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# The Development of a Fullerene Based Hydrogen Storage System

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## Abstract

This is the final report of a three-year, Laboratory Directed Research and Development (LDRD) project at Los Alamos National Laboratory (LANL). The project objective was to evaluate hydrogen uptake by fullerene substrates and to probe the potential of the hydrogen/fullerene system for hydrogen fuel storage. As part of this project, we have completed and tested a fully automated, computer controlled system for measuring hydrogen uptake that is capable of handling both a vacuum of 1 x 10-6 torr and pressures greater than 200 bars. We have first established conditions for significant uptake of hydrogen by fullerenes. Subsequently, hydrogenation and dehydrogenation of pure and catalyst-doped C60 was further studied to probe suitability for hydrogen storage applications. C60•H18.7 was prepared at 100 bar H2 and 400°C, corresponding to hydrogen uptake of 2.6 wt % . Dehydrogenation of C60•H18.7 was studied using thermogravimetric and powder x-ray diffraction analysis. The C60•H18.7 molecule was found to be stable up to 430°C in Ar, at which point the release of hydrogen took place simultaneously with the collapse of the fullerene structure. X-ray diffraction analysis performed on C60•H18.7 samples dehydrogenated at 454°C, 475°C, and 600°C showed an increasing volume fraction of amorphous material due to randomly oriented, single-layer graphine sheets. Evolved gas analysis using gas chromatography and mass spectroscopy confirmed the presence of both $H_2$ and methane upon dehydrogenation, indicating decomposition of the fullerene. The remaining carbon could not be re-hydrogenated. These results provide the first complete evidence for the irreversible nature of fullerene hydrogenation and for limitations imposed on the hydrogenation/dehydrogenation cycle by the limited thermal stability of the molecular crystal of fullerene.

## Background and Research Objectives

The acute need for an effective mode of hydrogen storage has been very clear to our team , having been involved for more than ten years in polymer electrolyte (PEM) fuel cell R&D for transportation applications. One daunting engineering challenge that remains to be solved in the context of transportation applications of PEM-type fuel cells is effective

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hydrogen storage, preferably in solid state and at weight percent exceeding the 1% level offered by metal hydrides. The other features required include reversibility of charge / discharge cycles and relatively low temperatures for such cycles of hydrogen uptake / release so that the waste heat from the fuel cell can be effectively tapped for hydrogen release. Prototype hydrogen fuel cell vehicles unveiled recently all use hydrogen gas stored in highly pressurized ( 3000-5000 psig ) gas cylinders -- the only way known at present to achieve storage levels of 5% hydrogen by weight. Safety concerns would generate high barriers for introduction of such pressurized cylinders to replace fuel tanks in passenger vehicles. Known and much safer hydrogen storage instruments, such as metal hydrides, are associated with energy densities that are too low for transportation applications and, hence, with a limited range per single refueling for a vehicle fueled by hydrogen and powered by a fuel cell vs. gasoline fueled vehicles powered by internal combustion engines. Unavailability of a solid, reversible mode of hydrogen storage at weight percent hydrogen well in excess of 1% is perhaps the most important reason for having to resort to on-board liquid fuel processing for generation of hydrogen-rich gas mixtures. Such hydrogen rich mixtures generated on board have served as fuel feed stream to the fuel cell stack in all demonstrations (or disclosures) made recently by the automotive industry -- a clear indication of the failure to date to develop an effective mode of hydrogen storage.

Recent (still controversial) claims that suggest high hydrogen storage capacity in graphite nanotubes and nanofibers, up to 300 weight percent, have stirred strong renewed interest in using various forms of carbon as substrate for hydrogen storage *(1)* . Previous to this recent work , suggestions have been made that $C_{60}$ and $C_{70}$ fullerene carbons could serve as substrates for hydrogenation/dehydrogenation. Preparation of $C_{60} \cdot H_x$ (x=2, 18, 36) molecules have been reported by a variety of methods which include Birch reduction *(2)*, direct hydrogenation of the solid phase *(3-5)*, aqueous electrochemical *(6)* and organic chemical *(7)*. However, there have been no complete reports regarding the reversibility of the process, specifically reports on conditions for dehydrogenation of hydrogenated fullerenes. The exception have been some claims of reversibility of hydrogen uptake by fullerenes, made particularly by one industrial laboratory *(8)*.

The purpose of this work has been to examine the suitability of fullerenes as hydrogen storage medium, particularly for potential transportation applications. We have completed and tested, as part of this project, a fully automated, computer controlled system for measuring hydrogen uptake that is capable of handling both a vacuum of $1 \times 10^{-6}$ torr and pressures greater than 200 bars. We have established conditions for significant uptake of hydrogen by fullerenes. During the last year of the project, hydrogenation and dehydrogenation of pure and catalyst-doped $C_{60}$ was further studied to probe suitability for

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hydrogen storage applications. Specifically, we have examined the integrity of the structure of fullerene with respect to hydrogen uptake and release -- a prerequisite for suitability as hydrogen storage medium.

