

II.K.2 Hydrogen Production and Fuel Cell Research*

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Hydrogen, Fuel Cells and Infrastructure Technologies
Program Multi-Year Research, Development and
Demonstration Plan:

(U) High Temperature Thermochemical Technology

Technical Targets

This project is conducting experimental studies of the UT-3 thermochemical cycle for hydrogen production. On the basis of these studies, thermodynamic analysis of the cycle will be conducted. A process energy efficiency of 40% is being targeted.

Accomplishments

- Thermodynamic simulations were conducted to find optimal operation conditions.
- The experimental set-up for kinetic studies was installed.
- Preparation methods for porous calcium oxide (CaO) pellets and films were developed.
- The CaO pellets and films were characterized using X-ray diffraction (XRD), mercury porosimeter, scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS).
- Kinetic studies on calcium oxide pellets and films are underway.

Task 1.1 Thermochemical Hydrogen Production

D.Y. Goswami, Man Su Lee, Elias Stefanakos

Task Start Date: July 2006
Projected End Date: June 2007

Objectives

- Investigate the feasibility of the UT-3 thermochemical cycle and conduct kinetic studies.
- Improve stability and performance of solid reactants for gas-solid reactions.
- Increasing hydrogen yield with an improved solid reactant formulation.
- Reduce operating cost by lowering the reactor operating temperature.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the



Introduction and Approach

The UT-3 thermochemical cycle is considered as one of the most promising cycles for hydrogen production. The UT-3 cycle is comprised of four heterogeneous reactions. In order to simplify the product separation in the cyclic system and operate the process continuously, the solid reactants and products should remain in the reactors while the gaseous reactants and products move from one reactor to the next. Acceleration of the reaction rate as well as long cyclic lifetime and durability of the solid reactants are important keys for the cycle to become practical. Therefore, pellets of the solid reactants with inert structural materials have been developed, but the processes seem rather complicated and expensive and the practicality of the pellet-type reactant is still in doubt. The hydrolysis reaction of hydrogen bromide, which is the slowest rate limiting step among the four reactions in the cycle, must be accelerated in order to improve the process efficiency.

In order to make the cycle practical and cost-effective, the solid reactants must be chemically reactive

and physically stable in cyclic operation and the reaction rates must be accelerated. For experimental research porous calcium oxide pellets and calcium oxide films have been successfully fabricated and characterized. The film structure is expected to increase the surface area of calcium oxide, reduce mass transfer resistance, maintain cyclic reactivity and have endurance in cyclic transformations, let alone simplification of the preparation steps. Chemical kinetic studies to evaluate and improve the cyclic life, reaction rates and conversion of the solid reactants are being conducted using lab-scale apparatus.

Results

Considering excess steam and other thermodynamic parameters, the optimum conditions and expected conversion of each reaction in the UT-3 cycle were determined.

The calcium oxide precursor was prepared by Sol-Gel chemistry following the metal alkoxide process and the film was fabricated by dip coating procedure. The bromination and hydrolysis reactions of the calcium oxide film were conducted using laboratory experimental set-up in order to examine the effects of volume changes on the stability of the film. The structure and composition of the film on the glass substrate were examined by SEM and EDS experiments. Based on SEM images and EDS spectra over one cycle of bromination and hydrolysis reactions, it can be observed that the film consists of interconnected agglomerates of the solid reactant particles and the particulate aggregate has continuous porous structure with high surface area. Before bromination, the film has rather loose agglomerates while the brominated film is comparatively close-packed. Also, it is seen that the agglomerates of the solid reactant have expanded and contracted according to the expected volume changes between oxide and bromide forms. EDS spectra verify that the bromination and hydrolysis reactions have occurred and the calcium oxide is regenerated after one cycle.

Conclusions and Future Directions

- Thermodynamic simulations were conducted to find the optimal operation conditions.
- The preparation process for calcium oxide films was developed. The bromination and hydrolysis reactions of the film were conducted and the change of structure and chemical composition by the reactions were examined using SEM and EDS.
- The preliminary kinetic experimental studies show that the calcium oxide film is a feasible structure of the solid reactants for the UT-3 cycle.
- The calcium oxide film coating will be applied to high porosity substrates for higher surface area.

- The cyclic reactivity and durability of the calcium oxide films will be evaluated and compared with those of calcium oxide pellets.
- The practical process efficiency will be determined using the experimental results and theoretical thermodynamic analysis.

