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MONTHLY PROGRESS REPORT

Hydrogen from Renewable Resources
University of Hawaii
Grant No. DE-FG04-94AL85804

February 1995

During February, we achieved two significant results in our hydrogen storage activites. Reversible hydrogen uptake and release was measured at room temperature, near ambient pressure on the ($IrClH_2(H_2)$ PPr^i_3) complex. Dr. Jensen also observed that certain polyhydride complexes catalyze the low temperature, reversible dehydrogenation of cycloalkanes to aromatic hydrocarbons at temperatures as low as 130 °C. This discovery may represent a breakthrough in chemical storage of hydrogen as all other cycloalkane dhydrogenation systems require temperatures in excess of 300 °C.

TASK 1 - Hydrogen Production

A. Photobiological Production - Kelton Mckinley and Dulal Borthakur

We have been working on genetics and physiological aspects of hydrogen production in cyanobacteria.

1. Development of a genetic system for *Spirulina pacifica* :

Until last month we were working on isolation and characterization of restriction enzymes from *Spirulina pacifica.* We evaluated the assay conditions for the enzymes isolated from *Spirulina* and compared with those for commercial isoschizomers. The *Spirulina* enzyme SpaI which is an isoschizomer of Tth111I shows high activity at 37°C compared to 65°C for Tth111I from *Thermus thermmmophilus* 111 (New England Biolab, MA). SpaI is inactivated quickly at 65°C. This enzyme shows high activity under a reaction condition with 100 mM NaCl and a pH of 7.0. SpaI may be the most predominant restriction enzyme present in *Spirulina* and its extraction procedure is relatively simple. Therefore, it may be easier and more profitable extract this enzyme commercially from *Spirulina* than from *T. thermmmophilus.*

The other three restriction enzymes isolated from *Spirulina*, namely SpaII, SpaIII and SpaIV, are isoschizomers of PvuI, PvuII and HindIII, respectively. These three

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endonucleases showed higher activity when the NaCl in the reaction is replaced with 100 mM KCl. These three enzymes showed maximum activity at pH 7.5.

The work on restriction enzyme isolation is complete now. Mr. Vincenz Tragut who has been working on this project during past few months will leave for Germany on March 2. We are now writing a manuscript on the above work.

2. Cloning of the *hupB* gene of *Anabaena* sp. strain 7120 : In January we reported cloning of an internal 300-bp region of *hupB* gene from *Anabaena* sp. strain 7120. We are now in the process of isolating a large fragment containing the complete *hubB* sequence from the genomic DNA library of this strain. We used this cloned DNA fragment as a probe against genomic DNA of *Anabaena* digested with EcoRI and HindIII. The probe hybridized strongly with an EcoRI fragment of approximate size of 3.0 kb and a HindIII fragment of 2.0 kb suggesting that the *hupB* sequences are located in these fragments. Currently we are constructing a cosmid clone library in the cloning vector pDUCA7 obtained from Dr. Willium Buikema of the University of Chicago. We are also making genomic DNA of *Anabaena* for library construction.

3. Physiology: A post-doctoral fellw to assist in physiological bio-production was brought on board effective February 1. Axenic cyanobacterial cultures from American Type Culture Collection are being cultured to supplement stocks already available in Hawaii. Parts have been ordered to assemble a bio-reactor to better quantify physiological response and hydrogen production rates in selected organisms.

B. Photoelectrochemical Production of Hydrogen - Richard Rocheleau

1. Modeling: Loss analysis modeling for tandem amorphous silicon structures was completed. With suitably active catalysts, some improvement in hydrogen production rates compared to triple junction devices is to be expected. Hydrogen production potential for the tandem and triple junction devices for different catalysts activities will be reported next month.