## Importance to LANL's Science and Technology Base and National R&D Needs

This project is strongly tied to the DOE mission in the context of the Partnership for New Generation vehicles (PNGV), to develop vehicles of efficiency equivalent to 80 mpg of gasoline and low tailpipe emissions. An important longer-term part of the PNGV effort is devoted to PEM fuel cells as new power sources for passenger vehicles. The most efficient PEM fuel cell based power system for transportation would use hydrogen fuel stored on-board the vehicle, preferably in solid form. The absence of solid forms of hydrogen storage at weight percentage hydrogen higher than about 1%, is a major reason for having to resort to complex systems for liquid fuel processing, generating hydrogen by a chemical process on-board the vehicle. Solid form of hydrogen storage with weight percent hydrogen stored >5% and associated with a reversible charge / discharge cycle could practically revolutionize the prospects for PEM fuel cells as effective power sources for transportation. All the above considerations are further amplified by recent interest in the option of fuel decarbonization, e.g., decarbonization of natural gas at the well head separating in the process hydrogen as a transportable, widely utilized clean fuel for the future. Development of an effective mode of hydrogen storage has been identified as a most important challenge on the way to implementation of such a scheme.

## Scientific Approach and Accomplishments
## A. Approach

Two experimental systems for the study of fullerene hydrogenation / dehydrogenation were developed for this work. The first was used to simply hydrogenate $C_{60}$ under constant $H_2$ pressure and constant temperature conditions. $C_{60}$ obtained from MER Corp. (99.5% purity) was loaded into a stainless tube. The tube was connected through one end to a pressurized cylinder of pure hydrogen. A furnace was placed around the other (closed) end of the tube with the $C_{60}$ sample. The hydrogen pressure over the sample was raised to 1500 psi and the sample temperature was raised to up to 400°C. The sample was equilibrated under such isobaric/isothermal conditions for 24 hours. The sample was then quenched to room temperature while the hydrogen pressure maintained at 1500 psi.

To study in detail the extent of hydrogen adsorption/desorption as function of hydrogen pressures up to 200 bar under isothermal conditions, we constructed an

automated system to measure hydrogenation and dehydrogenation of solid samples. A fullerene sample of typically 1-2 grams by weight was loaded into a stainless steel tube connected to a manifold equipped with pressure and vacuum measurement equipment. The manifold was valved to both an ultra-high-vacuum turbo pump and to a high pressure hydrogen source. A basic hydrogen adsorption/desorption experiment was conducted as follows: a known mass of fullerene was heated to a temperature between 25 to 400°C which was maintained throughout the experiment. The sample and manifold were evacuated to $10^{-6}$ torr and back-filled with He to 1 atm for sample volume calculation. The system was then re-evacuated and back-filled with $H_2$ at 1 bar. The sample volume was valved off so that the manifold could be equilibrated at a new $H_2$ pressure and, given a known system volume, the molar quantity of $H_2$ was then calculated. The sample volume leg was opened to the manifold volume and the new $H_2$ pressure was measured after new steady state was achieved in the system. The amount of hydrogen adsorbed was calculated from the difference between initial hydrogen pressure and the hydrogen pressure post equilibration over the fullerene sample, taking into account sample leg and sample volumes. The $H_2$ pressure was thus increased in several increments (to some maximum set value) to establish the complete pressure vs. gas adsorption relationship at the temperature of the experiment. After achieving maximum pressure, the process was reversed to measure quantity of hydrogen gas released as the pressure of hydrogen over the sample is lowered, i.e., during dehydrogenation.

A Perkin Elmer TGA-7 thermogravimetric analyzer (TGA) was used to characterize weight loss during dehydrogenation. Ultra-high purity (UHP) Ar was flowed through the TGA at 80 ml/min and temperature was ramped at a rate of 5°C/min. A Siemens D5000 X-ray diffractometer (XRD) with incident beam monochrometer was used for crystal structure analysis. Two different gas chromatography systems were used to analyze the gas evolved during TGA analysis. The first was a Hewlet Packard 5890 Series II gas chromatograph equipped with a thermal conductivity detector. This instrument was used to confirm the evolution of hydrogen from $C_{60} \cdot H_x$ samples dehydrogenated in the TGA. UHP Ar was used as carrier gas. 1000µl samples were withdrawn at regular temperature/time intervals while the TGA was performed. The second gas chromatograph was a Hewlet Packard GCD G1800B equipped with a mass spectrograph that was used to analyze TGA exhaust gas stream for hydrocarbon fragments. The mass spectrograph was used to determine the speciation of the TGA exhaust gas. UHP He was used as a carrier in this system.

## B. Accomplishments

### *Brief Summary*

The experiments described below confirmed that, unfortunately, fullerenes do not seem to satisfy the conditions for effective solid state hydrogen storage. Our experiments have first shown that varying hydrogen pressure over a fullerene sample at constant temperature (up to around 400°C) does not bring about reversible uptake/release of hydrogen. Subsequently, we explored dehydrogenation of hydrogenated $C_{60}$ at temperatures exceeding the hydrogenation temperature. We found that commensurate with dehydrogenation ,which takes place at temperatures exceeding 450°C, there is a significant chemical transformation of the $C_{60}$ crystal and molecule resulting in a graphite-like material. Finally, precious metal catalysts added to $C_{60}$ samples in some of our experiments have not been found to affect a significant change in this highly irreversible nature of hydrogenation of solid $C_{60}$.

