BES011

Exploration of Novel Carbon-Hydrogen Interactions

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Transformation of Hydrogenated Bucky-Balls at High pressure

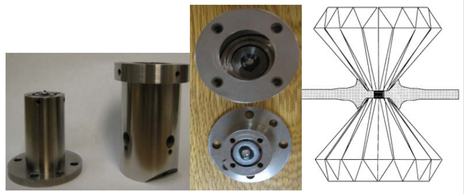
1 - Abstract

Thermodynamics dictate that pre-formed C-H structures will rearrange with increased pressure, yet the final carbon-hydrogen interactions may depend on the mechanism of hydrogen introduction.

- MD with ReaxFF used to model $C_{60}H_{36}$ and $C_{60}H_{18}$
- Investigate interplay between inter-ball polymerization into sp^3 geometries and on-ball sp^3 sites of H attachment
- Compress multiple crystal structures up to 30 GPa
- Develop a theoretical model for H release during hydrocarbon compression
- Test theory and models by comparison to experiment

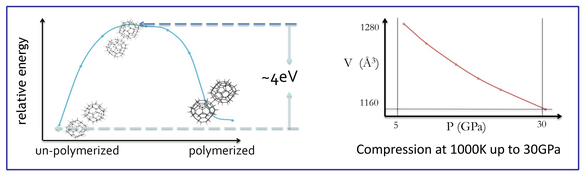
2 – Diamond Anvil Cell

Mao-Bell type piston-cylinder cells are used. Samples are loaded in a 250-300 μm hole in the metal gaskets and are compressed between the diamonds. High pressure gas can be loaded along with the sample as a pressure transmitting medium or reagent. Diamonds provide unique combination of optical clarity and high strength allowing for *in situ* Raman at GPa pressures

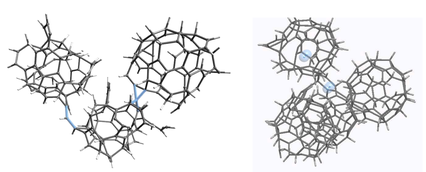


3 – Molecular Dynamics Simulation

Simulations imply that to automatically trap hydrogen gas during compression of $C_{60}H_{36}$ will require extreme conditions.



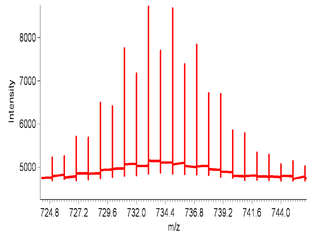
- $C_{60}H_{36}$ is stable against polymerization/dehydrogenation.
- Static Compression can't give rise to transformation. P-V relationship is smooth, and ball structure of $C_{60}H_{36}$ molecules remains at high pressures.
- Rapid (shock) compression may induce polymerization… Compression from ambient condition to 30GPA within 1ps, leads to failure of ball structure.

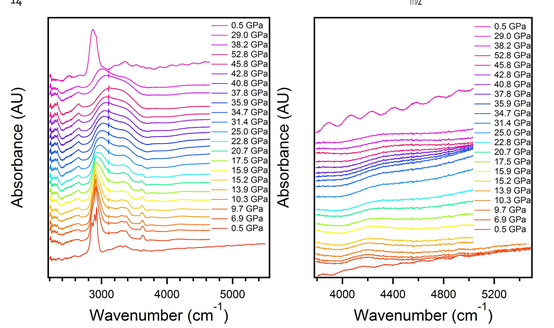


- … and also hydrogen release

4 – Experimental

A hydrogen transfer reaction between C_{60} and a complex amine, diethylene triamine, was used to synthesize $C_{60}H_{14}$ (as verified with ^{13}C NMR and FTIR).
At right, MALDI shows broad distribution of ions from 728 to 740 showing evidence of hydrogenation. Intense peaks at 734 confirm the formation of $C_{60}H_{14}$.





