

II.B.1 Bio-Derived Liquids Reforming

Yong Wang (Primary Contact), David L. King, Gordon Xia, Tom Peterson, and Xian-qin Wang
Pacific Northwest National Laboratory (PNNL)
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

Project Start Date: October 1, 2004
Project End Date: Project continuation and direction determined annually by DOE

but are amenable to low-temperature aqueous phase reforming. The goal is to maximize reactor volumetric productivity toward hydrogen production while maintaining high hydrogen selectivity, facilitating development of a commercially viable process. The focus of vapor phase reformation is on developing a catalyst and reactor system that can efficiently convert ethanol to hydrogen. A particular effort will be made to maintain moderate reforming temperatures (~500°C) in order to eliminate the need for costly high temperature alloys for reformer fabrication. A related objective is to develop the forming process so that it can be readily integrated with water-gas shift (WGS) or hydrogen separation to realize process intensification. Insights gained from these studies will be applied toward the development of a catalytic process that can potentially meet the DOE 2017 targets of <\$3.00/gge with 65-75% production unit energy efficiency.

Objectives

- Quantify hydrogen production rate from bio-derived liquids and determine the reaction mechanisms involved.
- Optimize catalyst and catalytic process that maximize the volumetric hydrogen production rates from bio-derived liquids.
- Demonstrate hydrogen production from bio-derived liquids can meet the DOE 2017 targets of <\$3.00/gge with 65-75% production unit energy efficiency.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section (3.1) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Reformer Capital Costs
- (D) Feedstock Issues
- (E) Greenhouse Gas Emissions

Technical Targets

This project focuses on the reformation of biomass-derived liquids for the production of hydrogen. Both aqueous phase reformation and vapor phase reformation are studied. The focus of aqueous phase reformation is on producing hydrogen from bio-derived liquids such as glucose and mixed sugars, and ultimately expanding the knowledge to less refined lignocellulosic biomass feedstocks. These feedstocks are too unstable and insufficiently volatile for conventional steam reforming,

Accomplishments

- Developed a Pt-Re/C catalyst and demonstrated that hydrogen productivity from a 10% ethylene glycol feed increased from ~500 to ~2,000 STD L H₂/L-cat/hr.
- It was found that the addition of KOH can significantly increase the hydrogen productivity by suppressing alkane formation.
- It was found that the degradation products of ethanol are insignificant at temperatures <600°C and our future studies should limit to temperatures <600°C to avoid the catalyst deactivation induced by ethanol thermal degradation.
- Developed a Pt-Re/C catalyst for ethanol vapor phase reformation which shows improved stability over the Rh/CeO₂-ZrO₂ catalyst due to its favored ethanol dehydrogenation-decarbonylation reaction pathways at low temperatures such as 350°C.



Introduction

Biomass sources include forest resources, agricultural resources, municipal solid waste, and animal waste. Our target biomass-derived feedstocks for hydrogen production include ethanol, sugars, sugar alcohols, and polyols, and less refined hemicellulose or cellulose. The cost of these feedstocks decreases as ethanol>sugar alcohols>sugars>hemicellulose or cellulose. Likewise the ease of conversion of these feedstocks also decreases in a similar order. Even for the most expensive bio-derived liquids under

our consideration such as ethanol, it may still be an attractive bio-derived feedstock for distributed hydrogen production. In general, poly-hydroxylated molecules such as sugars and sugar alcohols are thermally unstable at conventional reforming temperatures, but are good feedstocks for low temperature aqueous phase reforming. Ethanol, on the other hand, is thermally more stable, and reforming at higher temperatures in the gas phase becomes possible. Ethanol reforming therefore provides an opportunity for high reactor productivity, although at too high temperatures materials of construction become of concern and integration with WGS becomes less efficient. The major objective of this project is to research the options of aqueous and vapor phase reforming and develop feedstock flexible reformers for distributed hydrogen production.

Approach

Both aqueous phase reformation (APR) and vapor phase reformation are studied in this project. APR has the potential to produce a product rich in hydrogen and CO_2 , at elevated pressure, facilitating subsequent separation and recovery of hydrogen. It also appears possible to capture and sequester the byproduct CO_2 , making APR potentially a net reducer of CO_2 from the environment. Despite significant progress in APR over the past several years, challenges remain in developing a process that can meet the economic targets identified in the DOE Hydrogen, Fuel Cells, and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan. The challenges that we intend to address in our work include identification of catalyst and reaction conditions for optimizing activity, selectivity and stability; and reactor design to address heat and mass transport resistances, with the goal to improve volumetric productivity for the process.