### *Irreversibility of Hydrogen Uptake/Release Under Isothermal Conditions*

Irreversibility of hydrogen uptake/release by solid fullerene was first documented in this work by varying hydrogen partial pressure over a fullerene sample at constant temperature. Hydrogen pressure was cycled from lower to higher values and back under isothermal conditions. In Figure 1 we present six hydrogen adsorption/desorption experiments where the volume of hydrogen adsorbed and desorbed is measured versus hydrogen pressure. In the first three experiments, hydrogen uptake versus hydrogen pressure was measured for 2.38g of MER $C_{60}$ at 400°C. The three experiments were performed on the same fullerene sample. The same three experiments were also repeated with an identical volume of 10 gauge copper wire substituted for the fullerene sample. The latter served to generate a "blank" for the overall response of the system (reflecting any possible residual leak), with a sample of similar volume but zero hydrogen uptake reactivity. The results obtained during each adsorption/desorption cycle were corrected by the magnitude of this system blank. The flat branches seen on lowering hydrogen pressure over the fullerene sample indicate no dehydrogenation at a temperature as high as 400°C, and this is in complete agreement with the TGA dehydrogenation experiments presented above. The amount of hydrogen uptake for the first, second, and third consecutive cycles (weight percent) corresponds to 0.68, 0.40, and 0.26%, or a total of 1.34%, which is less than that obtained under prolonged isothermal/isobaric hydrogenation conditions. The difference in quantity is most likely due to slow hydrogenation kinetics in solid fullerene.

### *The Temperature Domain of Stability for Solid $C_{60}$*

Figure 2 is an XRD trace of pure $C_{60}$ as received from MER Corporation. The reflections were refined to an FCC unit cell with a=14.16Å and they are indexed

accordingly. This unit cell length compares favorably with a unit cell length of 14.11Å reported in the literature. TGA analysis of a sample weighing 52.288 mg is shown in Figure 3. Significant weight loss is seen to begin around 600°C. This is in accordance with a documented, unusually high vapor pressure of the $C_{60}$ phase. Several vaporization studies have been reported in the literature; at 500°C, the vapor pressure of $C_{60}$ is reported about $10^{35}$ times that of graphite (9, 10). Significant weight loss does not occur, however, until 600°C. The weight loss continued to increase rapidly with increasing temperature in the TGA experiment, until the experiment was terminated at 800°C.

### Sample Transformation During Dehydrogenation

The isobaric/isothermal hydrogenation system was used to prepare $C_{60} \cdot H_{18.7}$ at 1500 psi $H_2$ and 400°C. Commensurate with the weight gain was a change in color from black to dark red. Figure 4 is an XRD trace of this sample. Aside from a small change in relative intensities of the reflections, there is a lengthening of the unit cell to a=14.76Å. A 51.738-mg sample of this hydrogenated $C_{60}$ was loaded into the TGA. The TGA scan conditions were identical to those used to characterize the temperature response of pure $C_{60}$ except that the maximum scan temperature was increased to 1100°C. Figure 5 is a TGA trace showing dehydrogenation of this sample. The TGA curve for the $C_{60} \cdot H_{18.7}$ sample differs in several significant ways from that of pure $C_{60}$. Firstly, a weight loss appears at a temperature of 450°C. It is apparently associated with dehydrogenation but the amplitude of the weight loss is seen to be larger than expected for just loss of all hydrogen from $C_{60} \cdot H_{18.7}$ ( 2.61% by weight ). In addition, a stable plateau follows the weight loss that occurs around 450°C. Dehydrogenated $C_{60}$ is thus seen to no longer sublime as easily as pure fullerene. This suggests a substantial chemical change during dehydrogenation.

We further investigated the changes in the properties of $C_{60}$ during dehydrogenation by performing isothermal dehydrogenations and running XRD analysis on the dehydrogenated samples. A first sample of hydrogenated $C_{60}$ ($C_{60} \cdot H_{18.7}$) was placed into the TGA and equilibrated at 600°C in an atmosphere of UHP Ar until no further weight change was observed. The sample was cooled to room temperature removed and x-rayed. The XRD trace shown in Figure 6a. The broad amorphous peaks and high background intensity of this pattern has been seen in preparation of hard carbons from sugars or phenolic resins (11). It is characteristic of randomly oriented, single-layer graphine sheets. The broad reflection at 19° two-theta is the (002) Bragg peak. The presence of these rings and the complete lack of crystallinity in this XRD pattern explains the plateau region seen in the TGA data. A massive change of the fullerene crystal and molecule seems to take place commensurate with dehydrogenation. This change also explains why we see a weight change on dehydrogenation greater than the weight of the hydrogen uptake -- most

likely the balance of the weight loss is associated with some hydrocarbon formation in the process that transforms fullerene commensurate with dehydrogenation. Attempts to re-hydrogenate the sample at 1500 psi $H_2$ and 400°C were unsuccessful -- neither the typical color change nor the weight increase associated with hydrogenation of a fresh $C_{60}$ sample were observed.