FY 2007 Publications/Presentations

1. Man Su Lee, Yogi Goswami, Ben Hettinger, and Sanjay Vijayaraghavan, "Preparation and Characteristics of Calcium Oxide Pellets for UT-3 Thermochemical Cycle", Proceedings of 2006 ASME International Mechanical Engineering Congress and Exposition.
2. Man Su Lee, Yogi Goswami, Nikhil Kothurkar, Elias K. Stefanakos, "Fabrication of porous calcium oxide film for UT-3 thermochemical hydrogen production cycle", Proceedings of the ASME Energy Sustainability 2007 Conference.

Task 1.2 Hydrogen Production from Biomass

Yogi Goswami, Elias Stefanakos,
Nikhil Kothurkar

Task Start Date: October 2004
Projected End Date: October 2007

Objectives

Improve the hydrogen production process of conventional biomass gasification and reduce capital cost by combining steps. In the present approach the aim is to combine the two step shift and pressure swing adsorption (PSA) separation into a single step by integrating biomass steam gasification, CO₂ removal and hydrogen separation. The project also aims to improve the total hydrogen yield and overall process efficiency.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (T) Capital Cost and Efficiency of Biomass Gasification/Pyrolysis Technology

Technical Targets

- Energy Efficiency: 50%
- Plant gate cost: \$1.75/gge H₂

Accomplishments

- Experiments were conducted using CaO sorbent and pine mulch at gasification temperature in the range 500 to 700°C. Total gas yield in the presence of the sorbent more than doubled at a gasification temperature of 500°C and was almost 62% higher at 600°C over conventional biomass gasification. At 600°C, the hydrogen yield and carbon conversion efficiency increased by 48.6% and 83.5%, respectively while using sorbents.
- Tars and particulates reduced substantially while using the sorbent, suggesting that calcium oxide plays a dual role of sorbent and catalyst. Using the sorbent helped in improving the overall conversion of solid biomass into gas.
- Theoretical studies on sorbent regeneration were carried out. The chemical kinetics and thermodynamics of the reversible calcination-carbonation reactions were investigated and the factors leading to incomplete regeneration were identified.
- Cyclic performance of sorbents was enhanced by supporting on fibrous ceramics.



Introduction

Hydrogen yield of any carbonaceous fuel can be enhanced by using a simple inexpensive sorbent which absorbs one of the products of gasification (CO_2), thereby influencing the reactions in favor of hydrogen. Improvement of hydrogen yield will help in increasing the overall energy efficiency which is one of the technical targets of DOE. The process efficiency also depends on successful regeneration of spent sorbent which is also being simultaneously investigated.

Approach

Biomass feedstock common to Florida such as pine mulch was steam gasified in a batch type reactor. The effects of temperature, presence of sorbent (calcium oxide) and the form of sorbent (powder vs pellets) on the hydrogen yield were experimentally investigated. The initial experimental studies have shown a significant improvement in hydrogen and overall gas yield. After experimental investigation and studies on sorbent regeneration, cyclic performance of sorbents was improved by depositing them on fibrous ceramics such as Al_2O_3 .

Results

Experiments were conducted by steam gasifying pine mulch with and without calcium oxide sorbent. Five grams of palletized pine mulch was fed to the gasifier and

the temperature of the gasifier reactor was varied from 500°C to 700°C. The steam flow rate was set at 5 g/min and the sorbent to biomass molar ratio was maintained at one for all the experiments. Figure 1 shows the gas yields at 600°C with and without the sorbent.

The hydrogen yield while using the sorbent at 600°C increased by almost 48% as compared to the no sorbent case. It was also found that the hydrogen yield at 500°C and 600°C in the presence of the sorbent was comparable to the yield at 700°C for the no sorbent case. Hence, the gasifier can be operated at 100-150°C lower than the conventional gasification and still get the same hydrogen yield. It was also observed that the overall gas yield had increased and the product gas had less tars and particulates as compared to conventional gasification.

Studies on sorbent regeneration have identified two main factors (sintering and pore closure) that lead to incomplete conversion of calcium oxide to calcium carbonate. To overcome these problems CaO thin films were prepared on a ceramic substrate. CaO supported on Al_2O_3 fibrous paper (Figure 2), gave fast kinetics of CO_2 absorption and excellent cyclic performance. Degradation of absorption capacity over five cycles was not significant.

