

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: down-select preferred catalyst (Rh or Co) based on catalytic testing results combined with H2A analysis. Test criteria include activity, selectivity, life, and regenerability. Determine if catalyst performance at moderate temperatures meets criteria to justify scale up.
- Aqueous phase reforming: Identify and control the catalyst composition, reaction pathways, and catalyst preparation methods to enhance hydrogen selectivity, productivity, and catalyst life.

Technical Barriers

This project addresses the following technical barriers from the 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 is the cost of delivered hydrogen (non-compressed). This target is \$3.80/gge in 2012 and \$3.00 in 2017 (\$3.00/kg H₂). Our ethanol steam reforming work has especially focused on demonstrating performance under realistic conditions, especially in terms of conversion and product selectivity using realistic ethanol feed concentration and operating pressure. We have applied H2A methodology to determine these costs, leading to a down-selection from two to one primary catalyst. It is clear from the analysis that the cost of production is heavily tied to the cost of available ethanol. The cobalt-based catalyst system has the potential to meet the cost target for hydrogen production, if we can demonstrate acceptable catalyst life and regenerability.

For aqueous phase reforming, the costs targets remain the primary goal. We are not yet at the point of carrying out H2A analysis, although this has been provided by others working on this technology. For APR we are currently focusing on identifying the mechanistic pathways leading to desired and undesired products and understanding the pathways leading to catalyst deactivation. This improved understanding is expected to affect operating parameters that will lower cost of hydrogen production.

Accomplishments

Ethanol Steam Reforming:

- Demonstrated that Rh-based catalyst life can be significantly increased by operating at a significantly reduced weight hourly space velocity and balancing metal and support functions. Showed that Rh catalyst selectivity is driven by thermodynamic equilibrium, especially undesirable at elevated operating pressures.
- Quantified the performance of Co/ZnO catalyst over a range of conditions with realistic feed concentrations and conversion levels. Established substantially better performance of this catalyst at elevated pressures relative to the Rh catalyst in terms of hydrogen selectivity.
- H2A analysis based on both Rh- and Co-based catalysts indicates significant economic advantage of the Co catalyst and it has been down-selected for further work (Table 1).

TABLE 1. Rh and Co-based Catalysts compared to H2A Baseline

	PNNL-Rh	PNNL-Co	H2A Baseline
Capital Costs	\$0.51	\$0.46	\$0.58
Decommissioning Costs	\$0.00	\$0.00	\$0.00
Fixed O&M	\$0.16	\$0.16	\$0.20
Feedstock Costs	\$3.41	\$2.17	\$2.34
Other Raw Material Costs	\$0.00	\$0.00	\$0.00
Byproduct Credits	\$0.00	\$0.00	\$0.00
Other Variable Costs (including utilities)	\$0.08	\$0.05	\$0.05
Total	\$4.16	\$2.85	\$3.18

Aqueous Phase Reforming:

- Demonstrated that addition of Re to Pt/C catalyst significantly increases activity with modest decrease in H₂ selectivity.
- Provided increased fundamental understanding of the interaction between Pt and Re on carbon-supported catalyst, involving charge transfer from Pt to Re.
- Demonstrated that metal dispersion and particle size stability and therefore both catalyst performance is affected by the method of pretreating the catalyst prior to reduction (mild calcination).
- Quantified role of base addition on catalyst performance in terms of conversion and selectivity to hydrogen.



Introduction

The conversion of biomass-derived liquids to hydrogen is attractive because of the near carbon-neutral footprint and their availability in many regions of the U.S. Ethanol is an infrastructure fuel, thus it provides an avenue for early entry into distributed hydrogen. Ethanol is thermally stable, therefore steam reforming in the gas phase is practical and is our approach. Beyond ethanol, we target sugars and sugar alcohols, along with other polyols such as glycerol, again for distributed production of hydrogen. The other sugars and sugar are thermally unstable if vaporized to reforming temperatures, therefore an alternative approach based on aqueous phase reforming is practiced. We are addressing both feedstocks and technological approaches to producing hydrogen from bio-derived liquids.

Approach

Ethanol Steam Reforming

We are examining the catalytic reforming of ethanol at moderate temperatures (450-550°C). This approach provides the potential for hydrogen production using a single reactor, without the need for a subsequent water-gas shift step. The tradeoff of this approach is loss of activity compared with higher temperature reforming. The moderate temperature approach requires cost-effective, selective, active, and long-lived catalysts. We are examining and comparing precious metal (Rh) and base metal (Co) catalysts both for relative performance and for the ability of one or both to meet the hydrogen production cost targets.