We performed two more separate isothermal TGA experiments to check possible arguments that non-destructive dehydrogenation could possibly be achieved at lower temperatures, just above the threshold of 450°C defined by the results in Figure 5. The initial sample weight was recorded and the samples were dehydrogenated at 454°C and at 475°C in two separate experiments. Figures 6b and 6c are the XRD traces of $C_{60} \cdot H_{18.7}$ samples dehydrogenated at 454°C and at 475°C, respectively. The samples remained at temperature for 24 hours. While Figure 6b shows that the dehydrogenated sample retained some crystallinity at this lowest temperature of dehydrogenation with decrease in unit cell length to 14.57Å, there still is a substantial increase in the background intensity between 5 and 35 degrees two-theta. Increasing the dehydrogenation temperature somewhat to 475°C (Figure 6c) led to a predominant amorphous fraction in the sample such that the XRD trace begins to resemble Figure 5a. It must be re emphasized that a prolonged anneal at 475°C has little effect on a pure fullerene sample, aside from mass loss due to sublimation. No weight loss under isothermal conditions was measured below 400°C for $C_{60} \cdot H_{18.7}$.

To further confirm the decomposition of the fullerene molecule upon dehydrogenation, we used gas chromatography to verify evolution of hydrogen gas as weight loss occurs, and to detect the presence of hydrocarbon fragments from decomposition of fullerene. Figure 7 is a TGA curve of the dehydrogenation of the $C_{60} \cdot H_{18.7}$ sample. The right axis shows fraction of the hydrogen peak obtained from GC analysis, normalized to the largest peak detected. No attempt was made to quantify the percentage of hydrogen in the TGA exhaust. This GC analysis indicates that no $H_2$ evolved from the hydrogenated $C_{60}$ sample below about 430°C. This is close to the overall weight loss onset temperature of about 445°C for $C_{60} \cdot H_{18.7}$, as determined from the TGA trace in Figure 5. Most important for this work is the fact that such high temperatures are actually needed to recover hydrogen from the fullerene molecule. The dip in the relative $H_2$ content of the TGA exhaust ( Figure 7 ) might be caused by inconsistent injection into the GC.

The dehydrogenation experiment was repeated with an HP G1800B GC/mass spectrometer that was capable of resolving gas species of 10 to 400 amu. Below 400°C only $O_2$ and $N_2$ were found. Gas samples taken while the $C_{60} \cdot H_{18.7}$ sample was at 500, 525, and 570°C showed the presence of $CH_4$ and hydrocarbon fragments. A final gas

sample was taken at a sample temperature of 730°C and was found to be methane free. The presence of methane seems to explain the discrepancy between the magnitude of weight loss and the hydrogen content in $C_{60} \cdot H_{18.7}$, as recorded by TGA during dehydrogenation experiments: other reactions which involve breaking of carbon-carbon bonds apparently take place together with the dehydrogenation of fullerene.

### *Can Catalysts Help?*

It has been argued that the hydrogenation/dehydrogenation process could possibly be facilitated by catalyzation of the solid fullerene sample, particularly with precious metal catalysts known for their activity in other hydrogenation/dehydrogenation processes. In an attempt to facilitate reversible dehydrogenation, we studied mechanical mixtures of fullerene and ruthenium or platinum metal hydrogenation catalysts. A $Ru_3 \cdot C_{60}$ sample was prepared using coprecipitation from a miscible mixture of isopropyl alcohol and toluene. A second sample was prepared using 20 weight % Pt black. Both samples were hydrogenated at 400°C and 1500 psi $H_2$ for 24 hours. Hydrogen uptake and release by such catalyzed samples were studied, as well as the crystal structures after dehydrogenation. The addition of the hydrogenation catalyst was not found to lower the dehydrogenation temperature, nor did it prevent transformation of the fullerene structure upon hydrogen release. Figure 8 is the adsorption/desorption behavior of the $Ru_3 \cdot C_{60}$ sample and it clearly exhibits the same significant irreversibility. Identical behavior was seen for the Pt-catalyzed fullerene samples, and so catalyzation does not seem to improve on the irreversible nature of the hydrogenation process. Figure 9 is an XRD trace of the $Ru_3 \cdot C_{60}$ sample post dehydrogenation at 575°C. Reflections from the Ru metal catalyst are indicated. The significant chemical transformation upon dehydrogenation is very clear.

### *Overall Conclusion*

Although the use of fullerenes for hydrogen storage applications has been suggested and in fact advertised *(8),* we have shown in this work that solid fullerene could not be reversibly hydrogenated, either without or with added catalysts. The difficulty arises from sluggish hydrogenation of crystalline solid fullerene and, particularly, from the disintegration of the crystalline and chemical structure of $C_{60}$ upon dehydrogenation. Hence, fullerenes do not seem to have the properties required for an effective hydrogen storage system.

### Publication

E. L. Brosha, J. Davey, F. H. Garzon, and S. Gottesfeld, "Thermogravimetric and X-ray Diffraction Investigations of $C_{60} \cdot H_{18.7}$ Dehydrogenation", to be submitted *to J. Mater. Res.* (1997).

