

V.D.22 Dehydrogenation of Boron Nanostructures

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Objectives

The overall objective of this project is to explore the surface chemistry related to the possible use of metal catalysts to reversibly add hydrogen to various types of boron nanostructures. The nanostructures are being generated in two distinct ways. In the first method, we are studying the dehydrogenation chemistry of decaborane ($B_{10}H_{14}$) and carborane ($C_2B_{10}H_{12}$) on a catalytically active Pt surface using an array of surface sensitive techniques. In the second method, we are growing boron nanostructures by a simple chemical vapor deposition process using diborane (B_2H_6) gas. The high surface to volume ratio of these boron nanostructures suggests that if their surfaces can be hydrogenated, then materials with high hydrogen weight percentages should be obtained.

Technical Barriers

The use of complex hydrides constitutes one of the most promising routes for achieving high volumetric and gravimetric densities for the on-board storage of hydrogen for use in motor vehicles. Of the elements lighter than carbon, boron forms the most extensive array of compounds with hydrogen. Many of these compounds are stable at room temperature and would be attractive hydrogen storage materials if ways could be found to reversibly release hydrogen at low temperatures. In general, many metals are effective in catalyzing hydrogenation and dehydrogenation reactions, yet there has been essentially no prior work on metal catalyzed dehydrogenation/hydrogenation reactions of boranes and carboranes. This research project is designed to generate basic information on the surface chemistry associated with the making and breaking of B-H bonds with the hope that such knowledge will enable the potential of boron

nanostructures to serve as useful hydrogen storage materials to be realized.

Abstract

The surface chemistry of decaborane ($B_{10}H_{14}$) and carborane ($C_2B_{10}H_{12}$) on Pt(111) has been studied with reflection absorption infrared spectroscopy (RAIRS), temperature programmed desorption (TPD), and X-ray photoelectron spectroscopy (XPS). It is found that the Pt surface catalyzes the release of hydrogen from both molecules at temperatures much lower than their thermal decomposition temperatures. The partial decomposition of these molecules produces fragments that retain B-H bonds. The catalytic dehydrogenation of these molecules is thought to produce nanoclusters with structural features similar to those found in various boron-rich solids. Boron nanostructures have also been produced from a simple chemical vapor deposition process using diborane (B_2H_6) gas.

Progress Report

Given that there have been essentially no previous studies on the surface chemistry associated with the dehydrogenation of any borane or carborane on catalytically active metals, much of our experimental work to date has focused on studies of decaborane and carborane adsorption and dissociation on the Pt(111) surface. The work follows the same methodology widely used in studying the reactions of other small molecules on metal surfaces. The structures of decaborane and carborane are shown in Figure 1. Both structures feature a three-dimensional cage involving delocalized boron-boron bonding with hydrogen atoms decorating the exterior of the cage. Whereas carborane has a closed icosahedral structure with only terminal BH or CH bonds, decaborane has a more open structure with both terminal and bridging B-H bonds. In both

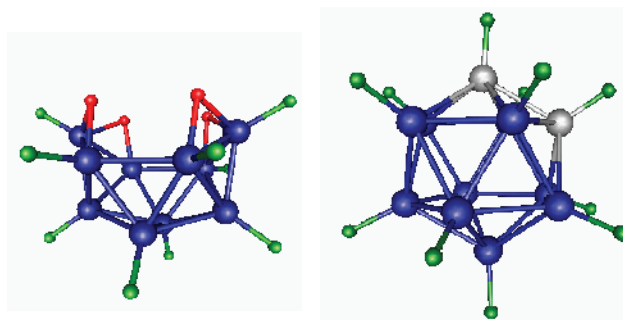


FIGURE 1. Structures of decaborane and o-carborane showing terminal hydrogens (green) and bridging hydrogens (red).

cases, the cage structures resemble the structures found in elemental boron and in boron carbide. In fact, carborane is used as a precursor for the growth of boron carbide thin films.¹ We find that the two molecules show similar behavior in that they adsorb molecularly on Pt(111) at 85 K, undergo some structural changes at low temperatures, and lose hydrogen in stages as the temperature is raised, as determined by both RAIRS and TPD. Figure 2 shows RAIRS spectra for a submonolayer coverage of decaborane on Pt(111) as a function of annealing temperature, while Figure 3 shows similar results for carborane. Figure 4 shows TPD results for H₂ desorption following decaborane adsorption on Pt(111). In recent years a variety of interesting nanostructures consisting of elemental boron and metal borides have been reported in the literature. For example, Prof. Rodney Ruoff's group at nearby Northwestern University has reported the growth of novel boron nanoribbons and nanoscrolls^{2,3}. With the assistance of his group, we have replicated their CVD apparatus in our lab and have succeeded in reproducing these structures. Figure 5 displays scanning electron microscopy (SEM) images of boron nanoribbons and a boron nanoscroll grown by us using a simple chemical vapor deposition method in which a gas mixture of argon and diborane is passed over Si surfaces in a heated tube furnace. Because the nanoscroll is only a few nm thick, a very high fraction of the boron atoms are present at the surface. In general, it has been found that the atoms at the surfaces of semiconductors such as silicon and germanium have reactive dangling bonds that readily form bonds to