Aqueous Phase Reforming

Aqueous phase reforming is becoming a recognized technology for the production of hydrogen from thermally unstable bio-derived sugars and sugar alcohols. Operation is at lower temperature (225-265°C) than ethanol reforming, placing an even greater demand on catalytic activity. The standard catalyst is platinum on carbon (Pt/C), which shows low activity but high hydrogen selectivity. Much development effort has been on catalyst modification to increase activity while preserving the good hydrogen selectivity. Addition of Re to Pt/C has been established as the leading candidate for enhanced aqueous phase reforming performance. Our approach has been to carry out detailed characterization of the Pt-Re/C catalyst in order to increase fundamental understanding of the promotional effect of Re, and as well to understand and optimize variables related to catalyst preparation, activation, and stabilization. We are also examining pH effects through the addition of

base on selectivity and performance, with the goal of increasing the overall understanding and control of the various reaction pathways available.

Results

Ethanol Steam Reforming

In our previous work, we found that Rh on ceria-based supports provided high activity for the conversion of ethanol, with gas phase selectivity toward hydrogen exceeding thermodynamic equilibrium. This catalyst, however, deactivated over relatively short time periods (approximately 100 hours). This year's studies have shown that by substantially lowering the space velocity, this same Rh-based catalyst gains significant stability (Figure 1). We have found that although operating at high space velocities could take advantage of the inherent activity of Rh, a non-negligible amount of the ethanol simply converted to acetaldehyde. Accumulation of acetaldehyde led to a condensation side reaction resulting in polymers that deactivated the catalyst. Operating at lower space velocities, the Rh function was able to convert acetaldehyde to H₂ and CO₂, avoiding the non-desirable polymerization reaction. This is shown schematically in Figure 2. However, we found that an inherent limitation of the Rh catalyst was the formation of methane as an intermediate, and the lowest achievable methane selectivity is at the thermodynamic equilibrium value. This leads to an undesirable loss of hydrogen and is especially deleterious at elevated pressure operation. Parallel examination of a cobalt catalyst, supported on zinc oxide (Co/ZnO) has shown better performance in terms of selectivity toward H₂ and CO₂ while minimizing methane formation (below equilibrium values). This same benefit is maintained at elevated pressure operation (to 100 psig;

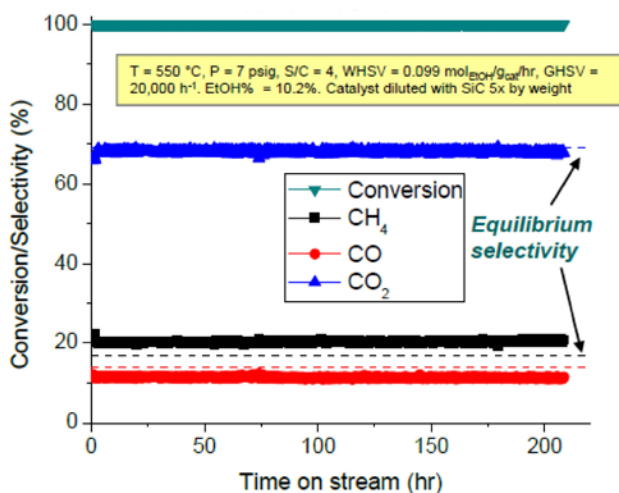


FIGURE 1. Performance of Rh/Y_{0.1}Pr_{0.2}Ce_{0.9}O₂ catalyst at reduced space velocity, showing stable operation for over 200 hours.

Figure 3). We believe this was due to different reaction mechanisms occurring on the cobalt metal with methane formation being a side reaction. Although the inherent activity of the Co catalyst is less than Rh, the need to operate the Rh catalyst at low space velocities minimizes the actual activity and productivity differences between the two. That fact, combined with the lack of a need for a water-gas shift step, the lower methane selectivity, and lower catalyst cost all contributed to a down-selection of the Co/ZnO catalyst.

Aqueous Phase Reforming

Our aqueous phase reforming work has focused on improving the understanding of catalyst performance and reaction pathways, primarily focusing on glycerol feedstock. Glycerol is a more tractable feedstock

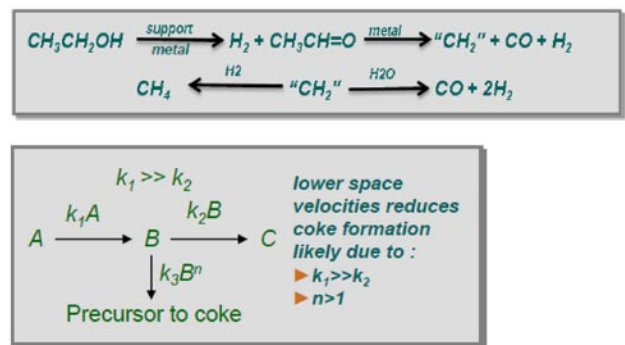


FIGURE 2. Schematic depiction of conversion of ethanol over Rh catalyst at high space velocity, leading to accumulation of acetaldehyde and production of undesirable coke precursors.