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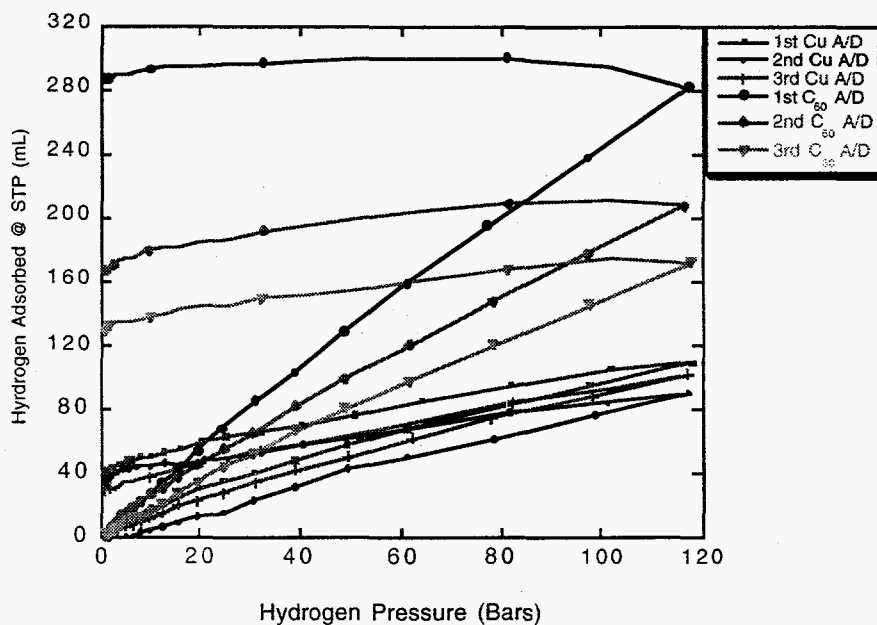
Figure 1. Quantity of hydrogen adsorbed and desorbed for pure $C_{60}$ (and copper of same volume as "blank" ) with respect to hydrogen pressure.
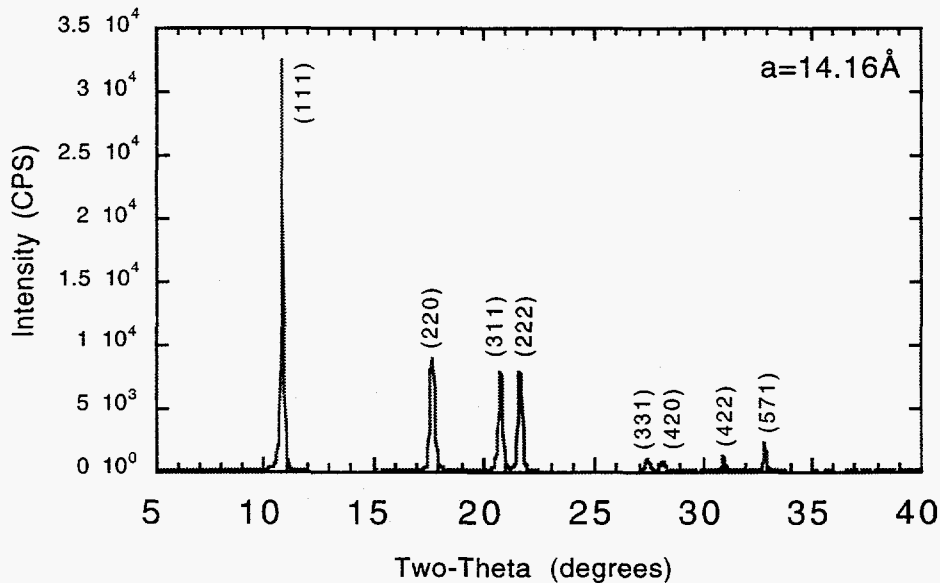