2. Photoelectrode Development: In January , we reported initial characterizations of the catalytic and optical properties of sputtered nickel oxide films deposited under different sputtering conditions. In February, we continued our investigation of NiOx films, using steady-state voltammetry, SEM, electron-dispersive spectroscopy (EDS) and photospectrometry to characterize a test matrix

of films deposited at various pressures, gas flows and DC sputtering powers. Through EDS and SEM we discovered that the NiOx film composition was not significantly altered by changes in deposition parameters, however, film morphology at the microstructural level varied dramatically. The catalyst films were amorphous at low sputtering pressure (2mTorr) with no observable features up to 30,000X but were clearly microcrystalline (0.1 to 0.25 micron crystallites) at pressures of 6mTorr or greater. The optical and electrochemical characterizations indicate that the microcrystalline films demonstrate improved catalysis (Figure 1) whereas the amorphous films exhibit superior transparency (Figure 2). Electrochromic behavior (i.e., film darkening in electrolytic media during O_2 formation) was also noted to change with the different film structures. These behaviors are being evaluated further.

The effects of both substrate temperature and iron dopants on catalysis and transparency of the sputtered NiOx films are currently under investigation. Results from these study will be available in next months report.

The plasma-enhanced CVD system was cleaned and re-assembled with a new electrode design which will minimize stray currents and contamination from scouring of the walls. Routine maintenance including a thorough leak-checking of the system, repair of a defective mass-flow controller, and clean-up of the exhaust system was completed. The system has now been pumped down, achieving the same vacuum levels as originally achieved. SiC depositions to make photoelectrodes for electrochemical characterizations and stability measurements will resume the first week of March.

3. System development: The key labware for gas evolution measurements finally arrived. The apparatus has been set up and initial tests conducted. Tests were run using 1-inch square stainless steel electrodes to demonstrate separation and collection of the hydrogen at the relatively low current densities and gas evolution rates expected from PEC's at 1 sun. Gas collection over 30 and 60 minute tests a current of 10 mA were the same as expected from calculations. Several dozen SS/nip/nip/nip/ITO solar cell samples each around $7cm^2$ have been received from ECD Inc. for photoelectrode fabrication These will be coated with our NiO_X films for testing.

Figure 1: O_2 Catalysis in 1N KOH of Microcrystalline vs. Amorphous NiOx Films

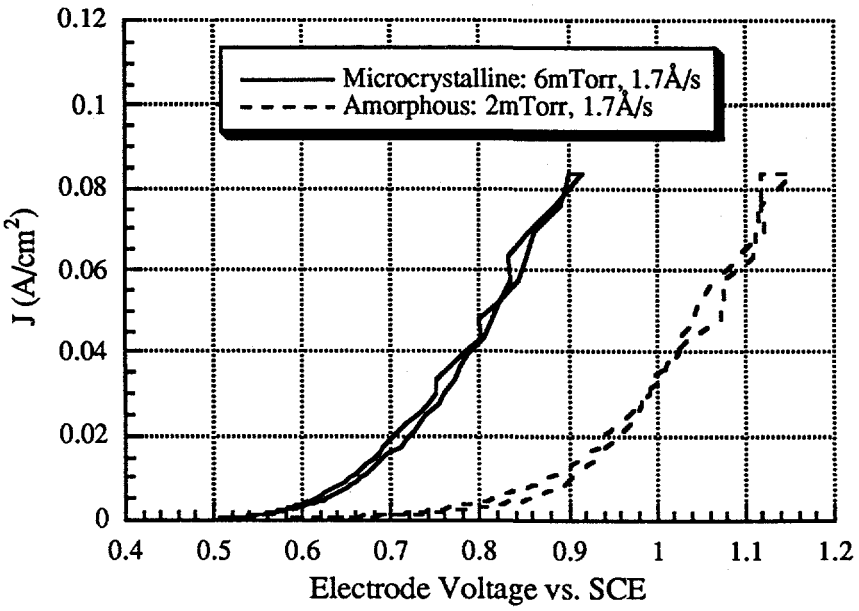
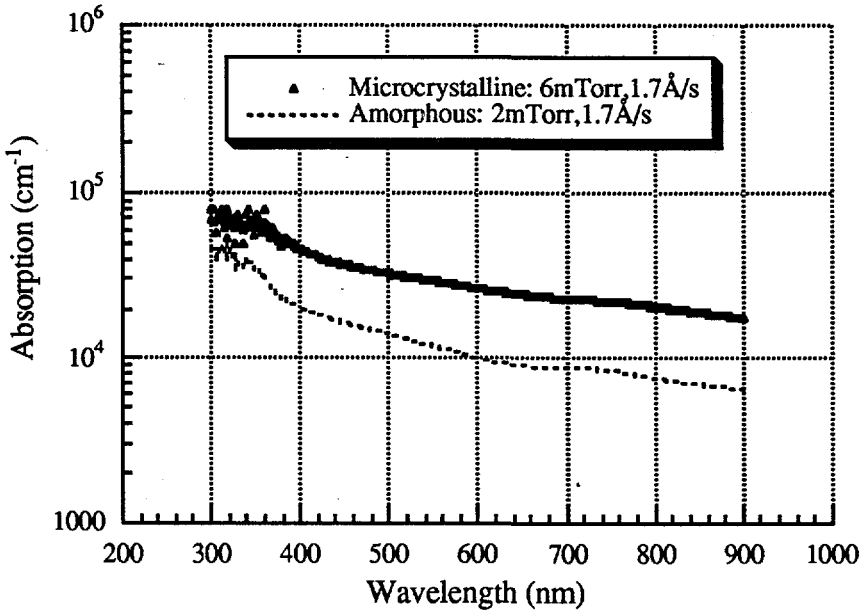


