid adsorption (physical and chemical). Although each storage method possesses desirable attributes, no approach satisfies all of the efficiency, size, weight, cost and safety requirements for transportation or utility use. Table I displays a compilation of the advantages and disadvantages associated with the various H_2 storage techniques.

Table I. Advantages and Disadvantages of Storage Techniques

Storage Technique	Advantages	Disadvantages
1. Compressed H_2	Well-developed technology base, good gravimetric performance, good dormancy characteristics	Large volume, compression cost, safety
2. Liquid H_2	Excellent volumetric and gravimetric energy density for large containers	Liquefaction cost, boil-off losses, poor performance in small systems
3. Gas-on-Solid	Fair volumetric and gravimetric densities, potentially inexpensive	Requires compression and cooling, complexity
4. Metal Hydrides	High volumetric energy density, safe	Poor gravimetric performance, trade-off between high wt% and high dissociation temperature
5. Chemical Storage	High gravimetric storage density	Toxicity, impure stream, re-hydrogenation reaction

Among other options, carbon-based hydrogen adsorption materials hold particular promise for meeting and exceeding the hydrogen storage energy density targets.

Fullerenes, a new form of carbon with close-caged molecular structure first detected by Smalley in 1985 [1], were selected for investigation as a potential hydrogen storage material based on their ability to react with hydrogen via hydrogenation of carbon–carbon double bonds. The theory predicts that a maximum of 60 hydrogen atoms can be attached both to the inside (endohedrally) and outside (exohedrally) of the fullerene spherical surface and that a stable $C_{60}H_{60}$ isomer can be formed loaded with ~ 7.7 wt.% hydrogen. Since many of the fullerene reactions appear to be reversible, if a 100% conversion of $C_{60}H_{60}$ is achieved, 30 moles of H_2 gas would be liberated from each mole of fullerene hydride:

$$C_{60}H_{60} \text{ « } C_{60} + 30\ H_2\ -$$

Since 1 mole of H_2 gas can produce 67.25 Wh (Watt x hour) of electric power, 30 moles of H_2 generated by 1 mole of $C_{60}H_{60}$ should produce 2017.5 Wh of electricity resulting in 2.6 kWh/kg or 4.4 MWh/m^3 power density (density of $C_{60}H_{60}$ is ~ 1700 kg/m^3).

The process of hydrogenation of fullerenes involves formation of C-H bonds as a result of breakage of C=C double bonds of fullerenes and H-H bonds of molecular hydrogen to form hydrogen atoms. Although the hydrogenation reaction is exothermic (the heat is released as a result of reaction), additional energy is required to break these bonds. Besides the thermodynamics involved into this process, certain energy barriers have to be overcome for the reaction to occur. From our experimental results of solid-state hydrogenation of fullerenes [12], the activation energy for the hydrogenation was estimated to be 100 kJ/mole (1.0 eV/H_2). Considering the dehydrogenation process, re-establishing C=C double bonds and re-forming molecular hydrogen is even higher - about 160 kJ/mole (1.6 eV/H_2) – than the potential barrier associated with the breakage of C-H bonds. The conceptual model for hydrogenation and dehydrogenation is schematically shown in Figure 1. Typically, high reaction temperatures (400 – 450^{0}C) and pressures (60 – 80 MPa) are required to overcome these barriers. That is why selection of the proper catalyst is crucial for facilitating the reactions at more mild condition.