Conclusions

- Total gas yield in presence of the sorbent more than doubled at a gasification temperature of 500°C and was almost 62% higher at 600°C over conventional biomass gasification. At 600°C the hydrogen yield and carbon conversion efficiency increased by 48.6% and 83.5%, respectively while using sorbents.
- The hydrogen yield for the sorbent case at 500°C and 600°C was more than the conventional hydrogen yield at 700°C. This suggests that the gasifier may be operated at 100-150°C lower while using the sorbent.

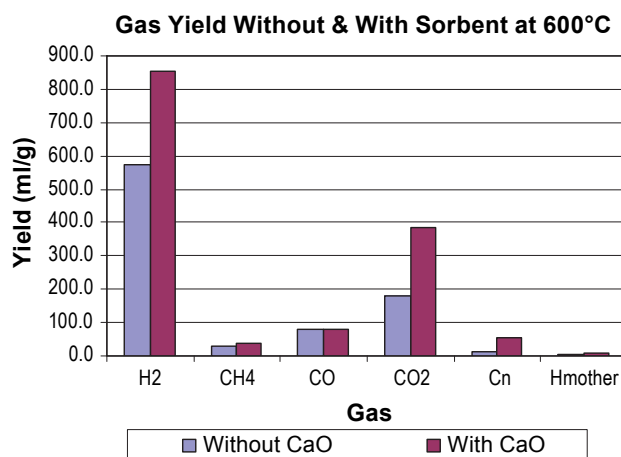


FIGURE 1. Effect of Sorbent on Gas Yield at 600°C

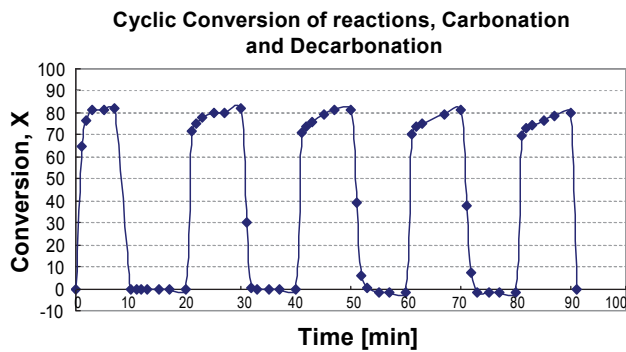


FIGURE 2. Cyclic carbonation and decarbonation of CaO film on Al_2O_3 substrate. Carbonation: 750°C , 20 Vol% CO_2 in N_2 for 10 min. Decarbonation: 750°C , Only N_2 for 10 min.

- Thin film CaO sorbent supported on a fibrous Al_2O_3 paper shows superior cyclic performance.

Future Directions

- Investigate the using alternative sorbents such as CaO-MgO, $\text{Ca}(\text{OH})_2$.
- Conduct additional studies on thin film sorbent to increase CaO loading and cyclic lifetime.

FY 2007 Publications/Presentations

- Mahishi MR, Sadrameli MS, Vijayaraghavan S, Goswami DY. A novel approach to enhance the hydrogen yield of biomass gasification using CO_2 sorbent: *Accepted for publication in the ASME Journal of Engineering for Gas Turbines and Power*.
- Mahishi MR, Goswami DY. An experimental study of hydrogen production by gasification of biomass in the presence of a CO_2 sorbent: *Accepted for publication in the International Journal of Hydrogen Energy*, Elsevier publications.
- Mahishi MR, Goswami DY. Thermodynamic optimization of biomass gasifier for hydrogen production: *under review with International Journal of Hydrogen Energy*, Elsevier publications.

Task 1.3 Photoelectrochemical Hydrogen Production

Yogi Goswami, Elias Stefanakos,
Nikolai Kislov, Sesha Srinivasan,
Nikhil Kothurkar

Task Start Date: July 1, 2006
Projected End Date: October, 2009

Objectives

- Develop a visible-light active TiO_2 photocatalyst modified by nitrogen doping and provide a detailed investigation of the effect of TiO_2 modification on the alteration of its photocatalytic activity.
- Optimize thermochemical ammonia treatment parameters (temperature, duration, ammonia gas flow rate).
- Provide comparative analysis of the temperature dependent structural material characteristics such as anatase and rutile particles size and anatase to rutile ratio in the relation to the photocatalytic activity of thermochemically treated titania.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (Y) Materials Efficiency
- (Z) Materials Durability