Figure 2.  XRD trace between 5 and 40° two-theta using $CuK_\alpha$ radiation of $C_{60}$ (99.5%) obtained from MER Corporation.  The pattern was indexed to a FCC unit cell with a = 14.16Å.
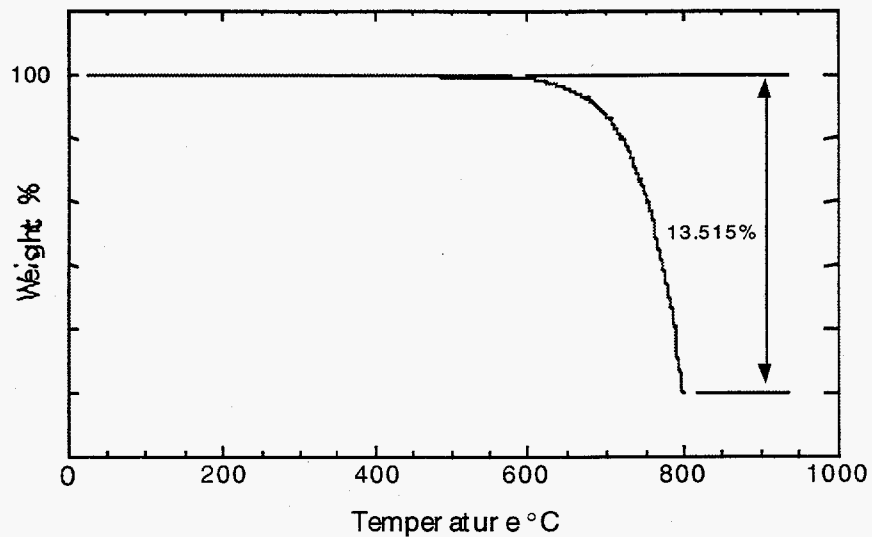
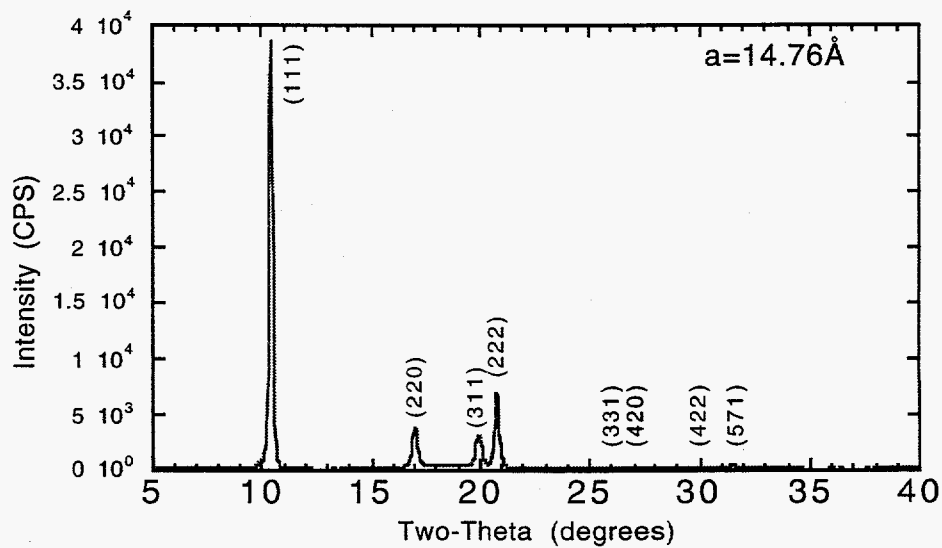Figure 3.  TGA (5°C/min under UHP Ar) of $C_{60}$ (99.5%) obtained from MER Corporation.



Figure 4.  XRD trace between 5 and 40° two-theta using $CuK_{\alpha}$ radiation of $C_{60} \cdot H_{18.7}$.

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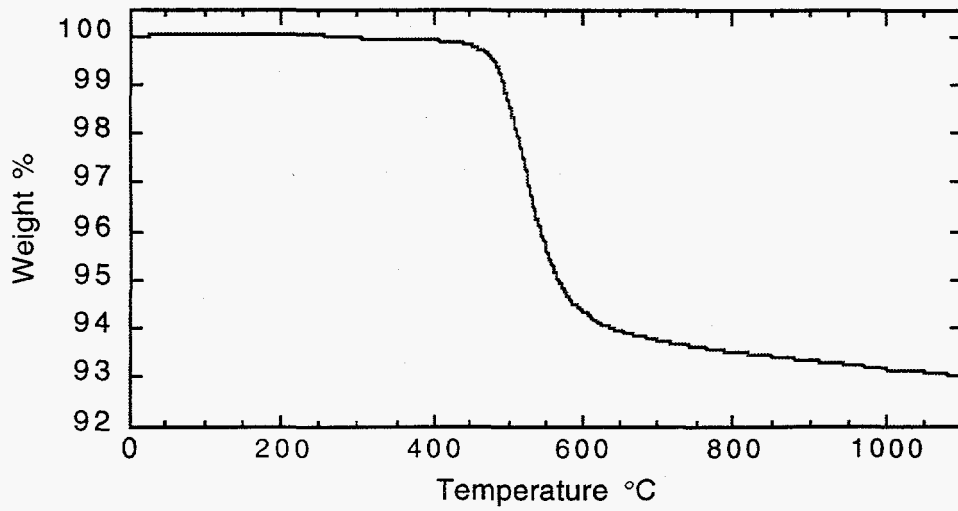
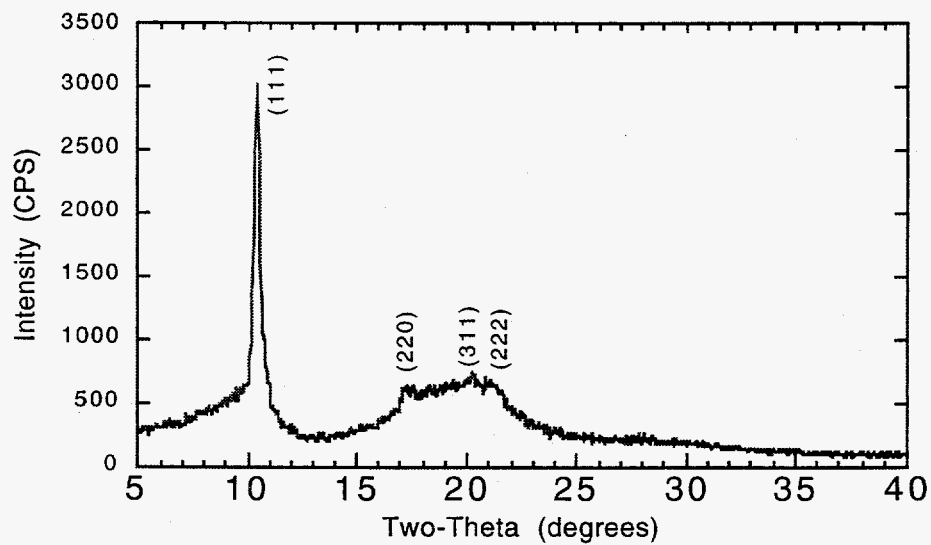Figure 5. TGA (5°C/min under UHP Ar) of $C_{60} \cdot H_{18.7}$.