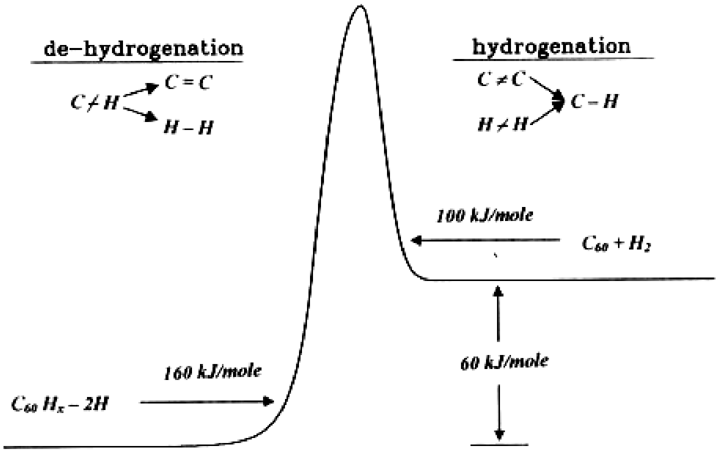


Figure 1 - Activation Energy of Hydrogenation and Dehydrogenation of Fullerenes

During the coarse of investigation, MER has explored various options to improve reversible hydrogen storage on fullerenes under moderate reaction conditions including a number of novel approaches, such as using liquid catalysts, molten salts, changing electronic structure of fullerenes, etc. As a result, significant progress was made in carrying out hydrogenation and dehydrogenation reactions at temperatures below 200^{o}C and moderate pressures. Although the percentage of reversibly exchangeable hydrogen in these systems still remains below the level required for efficient practical applications, the conducted research has produced an invaluable amount of unique knowledge and resulted in better understanding of the processes and mechanisms involved in hydrogen related chemistry of fullerenes.

This paper discusses the most interesting results, both theoretical and experimental, obtained during the course of the investigation that create basis for further research aimed at more complete realization of the hydrogen storage potential offered by fullerenes.

Thermodynamics of Fullerene Hydrides

As mentioned above, the reaction of hydrogenation of fullerenes generates heat, which is called the heat of hydrogenation. Together with the heat of formation required to form C-H bonds, it constitutes the heat of reaction. Depending on the degree of hydrogenation, the values of the heat of reaction vary. The average energy required to break a C-H bond in this system is given by 1/n times the heat of reaction (n=the number of hydrogen atoms). The corresponding values are generally reproduced accurately by the MNDO (*modified neglect of differential overlap*) and

AM1 (*Austin Model 1*) parameterization schemes [2]. Table II summarizes the calculated values of the heat of reaction for $C_{60}H_n$, n = 0 - 60.

Table II. Calculated heats of formation, heats of hydrogenation and average C-H bond energy of $C_{60}H_n$ at MNDO and AM1 levels [2]

Molecule	Symmetry	Heat of Formation[a]		Heat of Hydrogenation[a,b]		Bond Energy[c]	
		MNDO	AM1	MNDO	AM1	MNDO	AM1
C_{60}	I_h	869.3	973.3	-	-	-	-
$C_{60}H_{12}$	T_h	620.3	720.5	249.0	252.8	72.9	73.2
$C_{60}H_{18}$	C_3	532.9	626.9	87.4	93.6	70.8	71.3
$C_{60}H_{24}$	S_4	447.2	535.8	85.7	91.1	69.7	70.3
$C_{60}H_{30}$	C_3	337.7	419.3	109.5	116.5	69.8	70.6
$C_{60}H_{36}$	T_h	232.9	320.1	104.8	99.2	69.8	70.2
$C_{60}H_{42}$	C_3	244.4	315.2	-15.4	-10.7	66.9	67.8
$C_{60}H_{48}$	D	259.9	326.5	-15.5	-11.3	64.8	65.6
$C_{60}H_{54}$	C_3	274.0	331.3	-14.1	-4.8	63.1	64.0
$C_{60}H_{60}$	I_h	286.7	335.0	-12.7	-3.7	61.8	62.7

a) all values in kcal/mol, 1 kcal = 4.18 kJ
b) Energy released on hydrogenating the preceding derivative
c) 1/n times the energy of reaction

As can be seen from Table II, there is a large reduction in energy (~250 kcal/mol) on going from C_{60} to the T_h form of $C_{60}H_{12}$. Further hydrogenation of benzoid units leads to a roughly constant energy gain of 86-94 kcal/mol from $C_{60}H_{12}$ to $C_{60}H_{24}$.

