Evaluation of the physi- and chemisorption of hydrogen in alkali (Na, Li) doped fullerenes

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Abstract

In this study, alkali doped fullerenes synthesized by two different solvent assisted mixing techniques are compared for their hydrogen uptake activity. In particular, we investigated the interaction of hydrogen with lithium and sodium doped fullerenes via physisorption. In addition, we present the first mass spectrometric evidence for the formation of C₆₀H₆₀ via chemisorption. Hydrogen physisorption isotherms up to 1 atm at temperatures ranging from 77 K to 303 K were measured demonstrating an increase in hydrogen uptake versus pure C₆₀ and increased isosteric heats of adsorption for the lithium doped fullerene Li₁₂C₆₀. The hydrogen uptake in Na₆C₆₀, Li₆C₆₀, and Li₁₂C₆₀ was enhanced compared to pure C₆₀. However, despite these improvements the low amount of physisorbed hydrogen at 1 atm and 77 K in these materials suggests that fullerenes do not possess enough accessible surface area to effectively store hydrogen due to their close packed crystalline nature.

Keywords: Hydrogen Storage, fullerenes, C₆₀H₆₀, physisorption, chemisorption.

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1. Introduction

Storing hydrogen safely and efficiently with renewable resources is of great interest for the development of clean energy technologies incorporating hydrogen as an energy carrier. The most common approaches for storing hydrogen in materials are via physisorption in porous materials, storage in metal hydrides, chemical storage, or Kubas bound hydrogen (weak covalent bond) in which the intermolecular binding strength is between that of physisorption and chemisorption.^[1] It has been proposed by various theoretical studies that alkali decorated fullerenes could be capable of storing a significant amount of hydrogen in a Kubas fashion on the alkali metals bound to the fullerene cage.^[2-4] Investigation of hydrogen storage materials based on carbon is further inspired by the abundance of carbon on Earth, the wide range of material properties that can be obtained through various allotropes of carbon, and the low atomic mass of carbon. Since high gravimetric densities of hydrogen are required for application in light duty PEM fuel cell vehicles, light elements are required for chemisorption based materials. It is well known that the gravimetric hydrogen densities of many hydrocarbons, such as octane (15.8 wt% H₂), are sufficient to satisfy DOE requirements. Furthermore, the volumetric hydrogen density in octane (0.1109 g/mL or 0.055 mol H₂/mL at 25°C) is higher than that of liquefied hydrogen (0.07 g/mL or 0.0348 mol H₂/mL). Unfortunately, hydrogen storage applications for alkanes have been hindered by incomplete conversion to the alkene, low reversibility, and the requirement of precious metal catalysts.^[5] Therefore, the most logical carbon-based compounds for hydrogen storage would be materials, such as fullerenes, which are capable of complete reversibility without the need for precious metal catalysts. Previous work by our group has demonstrated enhancements in the hydrogen storage properties of complex metal hydrides using C₆₀ and carbon nanotubes.^[6-9] It was determined that the addition of C₆₀ to LiBH₄ lowers the

dehydrogenation temperature of LiBH_4 and the pressure and temperature requirements for its regeneration. It was also determined that carbon nanomaterials can have a catalytic effect on the dehydrogenation of NaAlH_4 by destabilizing the AlH_4 anion. We have also previously investigated alkali doped fullerenes by anelastic spectroscopy as well as other spectroscopic methods and reported a comparison of the chemisorption properties of sodium and lithium doped fullerenes by the hydride doping method.^[10-12] These previous results show increased hydrogen uptake for alkali hydride doped fullerenes.

