

## IV.H.10 Exploration of Novel Carbon-Hydrogen Interactions

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### Objectives

Hydrogen trapped in a carbon cage, captured through *repulsive* interactions, is a novel concept in hydrogen storage which borrows an idea from macroscale hydrogen storage (i.e. compressed gas storage tanks) and reapplies these concepts on the nanoscale in specially designed molecular containers. Under extreme conditions of pressure, hydrogen solubility in carbon materials is expected to increase and carbon is expected to restructure to minimize volume via a mixed  $sp^2/sp^3$  hydrogenated state. Our approach to form hydrogen caged in carbon relies on unique chemical reaction conditions provided by mechanochemistry, including dynamic shearing/compression via mechanical milling and static high-pressure chemistry in a diamond anvil cell. Materials are currently being characterized via multiwavelength in situ Raman spectroscopy to probe carbon-hydrogen interactions and structural changes in the carbon backbone. Complementary first-principles materials theory is being used to examine candidate carbon-cage structures to predict the characteristic Raman signatures of hydrogen held in place by either repulsive interactions (caged hydrogen) or attachment to the carbon backbone in mixed  $sp^2/sp^3$  states.

### Abstract, Progress Report and Future Directions

#### 1. Transformation of Hydrogenated Bucky-Balls at High pressure

Thermodynamics dictate that pre-formed C-H structures will rearrange with increased pressure, yet the final carbon-hydrogen interactions may be dependent upon the mechanism by which hydrogen is introduced. Molecular

dynamics with reactive force fields (ReaxFF) have been implemented in modeling compressed hydrocarbons and hydrogenated  $C_{60}$  (mainly  $C_{60}H_{36}$  and  $C_{60}H_{18}$ , systems also being investigated experimentally). The cage structure of  $C_{60}$  and the interplay between inter-ball polymerization into  $sp^3$  geometries and on-ball  $sp^3$  sites of H attachment could be beneficial for loading hydrogen into local traps. Compression of two initial crystal structures of  $C_{60}H_{36}$  was simulated by ReaxFF under a series of high pressures up to 30 GPa. Polymerization of hydrogenated  $C_{60}$  is not achieved under hydrostatic compression, but under shock compression it can be induced, with hydrogen released. A simple theoretical model for understanding the propensity for H release during compression of various hydrocarbon systems has been designed in which a volume is associated with each bond type (C-H, etc.). The model shows consistency with simple alkane molecules. The model needs more delicate tweaks to accommodate complex hydrocarbons such as hydrogenated  $C_{60}$  with the simulation support of first principle theory and ReaxFF.

Experimentally,  $C_{60}H_{14}$  has been synthesized to validate the ReaxFF models. A hydrogen transfer reaction between  $C_{60}$  and a complex amine, diethylene triamine, was used to synthesize the hydrogenated  $C_{60}$ . Synthesis and storage under inert atmosphere with no exposure to light ensured resistance to oxidation and cleavage of C-H bonds respectively. Hydrogenation of  $C_{60}$  and minimization of oxidation has been confirmed with solid state  $^{13}C$  nuclear magnetic resonance and Fourier transform infrared spectroscopy (FTIR). Matrix-assisted laser desorption/ionization mass spectrometry shows a broad distribution of ions from 728 to 740, and an intense peaks at 734 confirm the formation of  $C_{60}H_{14}$ . An FTIR experiment at static high pressure indicates no change in the C-H stretching region, consistent with the theoretical predictions. Ongoing Raman spectroscopy studies are being performed to analyze changes in the lattice modes and C-C bonding in the hydrogenated  $C_{60}$ . A combination of FTIR and Raman spectroscopy will be utilized to determine if  $H_2$  is evolved during the high pressure compression. Future work includes compression under non hydrostatic and shear conditions.

Compression of other hydrocarbons with the potential for release of  $H_2$  upon carbon polymerization are on-going. For example, compression of triptycene in the diamond anvil cell under non-hydrostatic conditions at room temperature led to polymerization at 25.4GPa. Future work will include compression of the same under hydrostatic conditions ( $H_2$  at 23,000psi) with resistive heating methods. The main goal is to find conditions for polymerization of triptycene under hydrostatic pressure and study the interaction of molecular  $H_2$  with the polymerized caged product. We are also studying

the diffusion and potential trapping of H<sub>2</sub> in pre-formed carbon materials such as glassy carbons and carbon onions. Parallel modeling studies include nanocage formation upon compression of triptycene and anthracene in the presence and absence of molecular H<sub>2</sub>.

## 2. In Situ Micro Raman Detection of Reversible Basal Plane Hydrogenation in Pt-doped Activated Carbon

Development of in situ spectroscopic measurement techniques capable of combined high-pressure and variable temperature measurements has allowed us to explore carbon-hydrogen interactions that are unresolved and debated in the literature. One such carbon-hydrogen interaction of particular interest is the binding mechanism between hydrogen and a carbonaceous support in the presence of a noble-metal dissociation catalyst, i.e. the hydrogen spillover mechanism [1]. Incorporation of a catalyst into nanoporous materials has led to several reports of particularly high hydrogen uptake at room temperature and pressures less than 100 bar [2], but the results are contested [3,4], reproducible by only a fraction of laboratories [5-7], and the active sites on the nanoporous support that bind reversibly with spilled over atomic hydrogen remains unclear [8,9]. We have investigated the local interaction between atomic H and the graphite basal plane adjacent to a Pt dissociation catalyst with in situ Raman spectroscopy and complementary density functional theory calculations. These results demonstrate spectroscopic evidence for hydrogenation of the carbon basal plane via the spillover mechanism; the feature is reversible for spillover to curved and defected oxidized activated carbon and irreversible to graphene and non-oxidized activated carbon. Poisoning of the catalyst eliminates the reversibility, showing desorption is through a reverse spillover mechanism. These results clarify whether H is chemisorbed or physisorbed, how reversibility is achieved, and how carbon structure and metal-carbon contact dictate the degree of reversibility.

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## Publications (including patents) acknowledging the grant or contract

1. Liu, X.M.; Rather, S.; Li, Q.; Lueking, A.D.; Zhao, Y.; Li, J. Hydrogenation of CuBTC framework with the introduction of a PtC hydrogen spillover catalyst. *J Phys. Chem. C*, *116* (5), 3477-3485, 2012.