Figure 2: Optical Absorption Spectra of Microcrystalline vs. Amorphous NiOx Films



C. Thermochemical Production of Hydrogen from Wet Biomass - Michael J. Antal , Yukihiko Matsumura, and Michael Onuma

1. Regeneration of spent catalyst X

Regeneration of spent catalyst X was performed successfully by supercritical water treatment. When 1.2 M glucose solution was decomposed with catalyst X, after 6 hours the on-stream carbon gasification efficiency began to decrease and tarry materials were observed in the liquid sample. This deactivation is a problem for long time operation needed in a practical plant. One approach we tried to regenerate the spent catalyst was to send supercritical water and gasify the deposited carbon. This is a convenient procedure since only switching glucose solution to water is required and there is no need for catalyst transportation nor a catalyst regeneration plant. Experiments on regeneration were made in three steps; 1) Measure the surface area number of spent catalyst X. 2) Measure the surface area number of regenerated catalyst X. 3) Measure the gasification characteristics of regenerated catalyst X. Cellobiose solution of 0.235 M was utilized as the feed to increase the deactivation rate. Decomposition proceeded at 600C and 5000 psi with flow rate of 1.0 ml/min and deactivation was observed within 4.5 hours. For regeneration supercritical water was sent under the same condition for 6 hours. Then the cellobiose solution was sent again under the same condition to find the gasification characteristics of the regenerated catalyst. The change of the surface area numbers is shown in Table 1. The regenerated catalyst has a surface area number as high as the original one and regeneration of surface area is confirmed. The time changes of gas generation rate and carbon gasification efficiency are shown in Table 2. Perfect reproducibility shown in the table assures the regeneration of catalyst not only for the surface area but also for the gasification characteristics. The mechanism of the deposit carbon gasification will be studied to find a proper condition for regeneration.

Table 1. Surface area numbers of catalysts.

Catalyst	Surface area number
Original catalyst X	1050
Spent catalyst X	365
Regenerated catalyst X	1263

Table 2. Gasification characteristics of original and regenerated catalysts.