An FT-IR experiment at static high pressure indicates no change in the C-H stretching region up to 52 Gpa, other than the expected red shift with pressure. A candidate H_2 stretch (at ~4250 cm^{-1}, right) is due to either H_2 evolution and subsequent physisorption or etalonging effects. Subsequent Raman experiments (with 458, 488, and/or 633 nm excitation) will differentiate.

4 – Conclusions and On-Going Work

Molecular dynamics simulations suggest rapid compression will polymerize $C_{60}H_{36}$, while slow compression will not. Experimentally, FTIR of $C_{60}H_{14}$ that has been compressed up to 52 GPa confirms static high pressure does not modify the C-H stretching region. Raman spectroscopy studies are on-going to analyze changes in the lattice modes and C-C bonding, and possible evolution of H_2 is being confirmed. Future work includes compression under non-hydrostatic conditions and compression of solid carbon materials in the presence of H_2.

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

1 - Abstract

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. In particular we focused on the hydrogen spillover mechanism via Platinum catalyst.

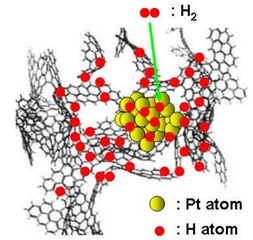
- *In situ* Raman and DFT to investigate local interaction between atomic H and the graphite basal plane adjacent to a Pt dissociation catalyst
- Demonstrate spectroscopic evidence for reversible hydrogenation of the carbon basal plane via the spillover mechanism

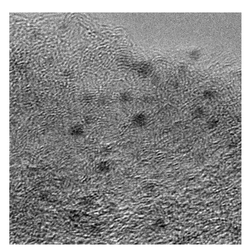
These results clarify C-H binding, mechanism for reversibility, and role of carbon structure and doping in mobility and reversibility.

2 –Structure and Characterization of AcOx

This presentation does not contain any proprietary, confidential, or otherwise restricted information.

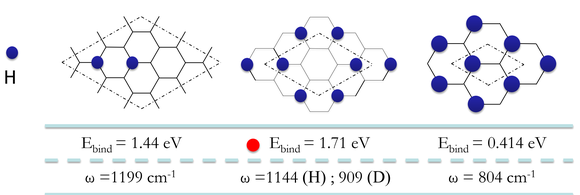
Raman spectroscopy shows the development of a C-H wag mode on exposure to H_2 and D_2 (above). AcOx particles are typically 3-5 nm thick and are curved on the nm length scale (TEM, below).





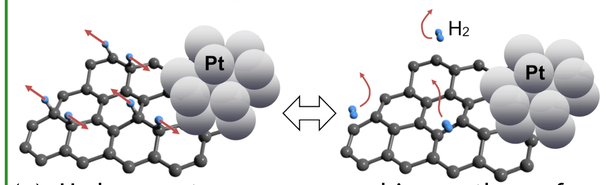
3 –Calculated H Binding Energies and Modes

First principle calculations show the 1160/1180 peak is consistent with C-H wagging, and when H is replace by Deuterium, the observed peak shift is as expected from theory. The exact frequency and binding energy varies with absorption density, and that this mode has a significant Raman intensity.



- Ten more configurations calculated but not shown here, among which this configuration has the lowest binding energy. Its Raman intensity ratio to that of the G peak is 0.086.

4 – Origin of Reversibility



(a) Hydrogen atoms may recombine on the surface via an Eley-Rideal mechanism. The kinetic barrier of this transition is about 0.5~1eV

(b) Hydrogen atoms may recombine on the catalyst, after surface diffusion. The barrier is also ~1eV

Pt poisoning experiments implicate the latter.

5 - Conclusions

This work gives spectroscopic evidence of hydrogen spillover onto an activated carbon. Simulations and theoretical calculations are used to confirm the origin of the spectroscopically observed C-H wag mode and develop thermodynamic arguments for adsorption by spillover and subsequent stability and desorption mechanisms.