

II.A.2 Distributed Hydrogen Production from Biomass Reforming

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

Objectives

- Evaluate and develop bio-derived liquid aqueous phase reforming (APR) technology for hydrogen production that can meet the DOE 2017 cost target of <\$3.00/gasoline gallon equivalent (gge).
- 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 Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Reformer Capital Cost
- (C) Operation & Maintenance
- (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). For APR, the cost targets remain the primary drivers. We have been focusing on identifying the specific role of the catalyst components, delineating the mechanistic pathways leading to desired and undesired products, and understanding the causes of catalyst deactivation. This

improved understanding is aimed at reducing operating costs, which will lower cost of hydrogen production.

Accomplishments

- Found evidence for dual-functionality of Pt-Re/C under a hydrothermal APR environment:
 - Pt-Re alloy formation provides increased activity toward H₂ production.
 - Acidic ReOx facilitates competitive dehydration pathways.
- Advanced the understanding of glycerol APR over Pt-Re/C:
 - Addition of Re increases conversion of glycerol, but also provides additional reaction pathways competing with the H₂-generating C-C cleavage pathway.
 - ReOx formed under APR conditions facilitates C-O scission, which consumes H₂ and leads to higher selectivity to alcohols and C₂⁺ alkanes.
 - H₂ productivity increases with addition of Re at expense of H₂ selectivity.
 - Addition of KOH to glycerol feed over Pt-Re/C neutralizes acidity of ReOx and depresses C-O scission pathways, resulting in increased H₂ productivity via C-C cleavage.
- Preliminary results from APR of sorbitol have been obtained, providing comparative behavior between APR of sorbitol and glycerol, indicating that maintaining selectivity toward C-C bond cleavage vs. C-O bond cleavage is even more challenging.



Introduction

The conversion of biomass-derived liquids to hydrogen is attractive because of their near carbon-neutral footprint and their availability in many regions of the U.S. We target sugars and sugar alcohols, along with other polyols such as glycerol, for distributed production of hydrogen. These sugars and sugar alcohols are thermally unstable if vaporized to reforming temperatures; therefore aqueous phase reforming is the technology of choice. Currently, many researchers are investigating the conversion of sugars and sugar alcohols to liquid products that are infrastructure compatible, with less attention being paid to hydrogen production from these same molecules. Our project focuses on this latter aspect, hydrogen production, which has perhaps a longer time horizon, but over the long-term is an

important approach to meeting the energy needs through the application of fuel cells.

Approach

APR is becoming a recognized technology for the production of hydrogen from thermally unstable bio-derived sugars and sugar alcohols. Operation is at relatively low temperatures (225-265°C), placing a significant demand on catalytic activity. The standard catalyst is platinum on carbon (Pt/C), which shows modest 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 APR performance. Our approach has included:

- Detailed study of Pt-Re/C catalyst:
 - Compare catalytic performance with Pt/C for glycerol feedstock.
 - Quantify the effect of Re addition on Pt/C performance.
- Develop advanced catalyst characterization methods to understand interactions between the Pt, Re, and C components: X-ray photoelectron spectroscopy, X-ray absorption near-edge spectroscopy, transmission electron microscopy.
- Examine and quantify effect of base addition on catalyst performance.
- Evaluate options for co-production of hydrogen with CH₄ for compatibility with solid oxide fuel cells (SOFC) for power generation.

Results

Our APR work has focused on correlating catalyst structure with performance, and delineating competing reaction pathways with the intention to maximize the H₂ production pathway. Work has progressed this year from glycerol to sorbitol feedstock.

Affect of Re Addition on Activity and Selectivity

Figure 1 compares the activity of 3%Pt/C, 3%Pt-1%Re/C and 3%Pt-3%Re/C catalysts. The figure provides this information on a turnover frequency basis, meaning moles (of glycerol converted or product formed) per active Pt metal site (based on CO chemisorption) per minute. It can be seen that the addition of Re dramatically increases turnover frequencies for both glycerol conversion and all products formed, indicating that Re addition more affects activity than selectivity. Figure 2 compares the product selectivity in greater detail for the 3%Pt/C and 3%Pt-3%Re/C catalysts. In this case, the space velocity (flow

