II.A.2 Distributed Hydrogen Production from Biomass Reforming

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Objectives

- Evaluate and develop bio-derived liquid reforming technologies for hydrogen production that can meet the DOE 2017 cost target of <$3.00/gasoline gallon equivalent (gge).
- Ethanol reforming: identify at least one catalyst having necessary activity, selectivity, and life at moderate temperatures to justify scale-up.
- Ethanol reforming: provide input for H2A analysis to determine potential economic viability and provide guidance to research and development effort.
- Aqueous phase reforming: identify and control the reaction pathways to enhance hydrogen selectivity and productivity as well as catalyst life.

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:

(A) Reformer Capital Cost
(C) Operation and Maintenance (O&M)
(D) Feedstock Issues
(E) Greenhouse Gas Emissions

Technical Targets

For production of hydrogen from bio-derived liquids, the primary target that we are focusing on is the cost of delivered hydrogen (non-compressed). The target is $3.80/gge in 2012 and $3.00/gge in 2017. We have carried out some very preliminary analyses by the H2A methodology to predict the production cost of hydrogen from moderate temperature ethanol reforming given the current status of development of the project, with several assumptions. The results of our preliminary analysis are summarized in Table 1. Assumptions in this analysis included no operating labor costs, 85% capacity factor, and maintenance and repair costs equal to 5% of capital costs. With those assumptions, the current estimated production cost of ~$3.00/gge is a lower bound to actual production costs. In addition to the assumptions cited above, the analysis does not address the following issues:

- Cost of catalyst regeneration (hence an assumption of very long catalyst life–not yet demonstrated).
- Cost of recycling any of the feed if incomplete conversion is obtained.
- Effect of elevated pressure operation: assumption that catalyst activity is maintained and there is no loss in hydrogen yield due to the potentially enhanced methane formation.

One clear conclusion from the preliminary H2A analysis is that the cost of production is heavily tied to the cost of available ethanol (assumed at $1.07/gallon).

TABLE 1. Preliminary H2A Analysis of Ethanol Production over Rh-Based Catalyst

Specific Item Cost Calculation	
Cost Component	**Hydrogen Production Cost Contribution ($/kg)**
Capital Costs	$0.463
Decommissioning Costs	$0.000
Fixed O&M	$0.156
Feedstock Costs	$2.344
Other Raw Material Costs	$0.000
Byproduct Credits	$0.000
Other Variable Costs (including utilities)	$0.055
Total	**$3.017**

We are addressing these targets in our work on ethanol steam reforming by developing highly selective catalysts that show long catalyst life. For aqueous phase reforming (for which we have not yet carried out H2A

analysis) we are focusing on identifying the mechanistic pathways leading to desired and undesired products and understanding the pathways leading to catalyst deactivation.

Accomplishments

Ethanol steam reforming:

- Improved the life of Rh-based catalysts by a factor of four by adjustment of pretreatment protocols and modification of support composition.
- Quantified the performance of Co/ZnO catalyst over a range of conditions with realistic feed concentrations and conversion levels.
- Provided test results from Rh/CeO_2-ZrO_2 catalyst to H2A analysis.

Aqueous phase reforming:

- Increased longevity of current best Pt-Re/C catalyst by 2x by support modification (based on a hypothesis on cause of deactivation).
- Extended the study of KOH and alternate base addition with glycerol and quantified the concentration effects on life and selectivity.

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Introduction

The conversion of biomass-derived liquids to hydrogen is attractive because of the low carbon footprint (nearly carbon neutral) and the availability of biomass in certain regions allowing for distributed (forecourt) hydrogen production. Our target biomass-derived liquid feedstocks include ethanol, sugars, sugar alcohols, and other polyols. Ultimately, the goal is to process less refined hemicellulose or cellulose directly to hydrogen. Ethanol is thermally stable, therefore steam reforming in the gas phase is practical and with the appropriate catalyst provides the opportunity for high reactor productivity. Most of the other sugars and sugar alcohols and polyols (with the possible exception of glycerol) are thermally unstable if vaporized to reforming temperatures, therefore an alternative approach based on aqueous phase reforming becomes attractive. We are addressing both technological approaches to producing hydrogen from bio-derived liquids. 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

Ethanol reforming

Cost-effective production of hydrogen from ethanol requires selective, active, and long-lived catalysts. General approaches to ethanol reforming include:

- High temperature reforming – challenges include decomposition of the ethanol prior to reaching the catalyst bed due to the high temperatures involved.
- Pre-reforming ethanol to methane-rich syngas and subsequent methane steam reforming.
- Low temperature reforming – challenges including reduced catalyst activity, catalyst selectivity, and catalyst deactivation.