Direct hydrogenation of fullerenes to produce fulleranes (hydrogenated fullerenes) is well known.^[13] It has been demonstrated that fulleranes more reduced than $\text{C}_{60}\text{H}_{36}$ can be produced with extreme conditions ($T = 400\text{ }^\circ\text{C}$, $P = 120\text{ bar}$). While the mixture of fulleranes possessed an average of ~ 31 hydrogens per C_{60} ,^[14,15] fulleranes with a hydrogen content greater than $\text{C}_{60}\text{H}_{36}$ were observed by mass spectrometry. It was further discovered that temperatures above $400\text{ }^\circ\text{C}$ can result in cage fragmentation. Recently, we have shown that lithium doped fullerenes can enhance the reversibility and reduce the temperature and pressure required ($T = 350\text{ }^\circ\text{C}$, $P = 105\text{ bar}$) to produce highly reduced fullerenes up to $\text{C}_{60}\text{H}_{48}$ with an average of ~ 40 hydrogens per C_{60} .^[16] Similar enhancements of the chemisorption of hydrogen in $\text{Li}_{12}\text{C}_{60}$ has also been demonstrated.^[17] It has also been previously reported by our group and Mauron et al that sodium doping of fullerenes leads to increased hydrogen capacities via chemisorption.^[18, 19]

Another avenue for hydrogen storage is via physisorption of hydrogen on alkali doped fullerenes. Density functional theory calculations suggest that lithium decorated fullerenes could store large amounts of hydrogen via physisorption with binding energies comparable to that of Kubas bound H_2 .^[4] The high hydrogen uptake predicted is attributed to a charge transfer of electron density to the fullerene cage from the lithium atom. Based on the DFT calculations, it

was predicted that the charge differential created would polarize the molecular orbital of hydrogen leading to an enhanced electrostatic attraction between the hydrogen molecule and lithium located on the surface of the fullerene cage. However, these theoretical studies were conducted on an isolated alkali doped fullerene and the actual solid state crystal lattice ensemble was not considered due to extensive computation requirements.

Herein, we report our efforts to experimentally evaluate the enhancement of hydrogen physisorption in alkali (Na, Li) doped C₆₀. We also report a comparison of different solvent assisted mixing methods (in THF or NH₃) and alkali metal source (hydride or metal). Additionally, we also examined the chemisorption of highly hydrogenated Na₆C₆₀ by LDI-TOF-MS. Hydrogen and deuterium chemisorption studies on this material are consistent with the formation of C₆₀H₆₀.

2. Experimental

2.1 Chemicals

Anhydrous ammonia was purchased from Air Gas and was delivered to reaction vessels through a drying tube filled with Dryrite. Sodium hydride (95 %), lithium hydride (95 %, 30 mesh), Sodium (99 %) and Lithium (99 %) were purchased from Sigma Aldrich and used as received. C₆₀ (99.5%) was purchased from SES corp. and was used without further purification.

2.2 Synthesis

Lithium and sodium doped fullerenes were prepared via two different methods, which will be referred to in this study as “hydride doped” and “NH₃ mixed”. Hydride doped sodium

and lithium C₆₀ were synthesized via solvent assisted mixing in THF, solvent removal, and annealing as described in previous work. [16, 18]

Lithium and sodium doped fullerenes were also prepared by solvent assisted mixing in liquid ammonia. Lithium and sodium to C₆₀ ratios 6:1 and 12:1 were prepared by adding the appropriate molar ratios of alkali metal and C₆₀ (250-500mg scale) to a 3-neck round bottom flask equipped with a dry ice/acetone condenser and flow control stopcocks under an Ar atmosphere. The apparatus was then connected to a Schlenk line and purged with UHP Ar, followed by addition of approximately 150 mL of liquid ammonia by condensation. Upon solvation of the lithium metal a deep red color is observed as well as solvation of the C₆₀. The reaction mixture was then stirred for 8-12 hours followed by solvent removal under Ar flow at ~80 °C. The product was then collected and annealed under vacuum at 200 °C.