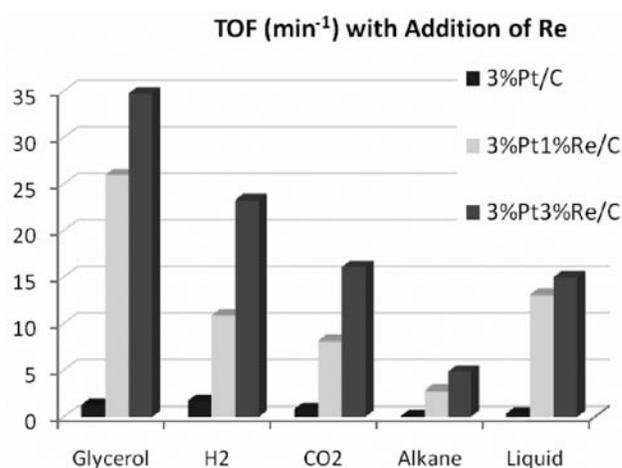


FIGURE 1. Comparative activities of 3%Pt/C, 3%Pt-1%Re/C, and 3%Pt-3%Re/C catalysts for APR of glycerol, expressed in terms of turnover frequency. The units are mol (product or glycerol)/g_{cat}-min. (Conditions: 226°C, 420 psig, feed rate 0.06 mol glycerol/g_{cat}-h.)

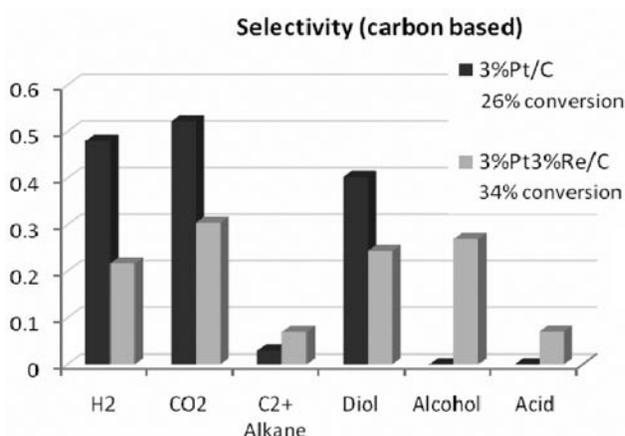


FIGURE 2. Comparative Product Selectivity of 3%Pt/C and 3%Pt-3%Re/C for APR of Glycerol at Near Constant Conversion Level (Conditions: 226°C, 420 psig, feed rate 0.06 mol glycerol/g_{cat}-h.)

rate) of the 3%Pt/C catalyst was substantially decreased in order to allow a comparison of performance over the two catalysts to be made at comparable glycerol conversion levels. The figure shows that the catalyst without Re addition is more selective toward H₂, CO₂, and diol formation, whereas addition of Re to the catalyst increases formation of alkanes, mono-alcohols, and carboxylic acids. We believe that the increase in alcohols and alkanes is the result of facilitating a dehydration pathway via the addition of Re, probably present as ReOx, in which diols are converted to mono-alcohols, and mono-alcohols converted to alkanes via successive dehydration/hydrogenation pathways. The reason for the increased formation of carboxylic acids is less clear.

Effect of Base Addition to 3%Pt-3%Re/C Catalyst

With the operating assumption being that the increase of mono-alcohols and alkanes was due to acidity present on the catalyst, we have explored the addition of 0.1% KOH base to neutralize the acidity of the catalyst. The net effect is a small increase in hydrogen selectivity, as shown in Figure 3, accompanied by a decrease in alkanes production, the result of significantly removing the dehydration pathway from mono-alcohols to alkanes. On the other hand, the addition of base results in the generation of more liquid phase product. We conclude that although base addition can have some positive effects in controlling reaction pathways, the amount of base added must be carefully controlled to maximize overall hydrogen productivity and minimize accumulation of liquid phase product.

Co-Production of Methane with H₂

This past year, we examined adjusting pH and operating conditions in an effort to maximize the combined production of H₂ and CH₄. The purpose for this was the potential utilization of the APR product with an SOFC, which is capable of processing CH₄. Figures 4 and 5 show that it is possible to maximize both H₂ and CH₄ through a combination of increased residence time and base addition.