Technical Targets

- Chemical conversion process efficiency (EC), $>10\%$
- Durability, $>1,000$ hours

Accomplishments

- Provided comparative analysis of the temperature dependent structural material characteristics such as anatase and rutile particles size and anatase to rutile ratio in relation to the photocatalytic activity of thermochemically treated titania.
- Discovered a 200% increase in photocatalytic efficiency of ammonia thermochemically treated TiO_2 catalyst at the following parameters: temperature - 675°C , gas flow - 12 mL/min, duration - 3 hours.
- The optimized thermochemically treated TiO_2 catalyst has about 50% mass fractional rutile to anatase ratio.
- The results suggest an important role of rutile phase in the enhanced photocatalytic activity of ammonia thermochemically treated TiO_2 particles.



Introduction

Our proposed research focuses on the processes of preparation and testing of the N-doped TiO₂ nanoparticulate photocatalytic material.

Approach

Photocatalytic efficiency was measured by analysis of kinetics of methyl orange (MO) photodegradation in combination with optical, Fourier transform infrared (FTIR), and structural (XRD, SEM) analyses to determine the relationship between the material characteristics and photocatalytic activity. The average surface area, pore size distribution and pore volume of thermally treated N-doped TiO₂ photocatalysts were found to be in correlation with the observed photocatalytic performance.

Results

Figure 3 shows that ammonia thermochemically treated TiO₂ has a 200% higher efficiency as compared to untreated TiO₂ (Degussa P-25) photocatalyst. The results observed also suggest an important role of the rutile phase in the enhanced photocatalytic activity of ammonia thermochemically treated TiO₂ particles, which is measured by MO decoloration rate.

Conclusions and Future Directions

- Thermochemical modification/improvement of photocatalytic properties of TiO₂ is an efficient method for the development of innovative solar light activated photocatalysts.
- The results suggest a synergistic effect between rutile and anatase TiO₂ particles in photocatalytic oxidation of methyl orange in aqueous solution.
- Investigation of structural and surface modifications of the photocatalyst after thermochemical treatment will lead to a better understanding of the photooxidation and photoreduction mechanisms with a focus on the surface-property relationships.
- Explore the influence of the nitrogen content and oxygen deficiency in the TiO₂ lattice.

FY 2007 Publications/Presentations

1. Quantum size effects in nanoparticulate ZnFe₂O₄: blue and “anomalous” red shifts in the optical absorption spectra, N. Kislov, S. Srinivasan, E. Stefanakos, and Yu. Emirov, Manuscript under preparation (2007).
2. Nanoclusters and nanocatalysts for environmental and energy storage applications, S. Srinivasan, Invited Talk, Indian Institute of Technology, Chennai, India.

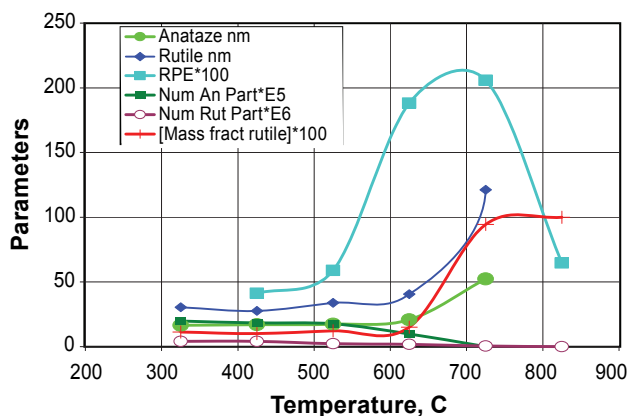


FIGURE 3. Relative photonic efficiency under visible light irradiation (RPE) of thermochemically treated photocatalyst (relative to untreated Degussa P-25, TiO₂ photocatalyst), anatase and rutile particle sizes, and mass fraction of rutile as functions of sintering temperature.

3. Nanomaterials for Energy Storage and Environmental Detoxification Applications, Sessa Srinivasan, Nikolai Kislov, Yogi Goswami, Elias Stefanakos, Yusuf Emirov, Symposium on “Recent Developments in Nanomaterials”, NanoScience Center, Department of Physics, Banaras Hindu University, Varanasi, India.