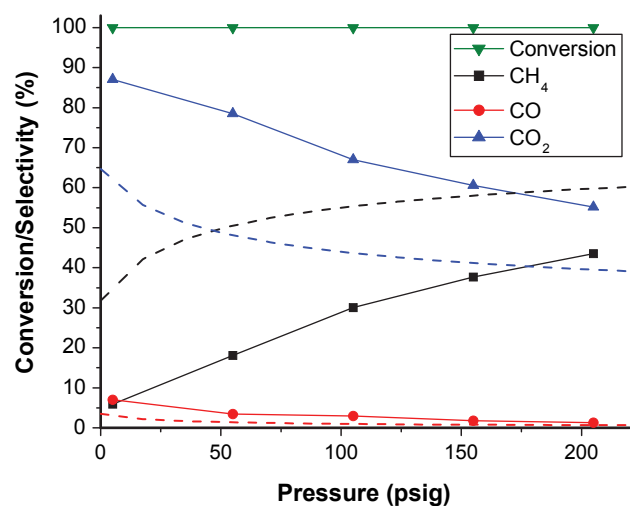


FIGURE 3. T = Performance of Co/ZnO catalyst as a function of operating pressure. Conditions: 450°C, S/C = 5, gas hourly space velocity = 11,000 h⁻¹, 4.7 % EtOH. Dashed lines correspond to predicted thermodynamic equilibrium concentrations.

that shows the same patterns of selectivity as do the sugar alcohols such as sorbitol, but with a significantly reduced product slate, simplifying the analysis. In previous work we have shown that the addition of Re to Pt/C increases the activity of the catalyst toward glycerol conversion, but the very high selectivity of Pt/C toward H_2 and CO_2 decreases upon addition of Re, with the resulting production of a significant level of light alkanes. A simplified reaction pathway analysis suggests that addition of Re has facilitated C-O bond cleavage, primarily dehydration, which sequentially can lead to alcohols and ultimately hydrocarbon formation. Addition of KOH to the aqueous phase feed provides a significant increase in H_2 /alkane ratio across the entire range of Re concentrations, as shown in Figure 4. We believe that the base addition deactivates acid sites that favor dehydration, although co-production of carboxylic anion byproducts occurs as a result of the parallel homogeneously catalyzed Cannizzaro reaction. Moreover, we observe catalyst deactivation which we believe to be due to formation of base-catalyzed aldol condensation products that deposit onto the catalyst surface and hinder active sites. We believe that by proper pH control with the appropriate base that the benefits of base addition without the liabilities may be realized. A major task in Fiscal Year 2009 is to gain a more basic understanding of the role of Re when it is added to Pt/C. The general understanding is that in the reduced form, Pt-Re is present as an alloy, and that the role of Re is to reduce the binding energy of CO, facilitating the adsorption and reaction of the glycerol substrate. Why Re retards CO adsorption is not fully understood, however. Work that we have carried out using in situ X-ray photoelectron spectroscopy (XPS) has indicated that in the formation of the Pt-Re alloy, electron density flows from the Pt to the Re, making Pt somewhat more electropositive, Figure 5. This is

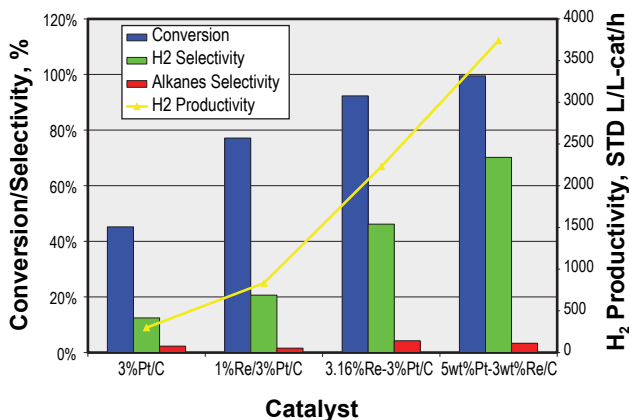


FIGURE 4. Effect of Re loading on Pt/C catalyst activity and relative hydrogen vs. alkane selectivity in the presence of 1% KOH addition to the feed.

