
II.A.4 Production of Hydrogen by Biomass Reforming

Yong Wang (Primary Contact), Dave King,
Gordon Xia, Alexander Platon

Pacific Northwest National Laboratory
P.O. Box 999
Richland, WA 99354
Phone: (509) 376-5117; Fax: (509) 376-5106
E-mail: yongwang@pnl.gov

DOE Technology Development Manager:
Arlene Anderson

Phone: (202) 586-3818; Fax: (202) 586-9811
E-mail: Arlene.Anderson@ee.doe.gov

Start Date: October 1, 2004

Projected End Date: September 30, 2009

Objectives

The objective of this project is to develop a cost-effective and feedstock-flexible technology for the conversion of biomass feedstocks to hydrogen that meets the DOE cost targets. Target feedstocks include:

- Ethanol
- Sugar, sugar alcohols (xylitol, sorbitol, glucose)
- Less refined starting materials such as cellulose, hemicellulose

Technical Barriers

This project addresses the following technical barriers from the Distributed Hydrogen Production from Natural Gas or Renewable Liquid Feedstocks section (3.1.4.2.1) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Fuel Processor Capital Costs
- (D) Feedstock Issues
- (E) Carbon Dioxide Emissions

Technical Targets

The goal of this project is to develop a cost-effective and feedstock-flexible technology for reforming of biomass feedstocks. The synergistic improvement in reforming catalysts and reaction engineering will help the reforming technology development that meets the following DOE 2010 targets for distributed production of hydrogen from bio-derived renewable liquids:

- Cost: \$3.60/gge
- Total Energy Efficiency: 66%

Accomplishments

- Comparison of conventional micro tubular and microchannel reactor tests was conducted which suggests that heat transfer limitation is a potential issue in a conventional micro tubular reactor for aqueous phase reforming of sorbitol. As a proof-of-principle, we showed that hydrogen productivity as high as of 700 L H₂/L catalyst/hr can be achieved using a single channel micro reactor.
- It was discovered that catalyst surface acidity and location where carbon-to-carbon (C-C) cleavage takes place can potentially affect hydrogen selectivity in aqueous phase sorbitol reforming.
- It was demonstrated that carbonaceous deposition on the Rh/CeO₂-ZrO₂ catalyst is a potential deactivation issue in low temperature ethanol steam reforming, i.e. 350°C. Additional effort is needed to develop strategies to mitigate the carbonaceous deposition on the catalyst, including modifying catalyst formulations and textural properties and identifying appropriate operating conditions.

Introduction

Biomass-derived feedstocks that can potentially be converted into hydrogen include ethanol, sugars, sugar alcohols, polyols, and less refined hemicellulose or cellulose. Catalytic conversion of these biomass feedstocks provides a means for hydrogen production through a renewable source. In general, the feedstocks with larger size carbohydrate-based molecules such as sugar or sugar alcohols are thermally unstable toward conventional steam reforming, and more amenable to low temperature aqueous phase reforming. Ethanol, on the other hand, is thermally more stable and may take advantage of reforming in the gas phase that allows higher space time yield due to the use of more concentrated feedstocks and relatively higher reforming temperatures. Because of the relatively high cost of biomass feedstocks compared to fossil fuels, biomass conversion processes must be highly efficient in terms of high productivity and hydrogen selectivity. The major objective of this project is to research the options of aqueous and gas phase reforming and develop feedstock flexible reformers for distributed hydrogen production. These efforts will lead to the improvement in hydrogen productivity and selectivity and allow potential reduction of unit operation steps, which will help reduce the capital and operational costs and meet DOE 2010 cost targets for distributed hydrogen production.

Approach

This project was stopped on January 1, 2006 due to DOE funding logistics. With the limited funding carried over from FY 2005, our effort in FY 2006 was focused on the identification of heat transfer issues in aqueous phase reforming of sorbitol, and the elucidation of catalyst deactivation in ethanol steam reforming at low temperatures. With improved heat transfer using a microchannel reactor, we also demonstrated that reaction pathways in aqueous reforming of sorbitol can potentially be studied under near isothermal conditions over a wide range of liquid hourly space velocities (LHSV). This may provide direction on future efforts in improving hydrogen productivity and catalyst durability.

Results

In discussion with Randy Cortright of Virent Energy Systems, he has indicated that heat transfer may limit the productivity of the catalysts toward production of hydrogen from sorbitol since sorbitol reforming is highly endothermic. In October and November of FY 2005, we conducted a direct comparison of hydrogen productivity in both a micro tubular reactor and a single channel microreactor using a 10% sorbitol aqueous solution at 225°C and 420 psi. The microtubular reactor had a 0.25" ID and was inserted in a furnace for heat supply. The microchannel reactor had an active heat exchanger with a short heat transfer distance (0.06") between the heat source and heat sink. A proprietary catalyst provided by Virent was used in both tests since it is the most active catalyst available to us. As shown in Figure 1, over the range of space velocities studied, the microchannel reactor outperformed the 1/4" microtubular reactor for hydrogen productivity. The level of hydrogen