Task 2.1 Development of High Performance, Low Cost PEM Electrolytes

Clovis A. Linkous

Task Start Date: October 1, 2004

Projected End Date: September 30, 2007

Objectives

- Decrease cost per unit power for proton exchange electrolyte membranes.
- Improve long-term chemical stability of fuel cell proton exchange membrane (PEM) electrolytes operating at ≤120°C.
- Maintain or improve high protonic conductivity of PEM electrolytes.
- Minimize water content necessary to support high conductivity under stated conditions.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (B) Cost
- (C) Performance

Technical Targets

This project is performing chemical modifications of polyetheretherketone (PEEK) polymer, converting it into a PEM electrolyte. Insights gained from these studies will be applied toward the design and synthesis of proton exchange membranes that meet the following DOE 2010 technical targets targets:

- Operating temperature: 120°C
- Conductivity at operating temperature: 0.1 S/cm
- Room temperature conductivity: 0.07 S/cm
- Inlet water vapor partial pressure: 25 kPa
- Cost: \$20/m²
- Durability: 2,000 hours at >80°C

Accomplishments

- Successfully prepared via cross-linking chemistry a membrane based on highly sulfonated (water soluble) sulfonated polyetheretherketone (SPEEK), with an equivalent weight of 534 g/equiv.
- Developed a synthetic approach for fabricating a proton exchange membrane made from the fluorosulfonic acid of PEEK. The procedure begins with bromination of the bis-acetamide derivative of 2,5-diaminobenzotrifluoride. Have successfully performed the amidization, the monobromination, and the sulfatodehalogenation of the starting material.
- Developed multiple characterization methods for monitoring peroxide attack.



Introduction

The PEM fuel cell is the leading fuel cell technology in applications ranging from vehicular transportation to portable appliances. In order to advance this technology, improvements have to be made on the solid polymeric electrolyte about which the cell is designed. Tasks involving fabrication and testing of new electrolyte materials are described with the goal of achieving DOE performance targets in terms of chemical stability and proton conductivity, while maintaining low cost and reducing dependence on water-saturating conditions.

Approach

We are attempting to fabricate a highly proton-conductive polymer membrane by heavily sulfonating,

and subsequently limiting water uptake and possible dissolution via cross-linking chemistry. Polymer membranes are fabricated and then subjected to accelerated life testing via exposure to hydrogen peroxide solution. Proton acidity will be increased by synthesizing the fluorosulfonic acid of the polymer.

Results

Water-soluble (85% degree of sulfonation) SPEEK was solution cast along with a cross-linking agent and catalyst and then heated briefly to 200°C. After leaching out the water-soluble catalyst, the equivalent weight was determined to be 534 g/equivalent, only slightly larger than that for the starting SPEEK material. Either only a small density of crosslinkages are tying up the polymer's sulfonic acid groups, or the crosslinking avoids the acid groups entirely.

Reacted acetic anhydride with 2,5-diaminobenzotrifluoride to make the diacetanilide derivative. Subsequently reacted with BBr₃ in tetrahydrofuran. The BBr₃ may be coupling with the amide oxygen, complicating formation of the monobromo-difluoromethyl product. Have successfully monobrominated model compounds and formed the sulfinic salt.

Conclusions and Future Directions

- Successfully showed that polymer equivalent weight could be reduced via more forcing sulfonation conditions, yet resist solubility because of covalent crosslinking groups introduced between polymer chains. The extent of crosslinking needs to be quantified.
- Developed multiple characterization methods for monitoring peroxide attack. Conductivity was the best monitoring method.
- Amine-protecting and trifluoromethyl brominating procedures have been combined into an overall scheme that will allow synthesis of a fluorosulfonic acid polymer. Conductivity and water uptake of the cross-linked SPEEK membranes will be determined.

FY 2007 Publications/Presentations

1. C.A. Linkous and B.P. Pearman, "Development of Procedures for Evaluating Oxy Radical Stability of Proton Exchange Membranes," poster presentation in Advances in Materials for Proton Exchange Membrane Fuel Cell Systems 2007, February 18 - 21, 2007, Pacific Grove, California.
2. C.A. Linkous and S.L. Rhoden, "Sustainable Fuel Cell Scenarios for the Caribbean," proceedings of SATIS (Sustainable Applications for Tropical Island States) 2007, Caribbean Solar Energy Society, June 3-6, 2007, Cape Canaveral, FL.