hydrogen to form a stable surface termination. Because boron is a semiconductor with some properties similar to other elemental semiconductors, a reasonable hypothesis is that boron surfaces, including the surfaces of boron nanoscrolls, can also be terminated by hydrogen.

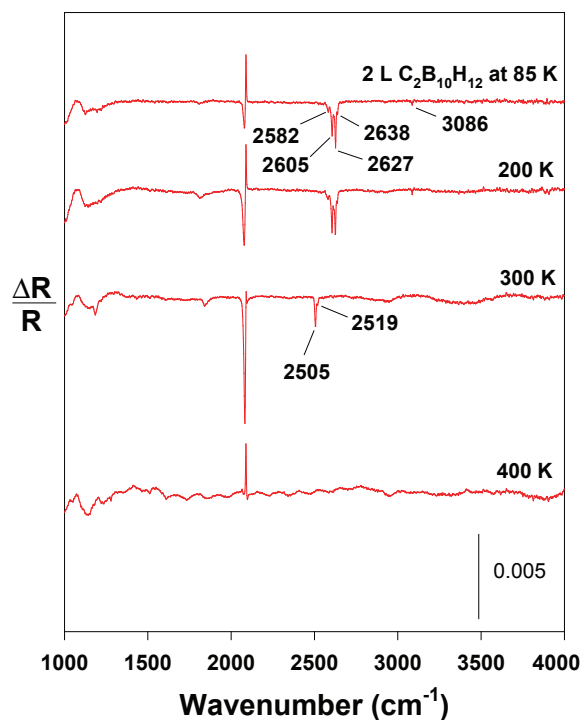


FIGURE 3. RAIR spectra of C₂B₁₀H₁₂ on Pt(111)

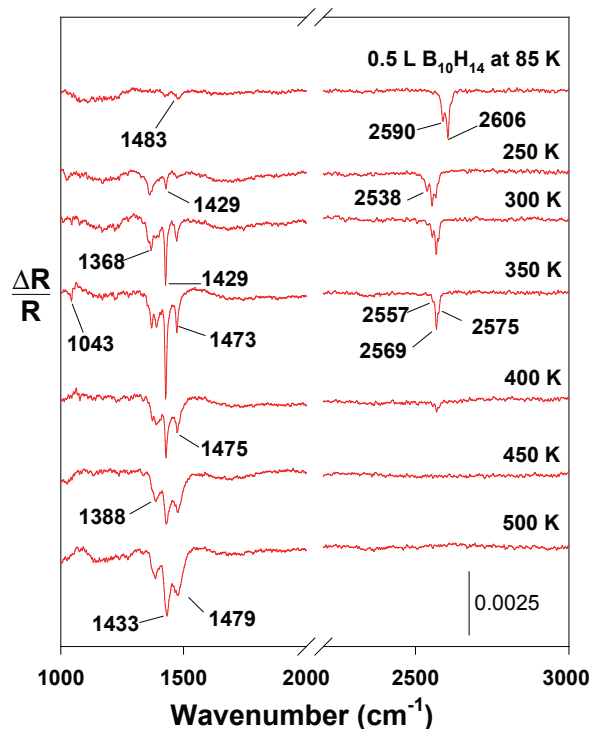


FIGURE 2. RAIR spectra of B₁₀H₁₄ on Pt(111)

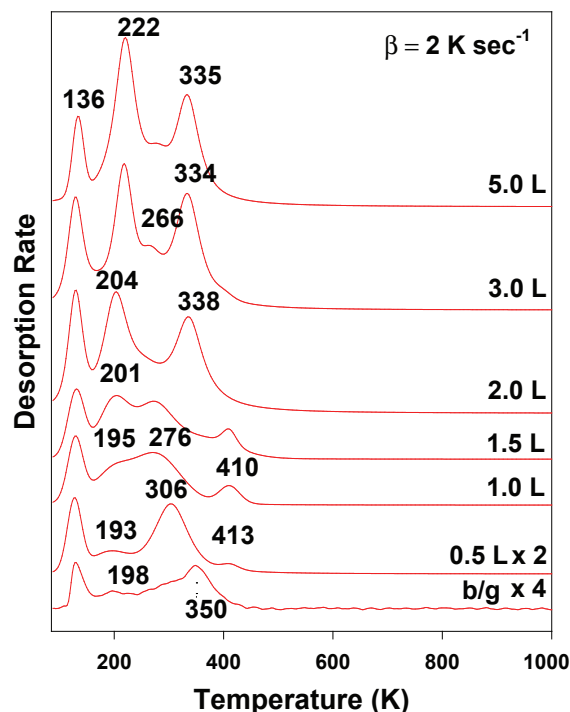


FIGURE 4. Hydrogen TPD of B₁₀H₁₄ on Pt(111)