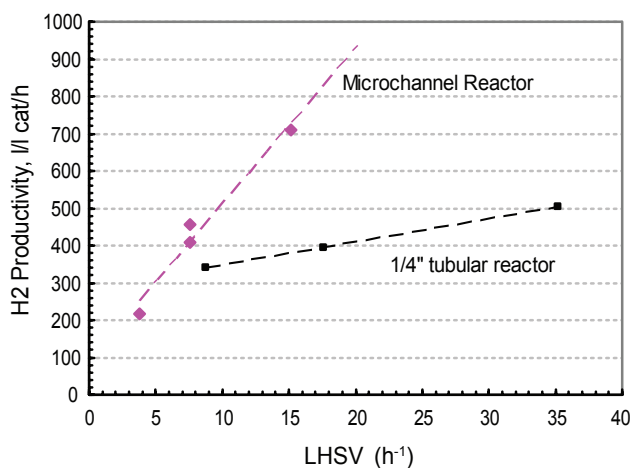


FIGURE 1. Comparison of Hydrogen Production Productivity in Microchannel and Micro Tubular Reactors (225°C, 420 psi, 10% sorbitol aqueous solution)

productivity enhancement in a microchannel reactor was more profound at a high LHSV, under which more heat was required. Hydrogen productivity as high as 700 L H₂/L cat/hr was observed at a LHSV of about 16 hr⁻¹, which is about a factor of two higher than that in a microtubular reactor under the identical reaction conditions. The improved heat transfer in a microchannel reactor also allowed us to study aqueous sorbitol reforming over a wide range of LHSV under near isothermal conditions, so that the reaction mechanisms on the catalysts could be elucidated. Our preliminary testing results indicated that random C-C cleavage of sorbitol took place on the Virent catalyst. In addition, rehydration and dehydration of aldehyde intermediates, likely due to the acidity of catalyst, can potentially contribute to the formation of undesired organic acid or saturated hydrocarbons, leading to poor hydrogen selectivity. Mechanistic insights thus obtained can potentially guide the improvement of catalyst formulations to enhance hydrogen productivity in aqueous biomass reforming.

In FY 2005, we developed Rh/CeO₂-ZrO₂ catalysts which are highly active for low temperature ethanol reforming. In particular, we demonstrated that a Ce/Zr ratio of 4 and the CeO₂-ZrO₂ support as-synthesized without calcination prior to Rh impregnation gave complete ethanol conversion at a high weight hourly space velocity (about 480,000 cc/g cat/hr) and exhibited higher than equilibrium hydrogen yield at 350°C. However, a major issue with these catalysts is their rapid deactivation under these conditions. In October and November of FY 2006, we preformed experiments with co-feeding of ethylene and/or acetaldehyde, the likely intermediates during ethanol reforming, and conducted detailed temperature programmed oxidation studies on spent catalysts. It was demonstrated that carbonaceous deposition on catalysts is a main reason for catalyst deactivation. It was not clear whether ethylene or acetaldehyde or other oxygenates are the coke precursors. It was also demonstrated that the deactivation rate is slower at higher steam reforming temperatures. However, coke formation due to gas phase reaction of ethanol may exist at high temperatures which could be different mechanisms for catalyst deactivation than that at lower temperatures. Further investigation is needed to improve the testing protocol to avoid the gas phase ethanol degradation and to develop robust catalysts for ethanol steam reforming.

Conclusions and Future Directions

- Heat transfer is an issue for aqueous phase reforming of sorbitol. A microchannel reactor with enhanced heat transfer showed improved hydrogen productivity at high LHSVs over a conventional micro tubular reactor. Mass transfer could affect

hydrogen productivity and its effects need to be studied.

- Further understanding of reaction mechanisms are needed to improve the catalyst selectivity and hydrogen productivity for aqueous phase biomass reforming.
- Carbonaceous deposition is a major factor for catalyst deactivation in ethanol steam reforming at low temperatures. Improvement in catalyst formulation and identification of appropriate reaction conditions to minimize the carbonaceous deposition are needed for robust ethanol steam reforming.

FY 2006 Publications/Presentations

Publications

1. H. Roh, Y. Wang, D.L. King, A. Platon, C. Chin "Low Temperature and H₂ Selective Catalysts for Ethanol Steam Reforming", *Catal.Letts.* 108 (1&2): 15-19 (2006).
2. H. Roh, Y. Wang, D.L. King, "Selective Production of Hydrogen from Bio-Ethanol at Low Temperatures over Rh/CeO₂-ZrO₂ catalysts", *Topics in Catalysis* (in press).
3. H. Roh, A. Platon, Y. Wang, D.L. King, "Catalyst Deactivation and Regeneration in Low Temperature Ethanol Steam Reforming with Rh/CeO₂-ZrO₂ Catalysts", *Catal.Letts.* (in press).
4. J. Cao, G. Xia, A. Platon, D.L. King, Y. Wang "Low Temperature Aqueous Phase Reforming of Sorbitol for Hydrogen Production", *Preprints - American Chemical Society, Division of Petroleum Chemistry* (2006), 51(1), 7-8.

Presentation

1. J. Cao, G. Xia, A. Platon, D.L. King, Y. Wang "Low Temperature Aqueous Phase Reforming of Sorbitol for Hydrogen Production", 2006 ACS Fall Meeting, Atlanta, GA, March 28, 2006.