Time on stream	Original catalyst X		Regenerated catalyst X	
[h]	Gas generation rate [10^{-3} mol/min]	Carbon gasification efficiency [-]	Gas generation rate [10^{-3} mol/min]	Carbon gasification efficiency [-]
1.0	5.77	1.04	5.47	0.95
2.0	5.28	-	5.68	0.96
3.0	5.30	-	5.16	-
4.0	4.89	0.90	4.99	0.91

-: no data

2. Improvement of the catalyst activity

Improvement of catalyst activity will permit longer operation without regeneration, and treatments of higher concentration solutions or slurries. For this purpose nickel chloride was applied as an additional catalyst. An experiment was carried out with a raw material of catalyst X treated with nickel chloride to find the effectiveness of nickel chloride. When a 1.2 M glucose solution was sent at 600C and 5000 psi, complete gasification was achieved. Since we do not observe such a high gasification rate with an untreated raw material of the catalyst, the treatment with nickel chloride is promising. Treatment of increasing surface area on this nickel treated raw material may result in a catalyst with higher performance. This experiment is now under way. Other salts such as nickel sulfate and potassium chloride will be tried, too.

Production of Catalyst X using hydrogen peroxide

Production of catalyst X in supercritical water using hydrogen peroxide can be a novel method of preparing this catalyst. Treatment of raw material with 0.9 wt % hydrogen peroxide solution at 375C and 5000 psi was performed but because of the

high reactivity of the material and oxygen, after a two-hour operation all the raw material was consumed by the reaction, leaving no catalyst. To find the reaction characteristics during this activation, gas and liquid samples from the experiment will be analyzed. A special gas chromatograph column for this purpose was ordered and the analysis will be made as soon as we get the column.

Fabrication of a new slurry feed reactor

The design of a new slurry feed reactor is progressing. Feeding a slurry into the reactor is an important process for wet biomass gasification to produce hydrogen gas. The present reactor has difficulty in sending concentrated slurry because of plugging, thus causing the stalling of the feeding system. To demonstrate the effectiveness of the supercritical water decomposition in wet biomass gasification, a reactor which can send concentrated slurry constantly is necessary. For this purpose, a new slurry feed reactor with auger feeding system was designed. Some of the equipment used for the old experiments can be used for the new system, but it is necessary to purchase an auger and reactor tubing. The auger has been ordered and will arrive by late March. We are now identifying candidate tubes for use as the reactor.

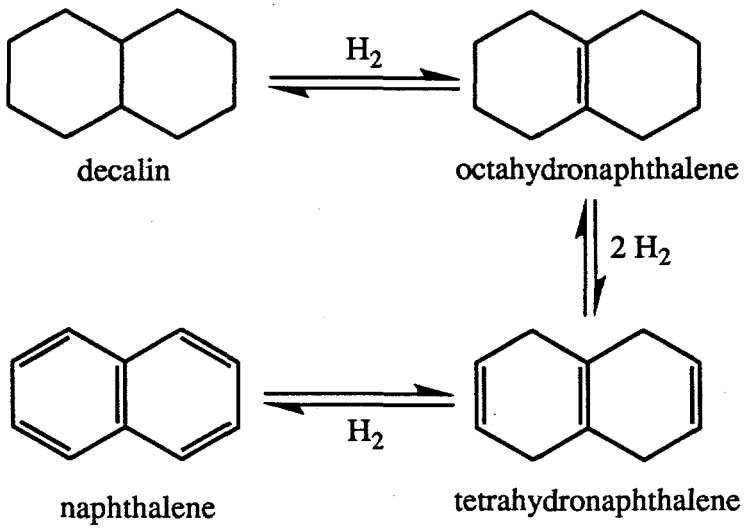
TASK 2 - Hydrogen Storage

A. Polyhydride Complexes for Hydrogen Storage - Craig Jensen

A serendipitous discovery has been made in our laboratory. We have found that certain polyhydride complexes act as catalysts for the low temperature, reversible dehydrogenation of cycloalkanes to aromatic hydrocarbons.

