
Dehydrogenation of Boron-Nanoclusters

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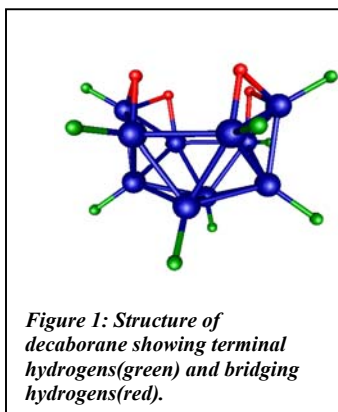
Program Scope

This new research program is designed to test the hypothesis that at a certain length scale the three-dimensional boron structural units found in certain boron-rich solids can be reversibly hydrogenated in the presence of a suitable catalyst to form boranes and/or carboranes with similar three-dimensional boron units. Of the elements lighter than carbon, only boron forms a rich array of compounds with high hydrogen weight percentages. The ability of boron hydrides to release their hydrogen and for the remaining boron nanoclusters to reabsorb hydrogen is being investigated. To promote the hydrogenation-dehydrogenation reactions, the boron clusters are being studied while in contact with a platinum surface, as platinum is a well-known hydrogenation-dehydrogenation catalyst. Since the reactions are intrinsically surface processes, a variety of surface science methods are being used, including reflection absorption infrared spectroscopy (RAIRS) and temperature programmed desorption (TPD). The PI's laboratory is well equipped to obtain RAIR spectra of molecules present at submonolayer coverages with exceptional sensitivity and resolution [1, 2]. The overall program entails the following components:

- RAIRS and TPD are being used to study the adsorption, chemical stability, and dissociation of decaborane, $B_{10}H_{14}$, on a Pt(111) surface under ultrahigh vacuum conditions.
- Analogous to the $B_{10}H_{14}$ /Pt(111) studies, other boron cage molecules such as carborane, $C_2B_{10}H_{12}$, will also be investigated by the same techniques.
- A new apparatus that will allow RAIRS studies of hydrogenation-dehydrogenation reactions under high $H_2(g)$ pressure conditions is being constructed.
- A second apparatus that will allow transmission IR studies of hydrogen interactions with boron nanowires prepared ex-situ is also being constructed.
- The interpretation of the experimental spectra is being aided with density functional theory calculations of small model clusters.

Recent Activity

Figure 1 shows the structure of a decaborane molecule, which has the structure of an 11-sided deltahedron lacking one boron atom and as is typical of the polyhedral boranes, it possesses terminal B-H bonds and bridging H-B-H bonds. Figure 2 shows hydrogen temperature programmed desorption (TPD) data after dosing decaborane onto the surface at low temperatures. It reveals that the molecule is dehydrogenated on the



surface in stages, with the final hydrogen loss occurring at 412 K. The lower temperature peaks are probably due to fragmentation associated with the desorption of a multilayer of decaborane, which gives rise to a peak at 255 K. More information on the thermal evolution of decaborane on Pt(111) is revealed by the RAIR

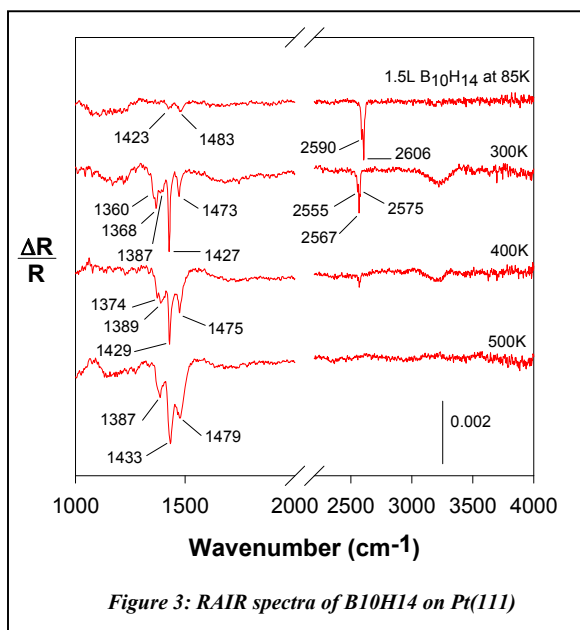


Figure 3: RAIR spectra of B₁₀H₁₄ on Pt(111)

spectra shown in Figure 3. After a 1.5 L (1 L = 1x10⁻⁶ Torr sec) exposure at 85 K, peaks in the BH stretch region at 2590 and 2606 cm⁻¹, and peaks at 1423 and 1483 cm⁻¹ that correspond to deformations of the boron cage structure appear. As the sample is annealed to increasingly higher temperatures, the changes in the spectra reveal that the molecule undergoes dramatic changes associated with dehydrogenation. The 300 K anneal results in a new set of B-H stretch peaks at 2555, and 2567, with a shoulder at 2575 cm⁻¹ along with a new set of more intense peaks in the boron cage region. The latter peaks persist even after the BH stretch peaks completely disappear after the 500 K anneal. The most obvious interpretation is that while hydrogen is removed from the molecule, the boron cage remains intact covering the surface with small nanoscale boron clusters. Moreover, the latter entities clearly have a high stability on the surface. Information on the structure of the boron clusters will be obtained by comparing the spectra to spectra calculated using DFT for clusters of various assumed structures. Experiments to determine if the boron structures can be hydrogenated are ongoing.