Comparison of APR of Glycerol with Sorbitol

We examined the effect of changing feedstock from glycerol to sorbitol on the conversion and product selectivity, keeping the same operating parameters for both. The comparative results are shown in Figure 6a. It can be seen that for the larger (sorbitol) molecule, the hydrogen selectivity is significantly lower. However,

Selectivity to Gas Phase Products on 3%Pt3%Re/C

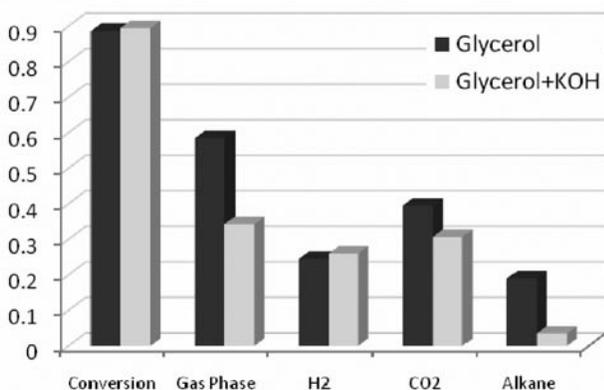


FIGURE 3. Comparative Gas Phase Selectivity for APR of Glycerol with 3%Pt-3%Re/C Catalyst With and Without 0.1%KOH added to the Feedstock (Conditions: 226°C, 420 psig, feed rate 0.06 mol glycerol/ g_{cat}-h.)

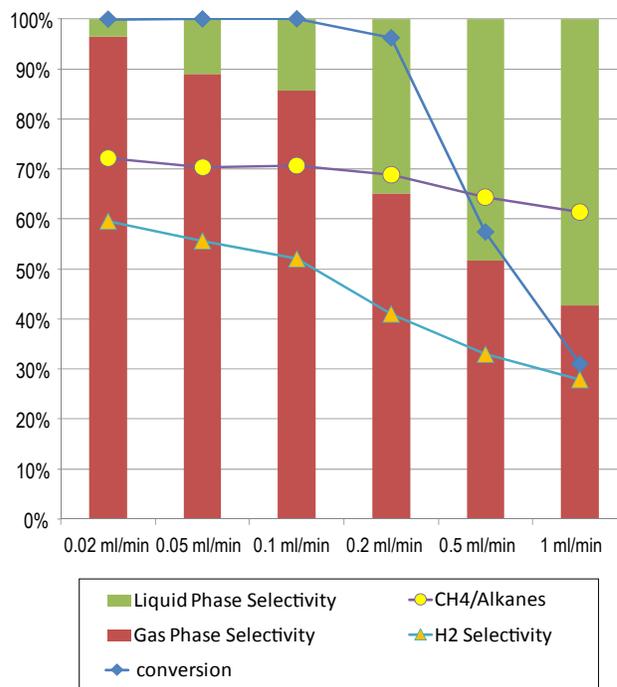


FIGURE 4. Effect of Feed Rate on the Conversion and Selectivity of 3%Pt-3%Re/C catalyst for the APR of Glycerol, Focusing on both H₂ and CH₄ Production (Conditions: 226°C, 420 psig.)

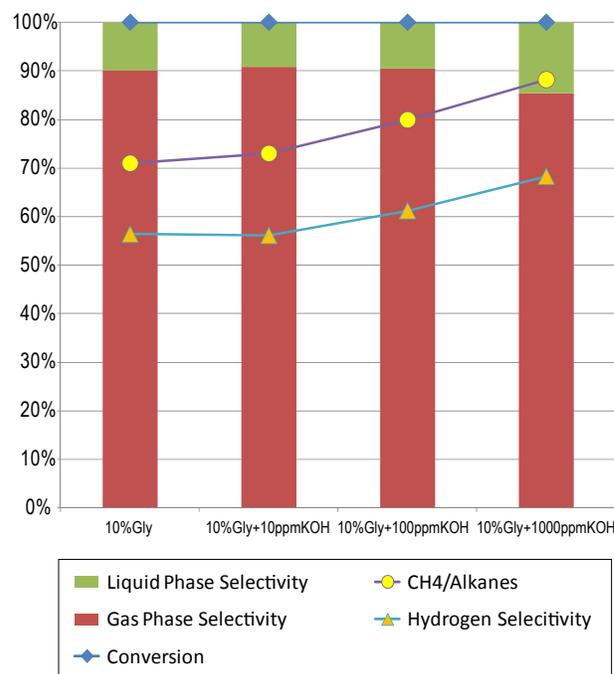


FIGURE 5. Effect of Added KOH at Various Concentrations on Activity and Selectivity of 3%Pt-3%Re/C Catalyst for the APR of Glycerol, Focusing on both H₂ and CH₄ Production (Conditions: 226°C, 420 psig, feed rate 0.06 mol glycerol/ g_{cat}-h.)