We are addressing the third option (low-temperature reforming) because we believe if a catalyst can be identified, this approach will provide the advantages of improved energy efficiency, easy integration with downstream water gas shift reactor, and lower material cost of reactor construction.

Aqueous phase reforming

Low temperatures are applied in aqueous phase reforming in order to maintain the system in the liquid phase. At temperatures of 225-265°C, operation occurs at approximately 30 bar. As with ethanol steam reforming, catalyst development is key because high activity, high selectivity, and long catalyst life are essential. We have identified a catalyst based on Pt-Re/carbon that shows good activity and selectivity with the addition of KOH in the feed, but shows some evidence of catalyst deactivation over the course of a few hundred hours of operation. Our focus on this project is to identify the reaction pathways that are followed in aqueous phase reforming (both desired and undesired) in order to gain insights that will lead to better catalyst formulations and better catalyst performance.

Results

Ethanol steam reforming

For ethanol steam reforming, we have focused on development of two types of catalyst formulations: Rh-based and Co-based. Rh catalysts have typically provided high activity and good selectivity toward hydrogen, but catalyst lifetime is much shorter than required for a successful process. Our approach to improving catalyst life has been based on modifying the catalyst support – we believe that the Rh metal is functioning properly and is not sintering, which would be a cause for deactivation. Rather, the catalyst support is implicated and supports that facilitate the reforming
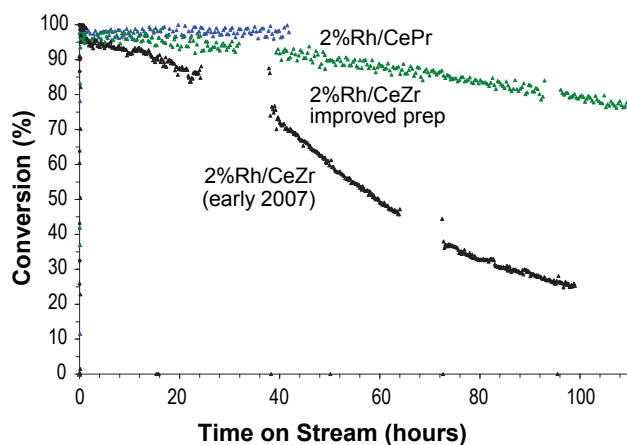
FIGURE 1. Steam Reforming of Ethanol over $Rh/Ce_{0.8}$-$Zr_{0.2}O_2$ and $Rh/Ce_{0.8}$-$Pr_{0.2}O_2$ Catalysts at 500°C and a Feed Rate of 1.2 mol $EtOH/g_{cat}$-h

FIGURE 2. Steam Reforming of Ethanol over Co/ZnO Catalyst at 450°C and a Feed Rate of 0.28 mol $EtOH/g_{cat}$-h

through water dissociation and/or oxygen transport to the Rh catalyst appear to be required. Most recently, our work has focused on modifying our current standard $Rh/Ce_{0.8}Zr_{0.2}O_2$ catalyst by replacing the ZrO_2 with praseodymium: $Rh/Ce_{0.8}Pr_{0.2}O_2$. Initial studies with this new catalyst show an increase in catalyst life, as shown in Figure 1. Although the length of the experiment was only 40 hours, a clear improvement in conversion maintenance at 100% is seen relative to the $Rh/Ce_{0.8}Zr_{0.2}O_2$ catalysts when operating at 500°C. The tests are run at very high space velocity, which demonstrates high catalyst activity, but also for the purpose of accelerating catalyst aging. Typical operating conditions in a plant would have feed rates at least one order of magnitude lower. During the test with the Pr-modified catalyst, hydrogen selectivity was maintained at 5 mol/mol EtOH fed (theoretical maximum is 6 mol/mol). Performance of this catalyst was modeled by the H2A analysis as described earlier.