2.3 Instrumental Techniques

Laser desorption ionization time-of-flight mass spectrometry (LDI-TOF-MS) was carried out on an Applied Biosystems Voyager DE-Pro using delayed pulse extraction in reflectron mode with a 337.1 nm nitrogen laser. Positive mode spectra were recorded with a spectrum consisting of 50 averaged spectra. Typical mass resolution ($m/\Delta m$) was 2,500 and was calculated using the full width half maximum approach. Samples were prepared, under an argon atmosphere, by spotting the plate with 1 μ L of a 0.5 mg/mL solution of the sample in THF. The sample plate was contained in an argon filled container for transfer to the spectrometer, but 5-10 seconds of air exposure were required to insert the sample plate into the instrument. In order to determine if oxidation had occurred, the samples were left in air overnight after measurements to observe differences between the two mass spectra. It was noticed that peaks consistent with

$C_{60}H_xO$ were noticed after overnight air exposure, but were not noticed in spectra with 5-10 seconds of air exposure.

The hydrogen chemisorption experiments were carried out on a HyEnergy PCT Pro 2000 (Sievert's Apparatus) with a sample size of ~ 100 mg with 100 bar of H_2 overpressure. The temperature was ramped from 25 °C to the target temperature (300 °C or 350 °C) over 1.5 hours followed by isothermal conditions for 11 hours at the temperature of interest.

Fourier-Transform Infrared spectroscopy (FT-IR) measurements were carried out on a Thermo Scientific Nicolet IR100 FT-IR in a nitrogen filled glovebox over the range of 500 to 3500 cm^{-1} . Samples were prepared as KBr pellets with a sample to KBr weight ratio of approximately 1:100. X-ray photoelectron measurements were performed using a PHI 3056 XPS spectrometer utilizing an Al X-ray source operated at 350W and 15 kV. Samples were pressed into indium sheets mounted on a sample holder in an argon filled glove box. The samples were load locked from the glove box into the XPS to prevent surface oxidation in a specially built transfer device. Charge calibrations, on the order of 0.2 eV, were made by assigning the first C peak a value of 284.8 eV. Hydrogen physisorption measurements were carried out on a Quantachrome AUTOSORB-1C instrument (Quantachrome Corporation, USA) using research grade hydrogen (99.9999 % purity). Measurements were made at 77K with 40 adsorption points and 40 desorption points in a 9mm cell with rod insert. Samples of approximately 100 mg were degassed for 1 hour at 300 °C prior to measurements. Hydrogen adsorption isotherms were fit to the one-binding site Langmuir model.

3. Results and Discussion

3.1 Physisorption

A series of physisorption measurements demonstrate that alkali metal doping enhances the hydrogen physisorption capability of fullerenes. Increased hydrogen uptake was noticed in fullerenes doped with alkali metals via both methods. Although the crystalline nature of C_{60} limits the accessible surface area resulting in low hydrogen capacities at ambient pressures, the focus of the study is to evaluate the effect of the dopant on the physisorption interaction of hydrogen with C_{60} . Variable temperature isotherms of $Li_{12}C_{60}$ (Figure 1A) and pure C_{60} (Supporting Information) were used to calculate the isosteric heats of adsorption of the materials. (2.97 KJ/mol for $Li_{12}C_{60}$ and 0.486 KJ/mol for C_{60}) These measurements demonstrate that alkali metal doping of fullerenes increase the isosteric heats of adsorption (Figure 1B) which improve the hydrogen uptake compared to pure C_{60} . Figure 2 shows the enhancement in hydrogen uptake via physisorption for the Li and Na hydride doped C_{60} (M_6C_{60}) compared to pure C_{60} at 77K. Hydrogen uptake was increased more than an order of magnitude for the hydride doped fullerenes Na_6C_{60} and Li_6C_{60} . At 1 atm the hydrogen uptake was 14.69 cc/gram, 8.64 cc/gram, and 0.39 cc/gram for the Li_6C_{60} , Na_6C_{60} , and pure C_{60} respectively.

Figure 1: A) Hydrogen isotherms of Li₁₂C₆₀ at different temperatures B) Isosteric heats of adsorption for Li₁₂C₆₀ and C₆₀ for an adsorption amount up to 0.40 cc/gram

Figure 2: Hydrogen physisorption curves at 77 K for C₆₀ (black squares), Na₆C₆₀ (blue triangles), and Li₆C₆₀ (red circles) from hydride synthesis.