Figure 6a

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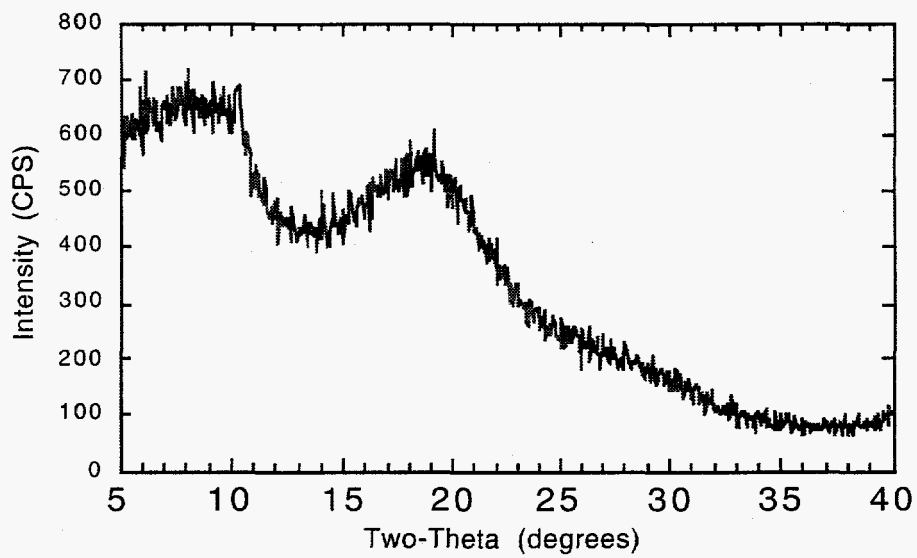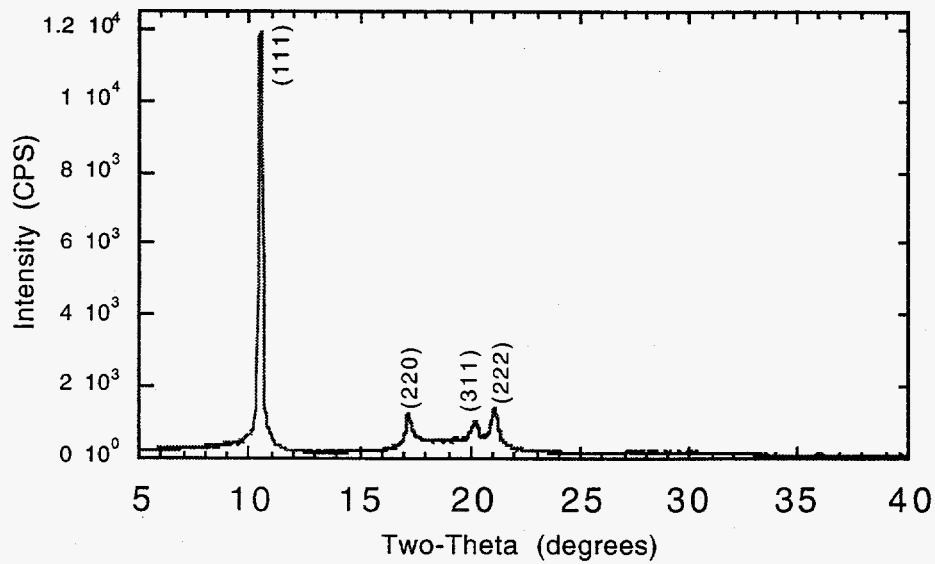
Figure 6b