Future Directions

a) RAIRS Studies under High H₂ Pressures

To fully explore the hydrogenation chemistry of boron cage structures, a new apparatus is being constructed that will allow RAIRS experiments under an ambient pressure of hydrogen up to one atmosphere. We will first prepare a Pt(111) surface covered with either fully or partially dehydrogenated boron cage structures, produced as described above from decaborane or carborane. The surface will then be exposed to a high pressure of H₂(g) to see if the formation of B-H bonds can be detected with RAIRS. Since H₂(g) does not absorb infrared radiation, the presence of gas phase hydrogen will not interfere with the RAIRS studies. With the new apparatus we will be able to investigate surface hydrogenation/dehydrogenation reactions at an unprecedented level of detail. All of the major components of the apparatus have been received, as has the custom-designed vacuum chamber. Assembly of the system will soon begin. Although the cost of the new apparatus was not included in the final budget from DOE, sufficient university funds were provided to support the instrumentation needs of this project. Use of the new apparatus should begin in the summer of 07.

b) Transmission IR Studies of Boron Nanowires and Nanoribbons

We have constructed a second new apparatus that will permit us to characterize the interactions of the boron nanoclusters with hydrogen using transmission IR spectroscopy. The design of the apparatus follows that of Yates and coworkers⁴, which has been used to characterize molecular adsorption on carbon nanotubes. More recently, they have used the same apparatus to characterize the interaction of hydrogen with TiO₂ nanoparticles.⁵ In our studies the boron nanostructures, such as those shown in Figure 5, will be pressed into a high transparency tungsten mesh, which is in good thermal contact with a sample holder. The IR spectra will then be obtained over a wide temperature range, from 77 to over 1,000 K. The ability to heat the structures to high temperatures in vacuum will cause any surface oxide to desorb, thus exposing boron dangling bonds at the surface. These bonds should then readily react with hydrogen to form a hydrogen-terminated surface. Given the strong IR absorption coefficients associated with B-H bonds⁶, and the high surface areas associated with the nanostructures, 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.

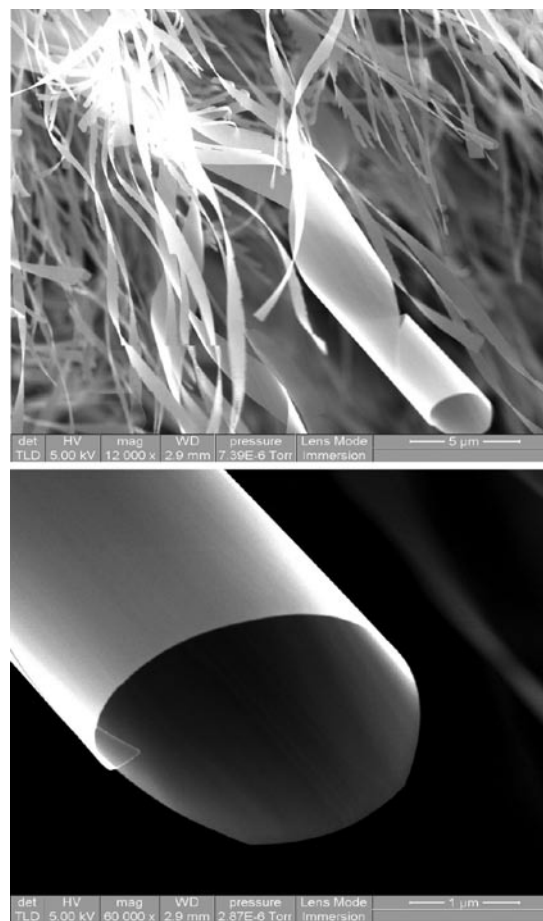


FIGURE 5. SEM images of novel nanostructures of pure boron grown by a low pressure CVD process. The structures on the left consist of "blades of grass" and a "nanoscroll". The image on the right is a magnified view of a boron "nanoscroll". These objects are a few μm wide, 10's of μm long, but only a few nm thick.

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