3.2 Chemisorption

The chemisorption properties of alkali doped fullerenes were further investigated to determine the possibilities of forming highly hydrogenated fullerene species ($>C_{60}H_{48}$). Figure 3 shows the positive mode mass spectra of hydrogenated Na_6C_{60} and Li_6C_{60} synthesized via liquid ammonia. Evidence for hydrogenated fullerenes up to $C_{60}H_{36}$ is clearly apparent in both lithium and sodium doped fullerenes hydrogenated at 300 °C and 100 bar of hydrogen overpressure. Laser desorption ionization time-of-flight mass spectrometry (LDI-TOF-MS) measurements confirm higher levels of hydrogenation for the alkali doped fullerenes than for pure C_{60} which displays a mass distribution corresponding to less than $C_{60}H_{18}$. (Supporting Information) The alteration of intensities between even and odd hydrogen containing ions (every 1 amu) is characteristic of LDI-TOF-MS spectra of hydrogenated fullerenes as shown in many works.^[13,16,18] Higher levels of hydrogenation in alkali doped fullerenes via the hydride doped synthetic methods have been demonstrated in our previous work.^[16,18] In this case, we demonstrate that alkali metal doped fullerenes created via the liquid ammonia synthesis also facilitate the chemisorption of hydrogen onto the fullerene cage.

Figure 3: Positive mode LDI-TOF-MS spectra of alkali doped fullerenes synthesized via liquid ammonia and hydrogenated at 300°C and 100 bar H₂. **A)** C₆₀H_x from Na₆C₆₀ **B)** C₆₀H_x from Li₆C₆₀

FT-IR was utilized to show the similarity between the Na and Li doped C₆₀ synthesized by alkali intercalation using liquid ammonia. The spectra displayed in Figure 4 shows the characteristic F_{1u} vibrational modes of C₆₀ (527 cm⁻¹, 577 cm⁻¹, 1183 cm⁻¹, 1428 cm⁻¹) in the alkali doped fullerenes synthesized in liquid ammonia.^[20] Broad peaks at ~2845 cm⁻¹ and ~2914 cm⁻¹, representing sp³ hybridized C-H stretching modes, are observed for the alkali doped fullerenes that were hydrogenated at 300 °C and 100 bar hydrogen. The disappearance of the F_{1u} vibrational modes in the hydrogenated samples is consistent with a breaking of the symmetry from hydrogen addition which is consistent with previous studies.^[21]

Figure 4: FT-IR spectra of Li and Na doped fullerenes synthesized via liquid ammonia in the hydrogenated and as prepared state.

To further understand the surface chemistry of the materials Na 1s and Li 1s XPS spectra were collected for the samples (presented in Figure 5) along with appropriate reference compounds. For the lithium doped fullerenes, there is a clear 2 eV shift in the Li species in the hydride doped samples to higher binding energies compared to the NH_3 mixed samples. This is consistent with a slight oxidation of Li or a decrease in electron density on the Li. The lower Li binding energy measured for pure LiH suggests that there is more electron density donation to the fullerene than to the hydride indicating the Li bound to the surface is more cationic in nature. A similar 1 eV shift in binding energy is observed between the hydride doped and NH_3 mixed sodium intercalated fullerenes. The re(de)hydrogenated samples (produced by the hydride doped synthesis) show similar binding energies as the starting material (MH:C_{60}) indicating that the alkali metals are present in similarly oxidized conditions.

Figure 5: XPS spectra for the Na and Li doped fullerenes synthesized by the hydride doping method (MH:C₆₀) and the liquid ammonia method (M:C₆₀). The re(de)hydrogenated species are the hydride doped samples.