For comparison, we have been investigating a cobalt-based catalyst (Co/ZnO) that has been reported in the literature to have high hydrogen selectivity. However, those tests were carried out with very high steam concentrations and at high dilution, both of which increase ethanol conversion but which results in an inaccurate view of performance under more realistic conditions. Figure 2 shows the performance of Co/ZnO operating at 450°C at a steam/carbon ratio of 4. The feed rate of ethanol per unit weight of catalyst for Co/ZnO is approximately 1/5 that of the Rh-based catalyst. Figure 2 shows high selectivity to CO_2 (it is desired that all carbon is converted to CO_2, which produces the highest corresponding amount of hydrogen). However, conversion in this experiment is limited to 30%, showing an even greater disparity in activity compared with Rh. Experiments aimed at increasing conversion of ethanol with the Co/ZnO catalyst by reducing flow rate or increasing temperature results in higher methane
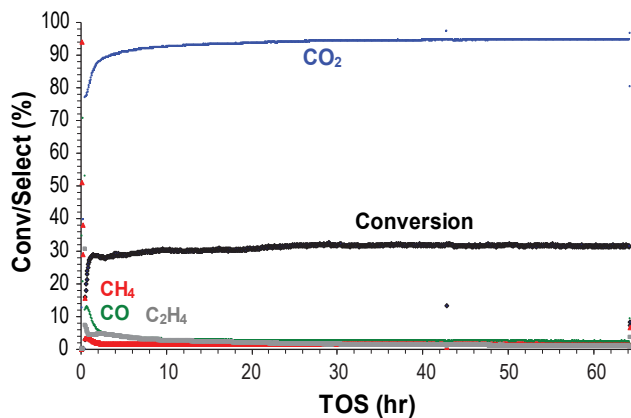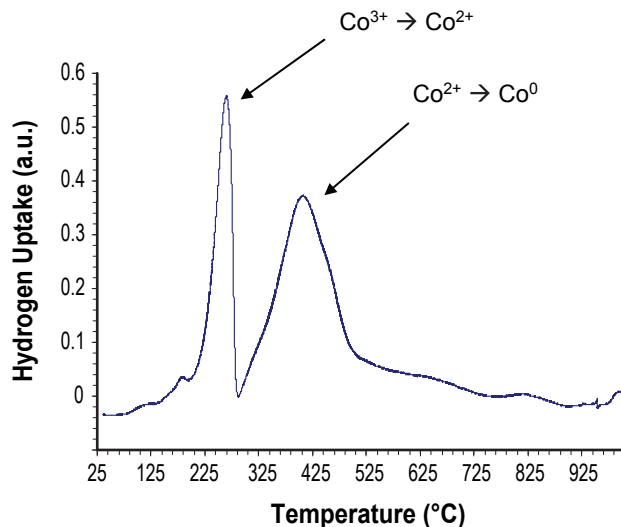

FIGURE 3. Temperature Programmed Reduction of Co/ZnO Catalyst

formation, which can only be counteracted by increasing steam concentration. We believe that the reason for the loss of selectivity at higher EtOH conversion is a change in the oxidation state of cobalt from partially oxidized to totally reduced. Figure 3 provides the results of temperature programmed reduction of the Co/ZnO catalyst. An initial reduction of Co^{3+} to Co^{2+} occurs at 240°C, and a second reduction of Co^{2+} to Co metal centered around 410°C and extending to higher temperatures. We are postulating that at our operation temperature of 450°C we are in the range of partial reduction of Co, which is accentuated at higher conversions where H_2 concentration is higher and H_2O concentration is lower. Co metal facilitates methane formation. Therefore, improved Co catalyst performance must deal with methods to maintain Co in a partially oxidized state at the temperatures of operation.

Aqueous phase reforming

Our aqueous phase reforming work has focused on improving catalyst performance and life. We have focused on glycerol reforming, as it is a relatively simple molecule but provides all the potential reaction pathways encountered with bio-derived sugar alcohols. All our catalysts are supported on carbon. We have found that although Pt is the best single metal for aqueous phase reforming of glycerol due to its very high H_2 selectivity, its overall activity is low. Addition of Re to the Pt increases the glycerol conversion substantially but at a loss of H_2 selectivity to CH_4, as shown in Figure 4. Addition of KOH to the aqueous phase feed decreases hydrogen selectivity with Pt only, but provides a significant increase in H_2 when Re is added (Pt-Re/C catalyst), as shown in Figure 5. The limitation to operating the Pt-Re/C catalyst under basic conditions

is catalyst deactivation, which is accompanied by a decrease in H_2 selectivity. We are continuing to map the reaction pathways by analysis of liquid phase products as well as gas phase products. Related to this, we are investigating the cause of this deactivation through several mechanistic studies, investigating the effects of alternative bases, and also modifying the carbon catalyst support in an effort to reduce the catalyst deactivation.