Ethanol, on the other hand, needs to be activated at higher temperatures than polyols and sugar alcohols, and vapor phase reforming may be more practical and economic. Reaction pathways and mechanisms of ethanol steam reforming are fairly complicated and there has been no general agreement. Methane is one of the major side products and is favored thermodynamically at lower temperatures. In addition, coke deposition precursors such as ethylene, acetaldehyde, and acetone are also thermodynamically favored at low temperatures. Therefore, the majority of literature has been focusing on high temperature ethanol steam reforming ($>500^\circ\text{C}$) to reduce the coke deposition due to the formation of coke precursors. Even high temperature reforming may introduce different carbonaceous deposition mechanisms. Deactivation of catalysts at high temperatures are not often reported since 100% ethanol conversion can be maintained, particularly at a short time on stream (<100 hours) typically reported in the literature. In addition, since the C-H bond in

methane is very difficult to activate, high temperatures such as those required for natural gas steam reforming may be employed, resulting in the requirement of high temperature (i.e. high cost) alloys and an unfavorable WGS equilibrium. Similar to natural gas steam reforming, highly endothermic ethanol steam reforming is potentially a mass and heat transfer-limited process. Our approach is to identify catalyst compositions and reaction conditions to address the activity and catalyst stability issues.

Results

Based on recent literature reports that addition of Re to Pt may increase the reactivity of Pt for C-C bond cleavage, we developed a new bimetallic catalyst, 3%Pt3-0%Re/C, on a hydrothermally stable carbon support. The Pt-Re/C catalyst exhibited superior hydrogen productivity and selectivity over one of the most active bimetallic catalysts previously developed at PNNL, Pt-Ru/C. As shown in Figure 1, using a 10% ethylene glycol feed, we demonstrated that hydrogen productivity increased from ~ 500 to $\sim 2,000$ STD L H_2 /L-cat/hr. On the Pt-Re/C catalyst, it was found that hydrogen productivity typically increases with the decrease of carbon number in monohydroxyl alcohols, polyols, and carbohydrates. For the feedstocks with identical carbon numbers, carbohydrates exhibit higher hydrogen selectivity than polyols and monohydroxyl alcohols. In general, dehydrogenation-decarbonylation of carbohydrates such as sorbitol, xylitol, glycerol and ethylene glycol are the preferred reaction pathways for selective hydrogen production. However, alkane products were formed which were most likely due to the dehydration reaction pathway catalyzed by acidic sites. Our preliminary results showed that addition of KOH can significantly suppress the alkane formation. The tradeoff is that KOH also increases acid formation likely

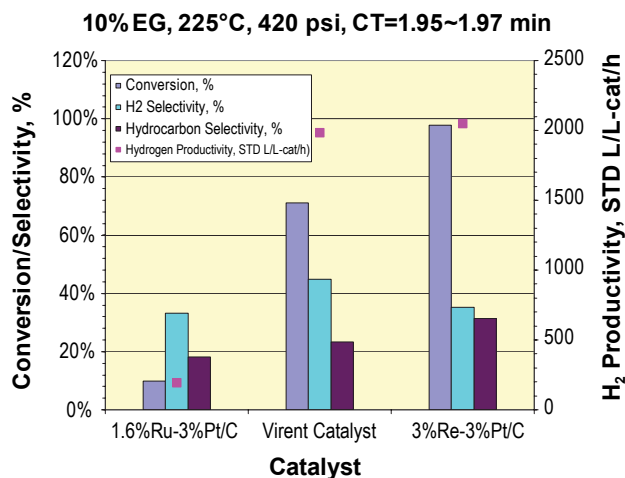


FIGURE 1. Catalyst Activity Comparison

due to the Cannizzaro reaction catalyzed by hydroxyl anions. We will optimize the reaction conditions to minimize both alkane and acid formations to increase the hydrogen productivity and selectivity.