In our continued effort to characterize the formation of alkali doped fullerenes under higher temperatures and pressures, we turned our focus to the chemisorption of hydrogen in Na₆C₆₀. The degree of hydrogenation in the material as a function of pressure and temperature was monitored by LDI-TOF-MS. A series of mass peaks consistent with the formation of C₆₀H₆₀ was observed when the sample was hydrogenated at 350°C and 100 bar H₂. Figure 6 shows the mass spectra of sodium doped fullerenes, synthesized by hydride doping and hydrogenated at 350 °C. The spectra display a large intensity distribution corresponding to C₆₀H₃₆, as evidenced by the peak ending at 755 m/z (C₆₀H₃₅⁺), with another distribution consistent with C₆₀H₆₀ at 780 m/z (C₆₀H₆₀⁺). In order to confirm the identity of the higher mass distribution, a series of mass spectrometric experiments were carried out to rule out other possible ions. First, the material was exposed to air overnight to insure that the distribution was not the result of oxidation. Figure 6B displays a mass distribution for the oxidized material shifted up by 16 m/z with no significant changes in intensity for the other distributions. Na₆C₆₀ was then deuterated in order to observe a shift by 2 amu for each deuterium compared to the 1 m/z shift for each hydrogen. The mass distributions observed for the deuterated fullerenes shifted by 36 m/z for the first distribution and

by 60 m/z for the second distribution which is consistent with $C_{60}D_{36}$ and $C_{60}D_{60}$ respectively. For comparison purposes, Na_6C_{60} was deuterated at 290 °C and only displays a mass distribution corresponding to $C_{60}D_{36}$ (792 m/z) demonstrating that the higher hydrogenation temperature favors the formation of $C_{60}D_{60}$. It is highly unlikely that this higher mass distribution is due to a sodium atom attached to the cage since this is not observed in the lower temperature hydrogenated samples. Furthermore, this would mean that deuterated samples would only attach 2 sodium atoms and hydrogenated samples would only attach 1 sodium atom. Again this is improbable and no higher mass distributions corresponding to multiple sodium atom addition is observed. Although there have been previous reports of $C_{60}H_{60}$,^[22-24] to our knowledge this LDI-TOF-MS data is the first to show mass spectrometric evidence for the existence of $C_{60}H_{60}$. Previous reports for the production of $C_{60}H_{60}$ utilized gravimetric methods to show that the weight change of the material corresponded to 60 hydrogens per fullerenes or isothermal conditions showing a pressure drop of hydrogen that corresponded to 60 hydrogens per fullerene cage. Meletov et al. used combustion analysis to confirm the hydrogen content in their material and Raman spectroscopy to show an increase in symmetry of the material as evidenced by a decrease in the number of vibrational modes. Although these techniques demonstrate hydrogen capacities corresponding to $C_{60}H_{60}$, none of these techniques completely rule out the possibility of cage fragmentation into polyaromatic hydrocarbons. This is known to occur in pure C_{60} hydrogenated under extreme conditions.^[25]

Figure 6: Positive mode LDI-TOF-MS spectra of hydride doped Na_6C_{60} A) hydrogenated at 350 °C and 100 bar H_2 B) hydrogenated at 350 °C and 100 bar H_2 air exposed overnight C) deuterated at 290 °C and 100 bar D_2 D) deuterated at 350 °C and 100 bar D_2 .

4. Conclusion

The physisorption measurements display low hydrogen uptake in the alkali doped C_{60} samples under 1 atm H_2 and 77K. However, the alkali doped samples demonstrated an order of magnitude increase in the hydrogen uptake relative to the pure C_{60} sample. We also observed an increase in the isosteric heat of absorption (2.97 kJ/mol) compared to pure C_{60} (0.486 kJ/mol). These findings demonstrate that the interaction strength between hydrogen and C_{60} is increased upon alkali doping with both sodium and lithium. The enhancement of adsorption upon alkali doping is believed to be due to the differential charge gradient produced on the surface of the