Figure 6c

Figure 6. XRD trace between 5 and 40° two-theta using CuK$_\alpha$ radiation of C$_{60}$•H$_{18.7}$ dehydrogenated at (a) 600°C, (b) 454°C, and (c) 475°C.
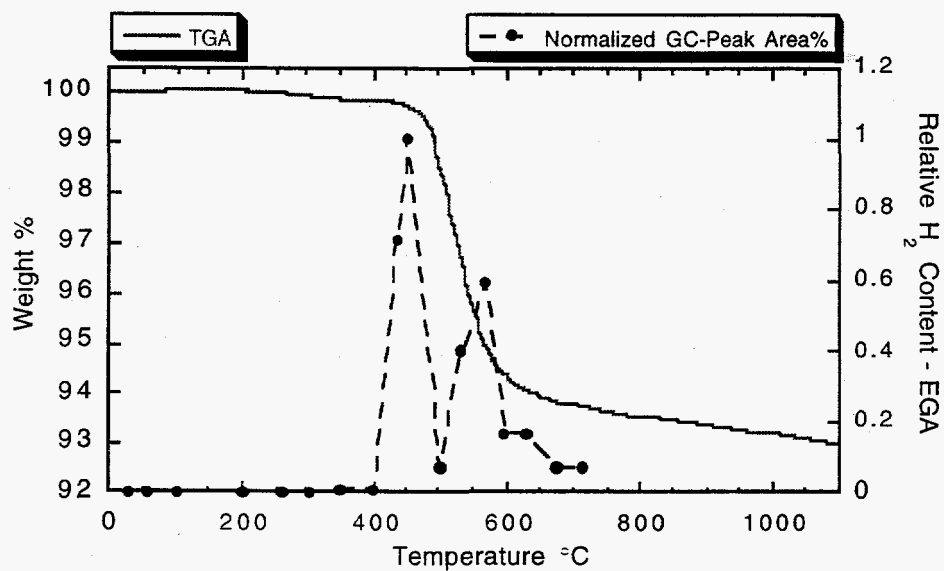
Figure 7. TGA (5°C/min under UHP Ar) of $C_{60} \bullet H_{18.7}$ and the normalized $H_2$ signal as obtained from gas chromatography.
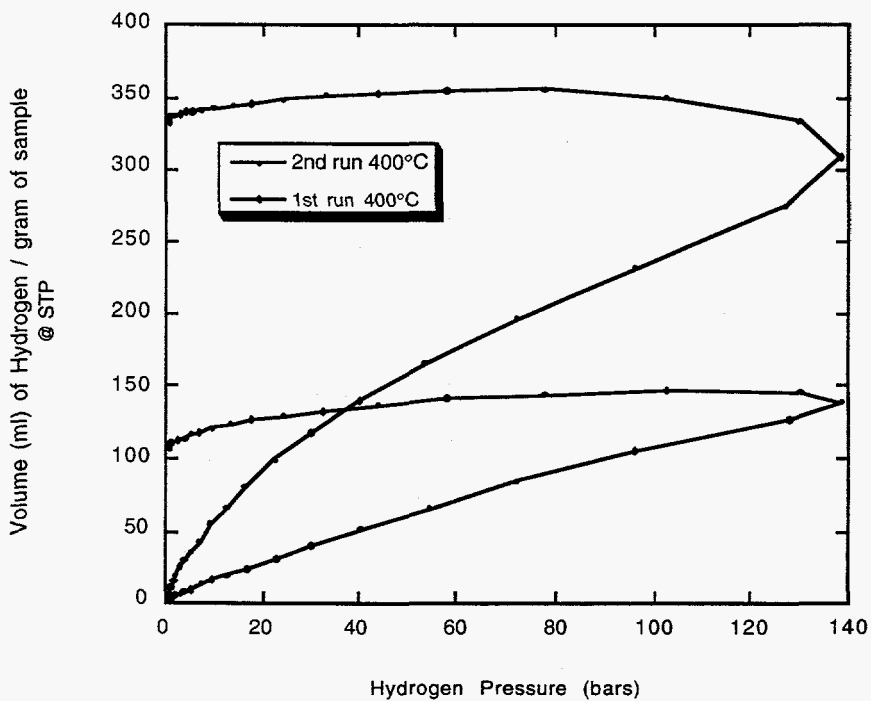


Figure 8. Quantity of hydrogen adsorbed and desorbed for $Ru_3 \bullet C_{60}$ with respect to hydrogen pressure corrected to volume adsorbed at standard temperature and pressure.
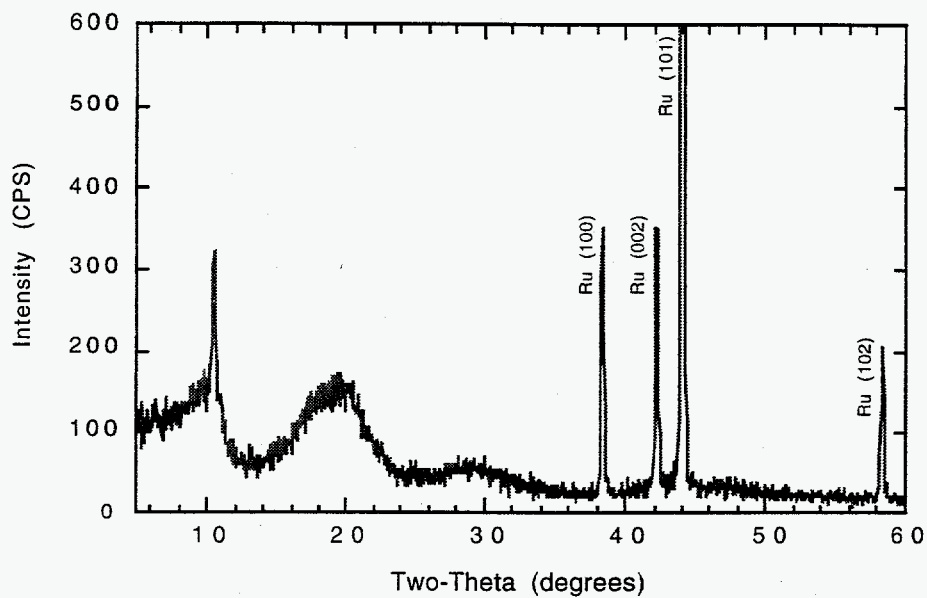
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Figure 9. XRD trace between 5 and 60° two-theta using $CuK_\alpha$ radiation of $Ru_3 \cdot C_{60}$ dehydrogenated at 575°C.