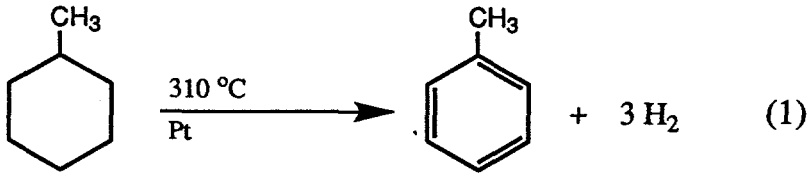
As part of our continuing studies of the reversible hydrogenation of unsaturated hydrocarbon ligands, we explored the reaction of polyhydride complexes with tetrahydronaphthalene. Instead of a stable h^4-tetrahydronaphthalene complex, we obtained a mixture of naphthalene, tetrahydronaphthalene, octahydronaphthalene and decahydronaphthalene (decalin) along with the original polyhydride complex. We have found that the resulting distribution of the bicyclic complexes seen in Scheme 1 is a

Scheme 1



function of the partial pressure of hydrogen above the solution. Furthermore, at a given partial pressure of hydrogen the same equilibrium mixture of products is obtained at 130 °C regardless of the starting distribution of the bicyclic complexes. Thus the polyhydride complexes act as both dehydrogenation and hydrogenation catalysts, depending on the partial pressure of hydrogen above the reaction mixture. This catalytic reaction may represent the basis for a system in which >7 weight percent of hydrogen can be stored and retrieved under mild conditions.

Reversible dehydrogenation of methylcyclohexane to toluene in the presence of platinum group metals, as seen in equation 1, has been explored as a method of hydrogen storage. However, dehydrogenation occurs in these systems only at temperatures in excess of 300 °C. This drastic energetic requirement has precluded such systems from consideration as practical methods for storing hydrogen as a fuel. Therefore, our



discovery of the catalytic dehydrogenation of cycloalkanes by polyhydride complexes may represent a breakthrough in chemical storage of hydrogen.

B. Polyhydride Systems Engineering - Richard Rocheleau and Ragaiy Zidan

We have started P-C-T testing of the complex hydride materials of the class $IrX\,H_2(H_2)\,PPr^i_3$ where X is a halide. The first materials investigated was $IrIH_2(H_2)\,PPr^i_3$ received in the fully hydrogenated state. A sample of 40 mg of $IrIH_2(H_2)\,PPr^i_3$ was loaded into the high pressure reactor under argon atmosphere. At room temperature (20.5 ^oC), the system was evacuated and kept under vacuum to detect possible hydrogen evolution from the as-received sample. No hydrogen release was observed under these conditions. The experiment was repeated at 60 ^oC for 2 hours but again no hydrogen release was observed. The sample was left over night under argon atmosphere at room temperature. Starting at vacuum, hydrogen was flowed into the reactor to detect any hydrogen uptake, but no hydrogen absorption was observed. We conclude that the hydrogen bonding in the $IrIH_2(H_2)PPr^i_3$ is too strong to be dehydrogenated at the conditions tested. Our ability to detect very small amounts of hydrogen that may have been adsorbing or desorbing were hampered by the very small test quantity of this material which was available. Rather than continue testing at more extreme conditions, we moved onto the Cl complexes which shown easier H_2 release in the IR and NMR characterizations. Although more stronger than to be released under these experimental conditions.

At this time, a 300 mg sample of ($IrClH_2(H_2)\,PPr^i_3$) has been loaded into the reactor. Preliminary testing very clearly shows indicate reversible hydrogen uptake and release under room temperature conditions.
The sample has undergone several cycles of hydrogenation/ dehydrogenation. Data are now being analyzed to quantify the hydrogen uptake and release and during March experiments will be conducted at lower temperatures and higher pressures. During March we also anticipate initial characterization of Fe complexes to examine their capacity and reversibility for hydrogen storage.