fullerene which gives rise to enhanced dipole interactions. The low hydrogen adsorption capacity is attributed to the low BET surface areas for C₆₀. Previous studies using nitrogen for BET experiments presented an average surface area less than 1 m²/g. ^[26] This is virtually negligible compared to the surface areas of MOF's which typically have surface areas greater than 2000 m²/g. ^[27] The low surface area of C₆₀ is attributed to the highly crystalline state and small pore sizes of our materials. To overcome this problem, recent theoretical work proposed the possibility of incorporating Li doped C₆₀ into a porous aromatic framework (PAF) with the consequent enhancement of the composite's physisorption capacity. ^[28] It has also been reported that hydrogen uptake can be enhanced in pure C₆₀ by high temperature activation with oxygen or carbon dioxide. ^[29, 30] These enhancements are likely due to an increased accessible surface area upon cage alteration. On the other hand, enhancements shown in our materials are due to the dopant (Na, Li) present in our materials and not an increase in accessible surface area.

Alkali doped fullerenes synthesized by the different techniques demonstrated in this work display slight differences in the hydrogen storage capacities via either a chemisorption or a physisorption mode. The differences observed are likely due to variable localized alkali metal clustering or changes in the alkali metal's locations on the fullerene due to the synthetic method used. Alkali doping also enhanced the chemisorption properties of fullerenes resulting in higher degrees of hydrogenation compared to pure C₆₀. It is evident that alkali doping of C₆₀ alters the electronic properties of C₆₀ as it enhances the interaction with hydrogen. Therefore, the most logical hypothesis is that the alkali metal is either dispersed differently within the two materials or has differing bonding with the fullerene cage. This may be due to a difference in the position on the fullerene cage that the alkali metal occupies or a difference in the number of alkali atoms on each fullerene cage. Although the molar ratio of alkali metal to C₆₀ in each case is

predetermined, the most stable and preferred number of alkali metal atoms on each fullerene cage may be different for each synthetic technique. Alkali decorated fullerenes synthesized by both techniques (hydride doped and NH_3 mixed) show enhancements in the chemisorption and physisorption properties of hydrogen compared to pure C_{60} . The enhancement in both physisorption and chemisorption properties is most likely due to the nature of the charge differential created from the electron density donation to the fullerene cage from the alkali metal.

We also present the first spectroscopic evidence for the formation of $\text{C}_{60}\text{H}_{60}$ when the material is doped with sodium. To our knowledge this is the first reported mass spectrometric confirmation of the molecular species $\text{C}_{60}\text{H}_{60}$. Deuteration experiments confirm that the additional mass observed on the C_{60} is from additional hydrogen and not another element. Currently the $\text{C}_{60}\text{H}_{60}$ is present in a mixture of other hydrogenated fullerenes, but these finding indicate that it may be possible to isolate $\text{C}_{60}\text{H}_{60}$ in pure form. Attempts to isolate and characterize $\text{C}_{60}\text{H}_{60}$ and other highly hydrogenated fullerene species ($>\text{C}_{60}\text{H}_{48}$) are currently under investigation.

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References

- 1) Jena, P. Materials for Hydrogen Storage: Past, Present, and Future. *J. Phys. Chem. Letters*, **2011**, 2, 206-211.
- 2) Chandrakumar, K. R. S.; Srinivasu, K.; Ghosh, S. K. Nanoscale Curvature-Induced Hydrogen Adsorption in Alkali Metal Doped Carbon Nanomaterials. *J. Phys. Chem. C* **2008**, 112, 15670-15679.
- 3) Sun, Q.; Jena, P.; Wang, Q.; Marquez, M. First-Principles Study of Hydrogen Storage on $\text{Li}_{12}\text{C}_{60}$. *J. Am. Chem. Soc.* **2006**, 128, 9741-9745.
- 4) Chandrakumar, K. R. S.; Ghosh, S. K. Alkali-Metal-Induced Enhancement of Hydrogen Adsorption in C_{60} Fullerene: An Ab Initio Study. *Nano Letters* **2008**, 8 (1), 13-19.
- 5) Jensen, C. M.; Sun, D.; Raman, S. S.; Murphy, K.; Niemczura, W. P.; Kumashiro, K. K.; et al. Catalytically enhanced systems for hydrogen storage. Proceedings for the 2002 U.S. DOE Hydrogen Program Review.
- 6) Shane, D. T.; Corey, R.; Rayhel, L.; Wellons, M.; Teprovich, J. A.; Zidan, R.; Hwang, S.; Bowman, R.; Conradi, M. S. NMR Study of LiBH_4 with C_{60} . *J. Phys. Chem. C* **2010**, 114, 19862-19866.
- 7) Teprovich, J. A.; Knight, D.; Wellons, M.; Zidan, R. Catalytic Effect of Fullerene and Formation of Nanocomposites with Complex Hydrides. *J. Alloys Compd.* **2011**, 509, S562-S566.