Future Plans

a) Dehydrogenation of Carborane on Pt(111)

Following the decaborane studies described above, we will shift to studies of the surface chemistry of 1,2-*closo*-dicarbadodecaborane, C₂B₁₀H₁₂, (also known as *ortho*-carborane, or just carborane) under ultrahigh vacuum conditions. This compound is an air stable solid with a modest vapor pressure at room temperature that can be easily dosed onto surfaces using standard techniques. It has the structure of a distorted icosahedron with

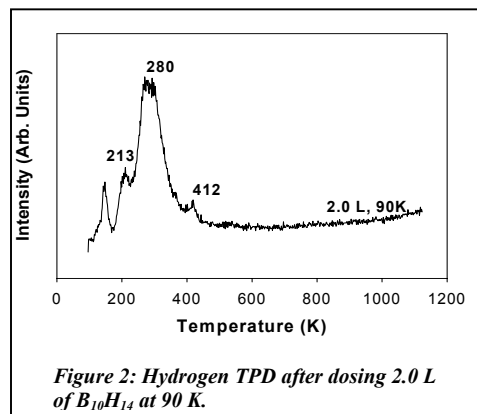


Figure 2: Hydrogen TPD after dosing 2.0 L of B₁₀H₁₄ at 90 K.

BH stretch region at 2590 and 2606 cm⁻¹, and peaks at 1423 and 1483 cm⁻¹ that correspond to deformations of the boron cage structure appear. As the sample is annealed to increasingly higher temperatures, the changes in the spectra reveal that the molecule undergoes dramatic changes associated with dehydrogenation. The 300 K anneal results in a new set of B-H stretch peaks at 2555, and 2567, with a shoulder at 2575 cm⁻¹ along with a new set of more intense peaks in the boron cage region. The latter peaks persist even after the BH stretch peaks completely disappear after the 500 K anneal. The most obvious interpretation is that while hydrogen is removed from

similar B-B bond lengths as in the distorted CB_{11} icosahedra that form the basic structural unit of boron carbide. Although carboranes have been used as precursors for the deposition of boron carbide thin films [3], their dehydrogenation chemistry has not been explored on surfaces. More importantly, it has not been established in previous studies if the boron cage structure of carborane remains intact in the course of the chemical reactions leading from molecular carborane to boron carbide films. Similarly, the ability of boron carbide thin films to be rehydrogenated to carborane-like entities has not been studied.

b) RAIRS Studies under High H_2 Pressures

To fully explore the hydrogenation chemistry of boron cage structures, a new apparatus will be constructed that will allow RAIRS experiments under an ambient pressure of hydrogen up to one atmosphere. As a homonuclear diatomic molecule, $H_2(g)$ does not absorb infrared radiation and the presence of gas phase hydrogen will not interfere with the RAIRS studies. The new apparatus will permit the investigation of surface hydrogenation/dehydrogenation reactions at an unprecedented level of detail. To help identify the surface species present, the experimental RAIRS spectra will be compared with spectra calculated for likely surface species using density functional theory calculations, as is currently done in the PI's laboratory [4].

c) Transmission IR Studies of Boron Nanowires and Nanoribbons

In a third phase of the project, the hydrogenation chemistry of boron nanowires and nanoribbons will be studied using transmission IR. An apparatus similar to one currently used elsewhere [5] for transmission IR studies of carbon nanotubes is being constructed. In these studies the boron nanostructured materials will be prepared in a simple CVD apparatus as developed elsewhere [6, 7] and then pressed into a high transparency tungsten mesh, which is in good thermal contact with a sample holder. The IR spectra will then be studied over a wide range of temperatures from 77 to over 1000 K. The ability to heat the structures to high temperatures in vacuum, will permit any surface oxide to desorb, thus exposing boron dangling bonds at the surface. These bonds should readily react with hydrogen to form a hydrogen-terminated surface. The B-H bonds can then be characterized with IR spectroscopy. Given the strong IR absorption coefficients associated with B-H bonds [8], and the high surface areas associated with the nanostructured material, we expect to have excellent signal-to-noise ratios in the BH stretch region. The studies will not only allow us to characterize the hydrogenated surface, but also to measure spectra as a function of annealing temperature to thereby establish the thermal stability of the hydrogenated structures.

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