The formation of $C_{60}H_{30}$, as well as $C_{60}H_{36}$, is calculated to be even more facile. The thermodynamic driving force for the formation of the T isomer of the latter from $C_{60}H_{30}$ is around 110 kcal/mol. Further reduction of the benzenoid rings is energetically unfavorable beyond $C_{60}H_{36}$. The highly hydrogenated structures $C_{60}H_{42}$, $C_{60}H_{48}$, $C_{60}H_{54}$ and $C_{60}H_{60}$ are calculated to be successively less stable.

Using the data described above, the free energy change, at which fullerene hydrides with a different degree of hydrogenation can be produced from C_{60} fullerene, was calculated as a function of temperature and pressure assuming the following reaction path:

$$C_{60} + nH_2 \rightarrow C_{60}H_{2n}$$

The Gibbs free energy ?G of this reaction can be expressed as follows:

$$?G = ?H_{r,T} – T?S \qquad (1)$$

where $?H_r$ is the heat of reaction and ?S is the entropy of reaction. Typically, the heat of reaction changes with temperature according to the expression:

$$?H_{r,T} = ?H_{r,298} + ?C_p\ (T-298) \qquad (2)$$

where $?C_p$ – is the difference in heat capacities between the products and the reactants. However, since $?C_p$ in this case is extremely low, the temperature effect on $?H_r$ can be neglected.

The enthalpy $?H_r$ and entropy ?S of the reaction can be expressed as follows:

$$?H_r = ?H_f(C_{60}H_{2n}) – [?H_f(C_{60}) +n\ ?H_f(H_2)] \qquad (3)$$
$$?S = ?S_f(C_{60}H_{2n}) –?S_f(C_{60}) +n\ ?S_f(H_2)] \qquad (4)$$

In the above expressions, the heat of formation of H_2 ($?H_f(H_2)$) is zero by definition and the difference of entropies of $C_{60}H_{2n}$ and C_{60} is assumed to be negligible in the presence of gaseous hydrogen. Hence, the above expressions can be presented in the simplified form as:

$$?H = ?H_f(C_{60}H_{2n}) - ?H_f(C_{60}) \qquad (5)$$

$$?S » n\ ?S_f(H_2) \qquad (6)$$

The entropy of H_2 can be calculated using statistical thermodynamics of the ideal gas, according to which ?S (H_2) consists of translational, rotational, vibrational and electronic components [3]. The last two are negligibly small as compared to the first two. This is why ?S (H_2) can be represented as follows:

$$?S\ (H_2) = S_{tr}(H_2) + S_{rot}(H_2) \qquad (7)$$

$$S_{tr}(H_2) = R[1.5\ln 2 + 2.5\ln T - \ln P - 1.1649] \qquad (8)$$

$$S_{rot}(H_2) = R[1 + \ln(T/sQ_{rot})] \qquad (9)$$

where $\Theta_{rot} = 83.35$ K and symmetry number $\sigma = 2$ for H_2.

Using the enthalpy and entropy data described above, it is possible to calculate the change of the Gibbs energy (?G) for the reaction of fullerene hydrogenation at different temperatures and hydrogen pressures. The results of these calculations performed for $C_{60}H_{36}$, $C_{60}H_{48}$ and $C_{60}H_{60}$ at 1 atm H_2 pressure are resented in Figure 2 below. As can be seen from the results of these calculations, the hydrogenation of C_{60} is favorable even at near room temperature and atmospheric pressure, however the kinetics of the reaction is expected to be extremely slow under these conditions. When considering higher temperatures for C_{60} hydrogenation, in an attempt to increase the kinetics, one should note that as it follows from the calculations $C_{60}H_{36}$ can be obtained in the entire temperature range of 25 to 500^0C (298 – 773 K), while further hydrogenation leading to $C_{60}H_{48}$ and $C_{60}H_{60}$ may occur only at temperatures below 400^0C (673 K) and 280^0C (553 K) respectively. This phenomenon is primarily attributed to the relative instability of highly hydrogenated fullerenes as indicated above.