Ethanol thermal degradation products include acetaldehyde from ethanol dehydrogenation, ethylene from ethanol dehydration, and acetone from aldol condensation of acetaldehyde which are the potential coke precursors. It was found that these degradation products are insignificant at temperatures $<600^{\circ}\text{C}$ and our future studies should limit to temperatures $<600^{\circ}\text{C}$ to avoid the catalyst deactivation induced by ethanol thermal degradation. The stability of Rh/CeO₂-ZrO₂ catalyst was studied at temperatures from 350 to 550°C. Although the deactivation rate decreases with an increase in reaction temperature, there is still potential catalyst deactivation at temperatures as high as 550°C as confirmed by a slight change in gas production distributions as well as the temperature programmed oxidation and Fourier transform infrared characterization of the spent catalyst. Alternatively, we have studied the Pt-Re/C catalyst which shows improved stability and superior activity over the Rh/CeO₂-ZrO₂ catalyst (2Rh/CZ) under the identical reaction conditions (Figure 2), due to its favored ethanol dehydrogenation-decarbonylation reaction pathways at low temperatures such as 350°C. The major disadvantage with the Pt-Re/C catalyst is that a significant level of methane is formed at low temperatures and an additional methane steam reforming step is required at high temperatures followed by a separate WGS conversion step. We will continue the development of catalyst compositions and reaction conditions to further improve the catalyst stability and overall performance.

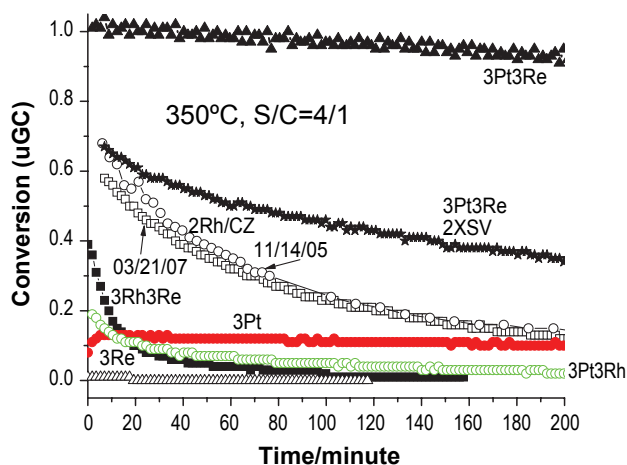


FIGURE 2. Improved Catalyst Activity and Stability

Conclusions and Future Directions

- Bimetallic catalysts exhibit improved hydrogen productivity from aqueous phase reforming of carbohydrates. Future optimization of catalyst compositions will be conducted to enhance catalyst activity and stability.
- Addition of KOH significantly enhances the hydrogen productivity by suppressing undesired alkane formation. KOH also increases acid formation likely due to the Cannizzaro reaction catalyzed by hydroxyl anions. We will optimize the reaction conditions to minimize both alkane and acid formations to further increase the hydrogen productivity and selectivity.
- Deactivation of the Rh/CeO₂-ZrO₂ catalyst cannot be avoided over the range of temperature studied. Catalyst composition can be tailored to facilitate the ethanol dehydrogenation-decarbonylation reaction pathways with mitigated catalyst deactivation. However, a significant level of methane formed by this approach requires an additional methane steam reforming step at a high temperature followed by a separate WGS, leading to increased capital and operation costs. We will develop an innovative reaction engineering approach to take advantage of the high selectivity and activity of the Rh/CeO₂-ZrO₂ catalyst while overcoming its deactivation problem.

FY 2007 Publications/Presentations

1. *Selective Production of H₂ from Bio-Ethanol at Low Temperatures over Rh/CeO₂-ZrO₂ Catalyst*, H.Roh, Y.Wang, D.L.King, accepted for publication in *Topics in Catalysis*.
2. *Deactivation studies of ethanol steam reforming catalysts*, A.Platon, H.Roh, D.L.King, Y.Wang, accepted for publication in *Topics in Catalysis*.
3. *Rh/CeO₂-ZrO₂ catalyst deactivation patterns during ethanol-steam reforming (ESR) at low temperatures*, X. Wang, A.Platon, H.Roh, G.Xia, D.King, Y.Wang, oral presentation in the 20th North American Catalysis Society Meeting, June 17–22, 2007, Houston.
4. *Hydrogen Production from Aqueous Phase Reforming of Sorbitol and Related Oxygenated Hydrocarbons*, G.Xia, X.Wang, J.Cao, A.Platon, C.Yang, T.Peterson, D.King, Y.Wang, oral presentation in the 20th North American Catalysis Society Meeting, June 17–22, 2007, Houston.
5. *Hydrogen Production via Bio-derived Liquids Reforming* by Yong Wang, U.S. Department of Energy Bio-Derived Liquids to Hydrogen Distributed Reforming Workshop, October 24, 2006, Baltimore, Maryland.
6. *Catalytic processes for biomass conversion to fuels and chemicals: an overview*, Plenary lecture by Y.Wang in 2007 symposium on biomass conversion and environmental catalysis organized by Japan Science and Technology, Catalysis Research Center, Hokkaido University, July 13–14, Sapporo, Japan.