Conclusions and Future Directions

Ethanol steam reforming

- An active and selective catalyst Rh-based catalyst $Rh/Ce_{0.8}Pr_{0.2}O_2$ has shown improved catalyst life relative to previous formulations and points to the potential of this catalyst system with planned further modifications to meet the requirements for H_2 production that can meet the DOE targets.

- The Co/ZnO catalyst provides very high H_2 and CO_2 selectivity but only at relatively low conversions. Methods to increase conversion result in increased methane formation, indicating that this catalyst in present form will not meet the guidelines and cost targets. Future work on this catalyst is focusing on methods to stabilize the Co in a partially oxidized state, possibly Co^{2+}, but specifically avoiding reduced Co metal.

Aqueous phase reforming

- Pt-Re/C is an attractive catalyst for the conversion of glycerol to hydrogen but requires the presence of base to maintain high H_2 selectivity. Base addition results in additional pathways being accessible which may lead to catalyst deactivation. Future work is focusing in two areas:
  - Specific experiments examining the effect of different bases on performance, including affixing a base function on the catalyst support rather than maintaining a basic aqueous solution. The aim is to adjust the reaction pathway so that deactivation, for example by production of polymeric species that block catalyst pores, is minimized.
  - Modifying the Pt-Re/C catalyst by developing methods to affix the metals to the support such that they do not deposit in the very small pores of the carbon. In such a case, deactivation may be facilitated by pore mouth plugging, denying access of the active catalytic metals to the feedstock.
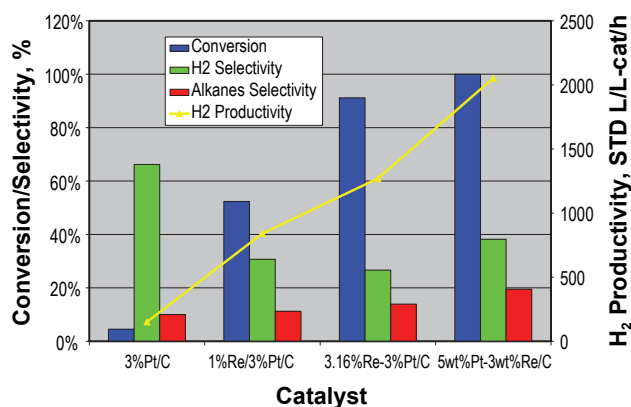

FIGURE 4. Effect of Re loading onto a Pt/C catalyst on catalyst activity and gas phase product selectivity for the aqueous phase reforming of glycerol in the absence of added base.
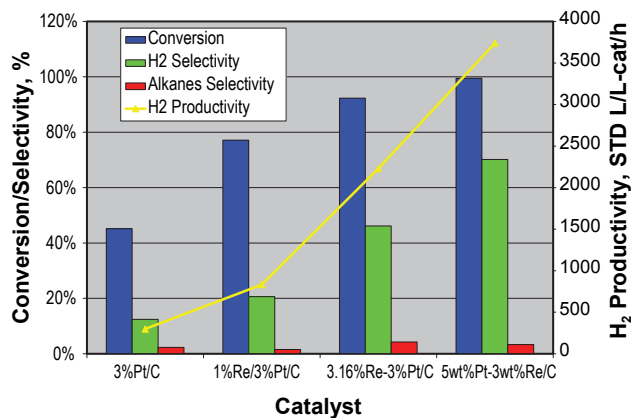

FIGURE 5. Effect of Re loading onto a Pt/C catalyst on catalyst activity and gas phase product selectivity for the aqueous phase reforming of glycerol in the presence of added KOH.

FY 2008 Publications/Presentations

Presentations

1. "Overview of Biomass Conversion to Hydrogen From a U.S. Perspective" presented by David King to the Task Force on Small Scale Reformers, IEA Meeting, Tokyo April 2008 (invited).

2. "Hydrogen Production from Bio-derived Liquids" presented by Yong Wang in 2008 Hydrogen Symposium, Purdue University, April 25, 2008 (invited).

3. "Overview of Hydrogen Production from Biomass" presented by Dave King in 2008 ACS Spring Meeting, New Orleans, April 7, 2008 (Keynote).

Publications

1. Platon, A., Roh, H-S., King, D. L., Wang, Y. "Deactivation studies of $Rh/Ce_{0.8}$-$Zr_{0.2}O_2$ catalysts in low temperature steam reforming", Topics in Catalysis (2007), 46, 374-79.

2. Roh, H.-S., Wang, Y., King, D. L. "Selective Production of H_2 from Ethanol at Low Temperatures over Rh/ZrO_2-CeO_2 Catalysts", Topics in Catalysis (in press).