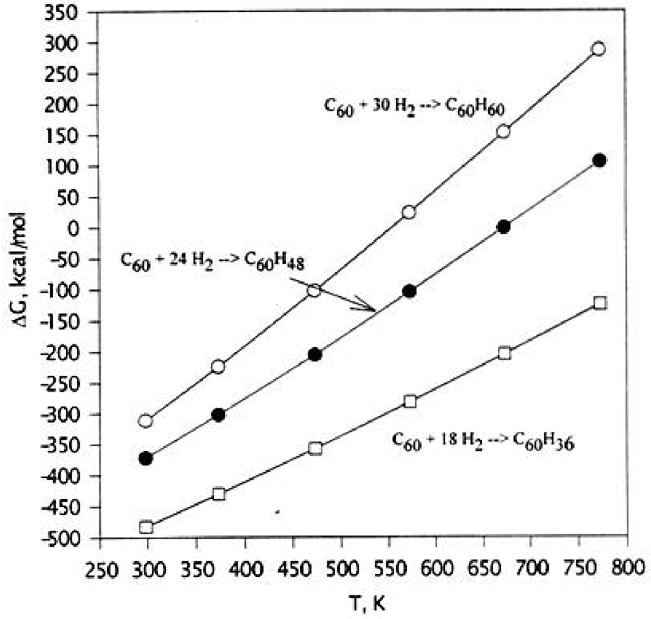
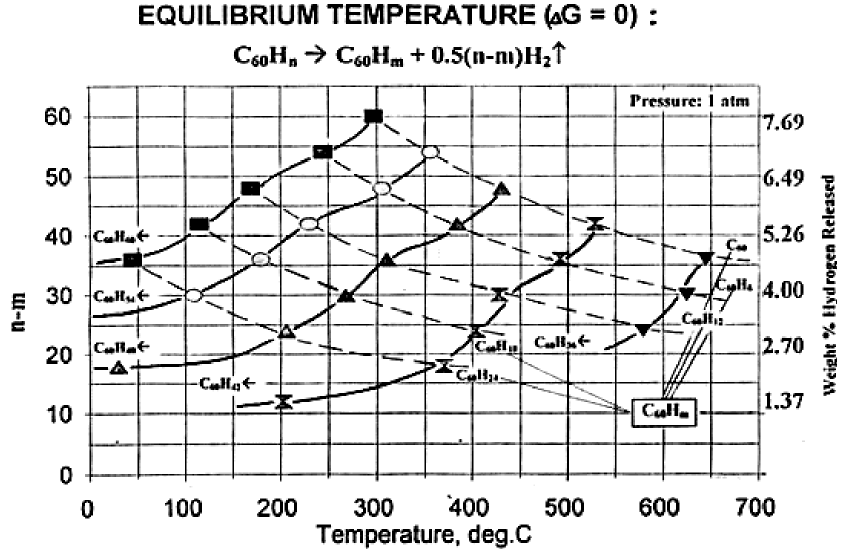


Figure 2 - Calculated Gibbs energy of the reaction vs. temperature.

A similar approach can be used to evaluate the free energy of dehydrogenation of fullerene hydrides at various temperatures. In this case, the results of calculations for equilibrium temperature ($\Delta G = 0$) are presented in Figure 3 and accompanying Table III.



Starting material	Dehydrogenation at 200°C		Dehydrogenation at 100°C	
	Product	Wt. % H	Product	Wt. % H
$C_{60}H_{60}$	$C_{60}H_{12}$	6.8	$C_{60}H_{18}$	5.8
$C_{60}H_{54}$	$C_{60}H_{18}$	5.0	$C_{60}H_{24}$	4.2
$C_{60}H_{48}$	$C_{60}H_{24}$	3.3	$C_{60}H_{36}$	1.7

Data presented above illustrate the fact that the temperature of dehydrogenation depends on the starting material. The higher is the hydrogen content of the starting fullerene hydride, the lower is the temperature of dehydrogenation. This can be explained by lower stability of highly hydrogenated fullerenes ($C_{60}H_x$, $x > 36$).

Thus, it is shown that hydrogenation and dehydrogenation of fullerenes and fullerene hydrides can thermodynamically be accomplished at relatively mild conditions. In order to achieve this in practice, a proper catalyst has to be selected and optimized.