- 8) Ward, P. A.; Teprovich, J. A.; Peters, B.; Wheeler, J.; Compton, R. N.; Zidan, R.
Reversible Hydrogen Storage in a $\text{LiBH}_4\text{-C}_{60}$ Nanocomposite. *J. Phys. Chem. C* **2013**, *117*, 22569-22575.
- 9) Berseth, P. A.; Harter, A. G.; Zidan, R.; Blomqvist, A.; Araujo, C. M.; Scheicher, R. H.; Ahuja, R.; Jena, P. Carbon Nanomaterials as Catalysts for Hydrogen Uptake and Release in NaAlH_4 . *Nano Letters* **2009**, *9* (4), 1501-1505.
- 10) Paolone, A.; Vico, F.; Teocoli, F.; Sanna, S.; Palumbo, O.; Cantelli, R.; Knight, D.; Teprovich, J. A.; Zidan, R. Relaxation Processes and Structural Changes in Li and Na Doped Fullerenes for Hydrogen Storage. *J. Phys. Chem. C* **2012**, *116*, 16365-16370.
- 11) Paolone, A.; Palumbo, O.; Leardini, F.; Cantelli, R.; Knight, D.; Teprovich, J. A.; Zidan, R. A Spectroscopic Investigation of Hydrogenated Li Doped Fullerene. *J. Alloys Compd.* **2013**, *580*, S67-S69.
- 12) Teprovich, J. A. Jr.; Knight, D. A.; Peters, B.; Zidan, R. Comparative study of reversible hydrogen storage in alkali-doped fullerenes. *J. Alloys Compd.* **2013**, *580*, S364-S367.
- 13) Jin, C.; Hettich, R.; Compton, R.; Joyce, D.; Blencoe, J.; Burch, T. Direct Solid-Phase Hydrogenation of Fullerenes. *J. Phys. Chem.* **1994**, *98*, 4215-4217.
- 14) Talyzin, A. V.; Tsybin, Y. O.; Purcell, J. M.; Schaub, T. M.; Shulg, Y. M.; Noreus, D.; et al. Reaction of Hydrogen Gas with C_{60} at Elevated Pressure and Temperature: Hydrogenation and Cage Fragmentation. *J. Phys. Chem. A* **2006**, *110*, 8528-8534.
- 15) Luzan, S. M.; Tsybin, Y. O.; Talyzin, A. V. Reaction of C_{60} with Hydrogen Gas: In Situ Monitoring and Pathways. *J. Chem. Phys. C* **2011**, *115*, 11484-11492.