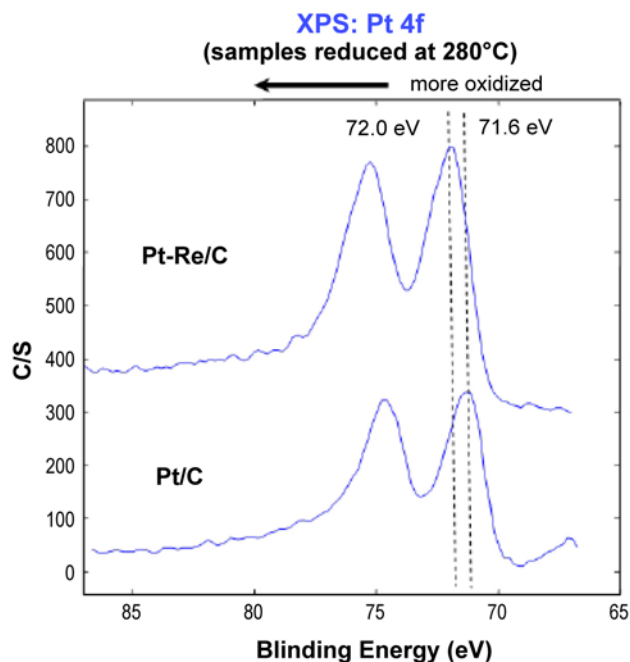


FIGURE 5. X-ray photoelectron spectra of Pt/C and Pt-Re/C catalysts following reduction at 280°C, indicating the transfer of electron density from the Pt to Re metal.

consistent with some recent theoretical calculations correlating higher CO adsorption strength with increasing electron density on the metal center [1].

Conclusions and Future Directions

Ethanol Steam Reforming

We have concluded that the Co/ZnO catalyst provides superior performance to the Rh/Ce_{0.8}-Zr_{0.2}O₂ catalyst and it has been down-selected for all future work. Remaining work with the Co catalyst will focus on catalyst life, including examination and possible verification of preliminary results indicating a significantly greater tendency of the Co catalyst to deposit filamentous carbon. Quantification of this effect and catalyst regenerability will be the focus of the work.

Aqueous Phase Reforming

- We have shown that the addition of Re to Pt/C catalyst increases activity and glycerol conversion to gas phase products, but at some loss of hydrogen selectivity relative to alkanes. Addition of 1% KOH base to the reaction mixture significantly increases hydrogen selectivity but results in some adverse effects such as carboxylate formation and catalyst deactivation. Some very preliminary results with formate base addition at lower concentrations has indicated that the deactivation of the catalyst can

be retarded with some increase in selectivity relative to the base case (no base addition). A combination of specific base effects (for example, formate may provide different chemistry from OH⁻) as well as overall pH effect are likely to be contributing to this result. In future work we intend to examine the effect of base concentration and base identity on Pt-Re/C performance with glycerol.

- Our work by XPS, along with some preliminary X-ray absorption near-edge spectroscopy studies, has shown that addition of Re to Pt results in a small shift in electron density from the Pt to the Re. Further work is required and planned to better quantify this effect, including the concentration dependence of Re and oxidation state of both Pt and Re in the presence of steam as well as syngas.

FY 2009 Publications/Presentations

1. D.L. King, Y. Wang, G. Xia, Y. Yang, D. Heldebrant, L. Zhang, and T. Peterson; “Aqueous Phase Reforming of Glycerol: Reaction Pathways, Base Effects, and Catalyst Deactivation.” Presented orally at the 21st meeting of the North American Catalysis Society, San Francisco, June 2009.
2. A. Karim, Y. Su, J. Sun, V. Lebarbier, J.J. Strohm, D. King and Y. Wang; “Highly Stable Catalysts for Ethanol Steam Reforming”. Presented orally at the 21st meeting of the North American Catalysis Society, San Francisco, June 2009.
3. L. Zhang, Y. Yang, G. Xia, D. Heldebrant, D. King, and Y. Wang; “Effect of Pt-Re Interaction on the Aqueous Phase Reforming of Glycerol over Pt-Re-C Catalysts”. Oral and poster presentations at the 21st meeting of the North American Catalysis Society, San Francisco, June 2009.

References

1. S. Kathman, D. Mei, R. Rousseau, J. White, M. Gerber, and D. Stevens; “Computational Study of Ethanol Synthesis from Biomass-Derived Syngas Using Rh-Based Catalysts”. Presented at the 21st meeting of the North American Catalysis Society, San Francisco, June 2009.