Practical Approaches to Hydrogen Storage on Fullerenes

In its earlier works, MER demonstrated direct hydrogenation of solid fullerene powder without catalysts in the presence of hydrogen gas under elevated temperatures and pressures (350 – 450^{0}C, 60 – 80 MPa). This is a convenient process for producing pure fullerene hydrides with various hydrogen contents; however its practical applications are limited because of the severe conditions. Direct dehydrogenation of fullerene hydrides requires even higher temperatures (up to 550 – 600^{0}C) and, therefore, is not practical either. It has been found, however, that the following conditions may help facilitate both reactions of hydrogenation and dehydrogenation at relatively mild conditions:

- Selection of the appropriate catalyst,
- Conducting the reactions in the liquid phase, and
- Modifying the electronic structure of fullerenes.

In order to satisfy the first two conditions, an extensive search for and testing of the catalysts, dehydrogenation agents and solvents has been carried out. As a result, it was found that the most promising were the transition metal-based liquid-state catalysts, such as $Ti(OPr^i)_4$, $Zr(OBu^t)_4$, $VO(OC_3H_7)$, $Ta(OC_2H_5)_5$, $Nb(OC_2H_5)_5$, etc. Implementation of these catalytic materials enables a liquid-state introduction of Ti, Zr, V, Nb, Ta ions to the fullerene solid, resulting in a markedly improved catalytic effect on fullerene hydrogenation and dehydrogenation due to a much higher contact surface area. Such materials were also reported to be capable of catalyzing the reaction of dehydrogenation of $NaAlH_4$ and Na_3AlH_6 [4].

As a result of conducting a series of experiments, it was shown that reversible hydrogenation of fullerenes and dehydrogenation of fullerene hydrides can be achieved in the temperature range of 150 – 200^0C in the presence of liquid transition metal catalysts. For example, when a $Zr(OBu^t)_4$ catalyst was used, the percent of reversible hydrogen was found to be between 1.53 and 2.82 wt.%. The reaction conditions and the amounts of the substrate and the catalyst are summarized in Table IV. The kinetics of the reaction is illustrated in Figure 4.

Another approach utilized in this work was based on changing the electronic structure of fullerenes by doping with alkali metals (Na, K, Li). When reacting with fullerenes, alkali metals donate their electrons to the fullerenes causing charge transfer and resulting in formation of *fulleride anions* [5,6]:

$$C_{60} + n\,e \rightarrow C_{60}^{n-},\ n = 1, 2, 3, 4, 5, 6$$

Resulting alkali metals – fullerene compounds appeared to be more reactive with hydrogen under mild conditions without requiring additional catalyst. The experimental results of hydrogenation of Na-doped fullerenes are shown in the Table V.

Table IV. Summary of the fullerene hydride dehydrogenation - hydrogenation cycling experiments in presence of $Zr[OBu^t]_4$ liquid catalyst [$(C_{60}/C_{70})H_x$ - 0.20 g, catalyst: 0.30 ml]

Step	Process Parameters	Starting material	Product	Hydrogen weight loss/gain, %
I	DH: 150^o C, 6 h (ΔP=5.65 psi) 200^o C, 6 h (ΔP=8.77 psi)	$(C_{60}/C_{70})H_{36}$ 4.65 %H	$(C_{60}/C_{70})H_{22}$ 2.91 %H	- 1.74
II	H: 150^o C, 12 h, 525 psi (ΔP=23.3 psi at 26^o C)	$(C_{60}/C_{70})H_{22}$ 2.91 %H	$(C_{60}/C_{70})H_{45}$ 5.73 %H	+ 2.82
III	DH: 200^o C, 6 h (ΔP=13.6 psi) at 29^o C	$(C_{60}/C_{70})H_{45}$ 5.73 %H	$(C_{60}/C_{70})H_{32}$ 4.14 %H	- 1.59
IV	H: 150^o C, 6 h, 535 psi (ΔP=13.0 psi at 26^o C)	$(C_{60}/C_{70})H_{32}$ 4.14 %H	$(C_{60}/C_{70})H_{44}$ 5.67 %H	+ 1.53
V	DH: 200^o C, 12 h (ΔP=14 psi at 27^o C)	$(C_{60}/C_{70})H_{44}$ 5.67 %H	$(C_{60}/C_{70})H_{31}$ 4.0 %H	- 1.67