- 16) Teprovich, J. A.; Wellons, M. S.; Lascola, R.; Hwang, S.; Ward, P. A.; Compton, R. N.; et al. Synthesis and Characterization of a Lithium-Doped Fullerane ($\text{Li}_x\text{-C}_{60}\text{-H}_y$) for Reversible Hydrogen Storage. *Nano Lett.* **2012**, *12*, 582-589.
- 17) Mauron, P.; Gaboardi, M.; Remhof, A.; Bliersbach, A.; Sheptyakov, D.; Aramini, M.; Vlahopoulou, G.; Giglio, F.; Pontiroli, D.; Ricco, M.; Züttel, A. Hydrogen Sorption in $\text{Li}_{12}\text{C}_{60}$. *J. Phys. Chem. C* **2013**, *117*, 22598-22602.
- 18) Knight, D. A.; Teprovich, J. A. Jr.; Summers, A.; Peters, B.; Ward, P. A.; Compton, R. N.; Zidan, R. Synthesis, characterization, and reversible hydrogen sorption study of sodium-doped fullerene. *Nanotechnology* **2013**, *24*, 455601 (7pgs).
- 19) Mauron, P.; Remhof, A.; Bliersbach, A.; Borgschulte, A.; Züttel, A.; Sheptyakov, D.; Gaboardi, M.; Choucair, M.; Pontiroli, D.; Aramini, M.; Gorreri, A.; Ricco, M. Reversible hydrogen absorption in sodium intercalated fullerenes. *Int. J. Hydrogen Energy* **2012**, *37*, 14307-14314.
- 20) Rao, A. M.; Eklund, P. C.; Hodeau, J.-L.; Marques, L.; Nunez-Reguerio, M. *Phys. Rev. B* **1997**, *55*, 4766-4773
- 21) Bini, R.; Ebenhoch, J.; Fanti, M.; Fowler, P. W.; Leach, S.; Orlandi, G.; Ruchardt, Ch.; Sandall, J. P. B.; Zerbetto, F. The vibrational spectroscopy of $\text{C}_{60}\text{H}_{36}$: An experimental and theoretical study. *Chem. Phys.* **1998**, *232*, 75-94.
- 22) Cataldo, F.; Milani, P. Fullerenes: The Hydrogenated Fullerenes, Springer, 2010, New York, NY.
- 23) Meletov, K. P.; Bashkin, I. O.; Shestakov, V. V.; Tartakovskii, I. I.; Maksimov, A. A.; Arvanitidis, J.; Christofilos, D.; Kourouklis, G. A. Comparative Raman Study of the

$C_{60}H_{36}$ and $C_{60}H_{60}$ Fullerene Hydrides. *Fullerenes, Nanotubes, and Carbon*

Nanostructures, **2008**, *16*, 593-596.

- 24) Schur, D. V.; Zaginaichenko, S. Y.; Savenko, A. F.; Bogolepov, V. A.; Anikina, N. S.; Zolotarenko, A. D.; Matysina, Z. A.; Veziroglu, T. N.; Skryabina, N. E. Experimental evaluation of total hydrogen capacity for fullerite C_{60} . *Int. J. Hydrogen Energy* **2011**, *36*, 1143-1151.
- 25) Talyzin, A. V.; Luzan, S.; Anoshkin, I. V.; Nasibulin, A. G.; Kauppinnen, E. I.; Dzwilewski, A.; Kreta, A.; Jamnik, J.; Hassanien, A.; Lundstedt, A.; Grennberg, H. Hydrogen-Driven Cage Unzipping of C_{60} into Nano-Graphenes. *J. Phys. Chem. C* **2014**, *118* (12), 6504-6513.
- 26) Mackeyev, Y. A.; Marks, J. W.; Rosenblum, M. G.; Wilson, L. J. Stable Containment of Radionuclides on the Nanoscale by Cut Single-Wall Carbon Nanotubes. *J. Phys. Chem. B* **2005**, *109*, 5482-5484.
- 27) Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M. The Chemistry and Applications of Metal-Organic Frameworks. *Science* **2013**, *341*, 1230444.
- 28) Ahmed, A.; Thornton, A. W.; Konstas, K.; Kannam, S. K.; Babarao, R.; Todd, B. D.; Hill, A. J.; Hill, M. R. Strategies toward Enhanced Low-Pressure Volumetric Hydrogen Storage in Nanoporous Cryoadsorbents. *Langmuir* **2013**, *29* (50), 15689-15697.
- 29) Deng, S.; Saha, D. Hydrogen adsorption on partially truncated and open cage C_{60} fullerene. *Carbon* **2010**, *48*, 3471-3476.
- 30) Loutfy, R. O.; Wexler, E. M. Feasibility of Fullerene Hydride as A High Capacity Hydrogen Storage Material. *Proceedings of the 2001 DOE Hydrogen Program Review*, **2001**.