Notes: 1. DH – dehydrogenation , H – hydrogenation
2. Hydrogen storage capacity was determined based on fullerene/fullerene hydride weight only

Table V. Hydrogen Storage Capacity of Na - Doped Fullerenes at 200°C

Starting Material	Process parameters Pressure, psi	Time, hr	Final Product	Wt.% Hydrogen
1. (MF)Na_3	600	6	$C_{60}Na_3H_{19}$	2.3
3. (MF)Na_3	1500	6	$C_{60}Na_3H_{23}$	2.74
4. (MF)Na_3	2000	6	$C_{60}Na_3H_{26}$	3.19
5. (MF)Na_3	2000	24	$C_{60}Na_3H_{33}$	3.91

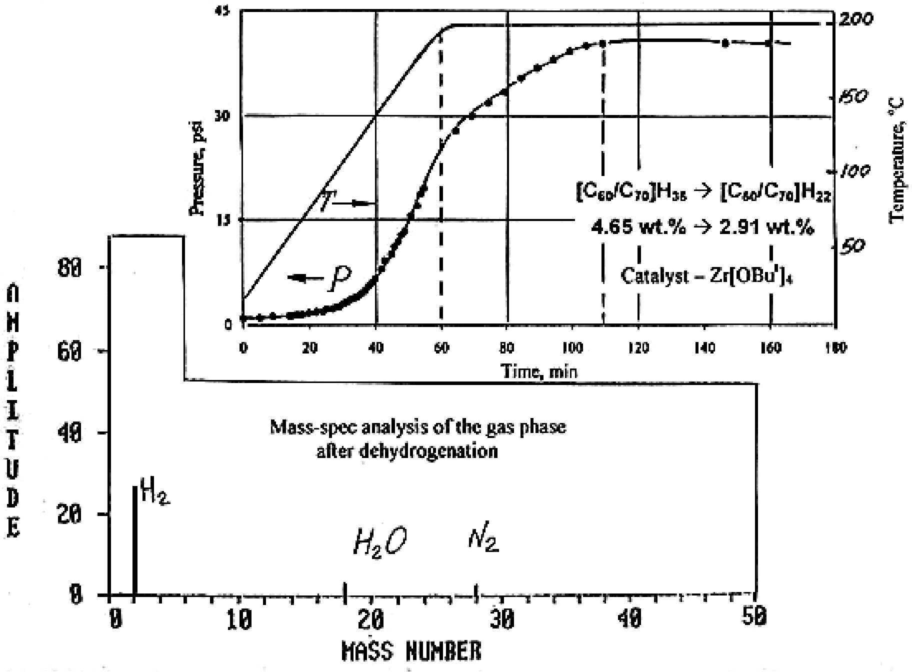


Figure 4 - Pressure change vs. time (a) and mass spectrum of the reaction products (b)

However, the dehydrogenation of the produced hydrides still remains a problem, and only about 1.1 wt.% of hydrogen was released by heating a hydrogenated sample of $C_{60}Na_3H_{33}$ to 200°C in vacuum for 6 hours. In addition, other approaches were utilized to facilitate hydrogen storage in fullerenes including liquid metal catalysts, molten salts, solvents, etc; however, no significant improvement was observed.

Conclusions

Based on extensive theoretical and experimental research, it was shown that fullerenes have a potential to be used as a high capacity, light weight hydrogen storage material capable of storing up to 7.7 wt.% hydrogen provided the optimal conditions necessary to facilitate the hydrogenation/dehydrogenation reactions are established. It was thermodynamically demonstrated that hydrogen can be storage in fullerenes at relatively mild temperatures; however, experimental testing showed only partial improvement in the reaction conditions. This suggests that further research and new approaches are required to ensure the full benefit o offered potential is realized.

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