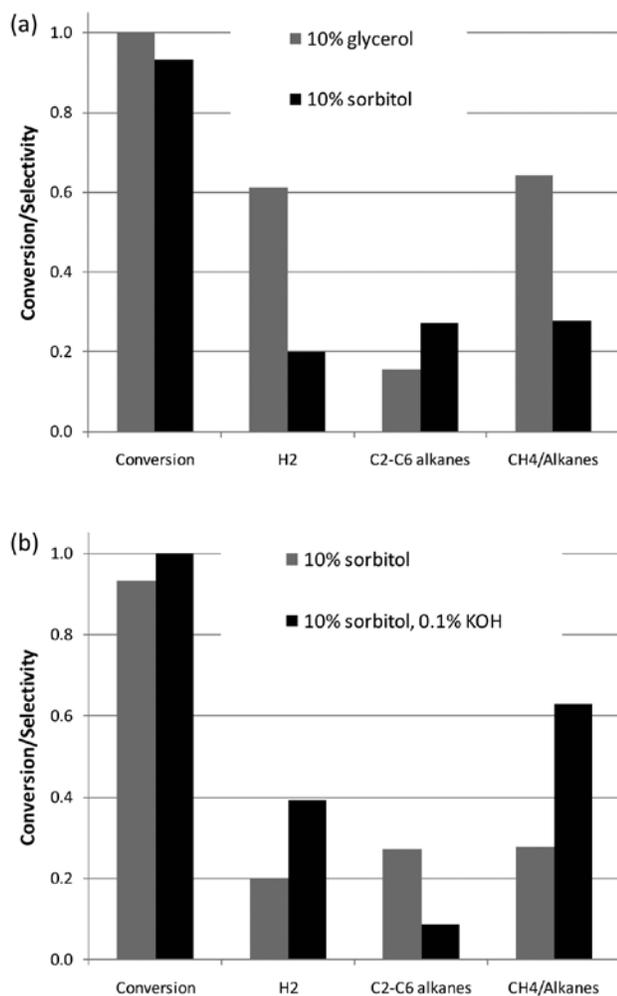


FIGURE 6. Comparison of APR Performance of 3%Pt-3%Re/C Catalyst for the APR of Glycerol and Sorbitol — Upper figure (a): glycerol vs. sorbitol in the absence of base; (b) sorbitol feed with added KOH at 0.1% concentration. (Conditions: 225°C, 375 psig, feed rate 0.01 ml/min.)

addition of base appears to be quite beneficial in terms of increasing the hydrogen selectivity from sorbitol, as seen in Figure 6b. The relative selectivity of methane vs. other alkanes is also increased on addition of base, pointing toward the possible realistic application of coupling the APR reformer with an SOFC.

Economic Benefits of Coupling APR with an SOFC

Based on a combination of Aspen modeling and H₂A analysis, a qualitative assessment of the potential benefits of combining APR of sorbitol with an SOFC was made. These results are summarized in Table 1.

TABLE 1. Potential Benefits of Combining APR of Sorbitol with an SOFC

	70% Sorbitol @ \$0.12/lb	70% Sorbitol @ \$0.30/lb
Fuel Cell Waste Heat	3.06	7.61
Reformate	4.29	10.65

Two conclusions can be drawn from the economic analysis:

- The use of fuel cell waste heat to drive the endothermic APR reaction provides a significant saving on cost of delivered H₂.
- The overall production cost for hydrogen is significantly impacted by the cost of the feedstock.

Conclusions

- We have quantified the effect of the addition of Re to Pt/C catalyst in terms of catalyst activity and selectivity. Re addition increases overall catalyst activity, but at a loss of hydrogen selectivity relative to alkanes.
- Addition of KOH base to an aqueous 10% glycerol feed increases hydrogen productivity modestly with 3%Pt-3%Re/C catalyst, primarily through shutting down the production of light alkanes. However, more liquid products are also seen.
- Residence time is important in glycerol APR with the Pt-Re/C catalysts. Longer residence time increases gas phase products, hydrogen, and methane (relative to light alkanes).
- Hydrogen productivity with sorbitol declines relative to glycerol, primarily because more pathways are available, predominantly via dehydration/hydrogenation pathways. This can be ameliorated by employing longer residence times and adding base to the aqueous feed.

Future Directions

We will focus on the following:

- Catalyst synthesis and characterization, focusing on a number of synthesis variables including support characteristics, metal loading, and pretreatment conditions.
- Long-term testing to assess catalyst life.
- Screen catalysts to identify possible replacements for Re as a promoter for Pt, due to the undesired dehydration selectivity associated with Re addition.
- Explore alternate feedstocks, including less pure sorbitol and the effects of impurities on catalyst performance. Also identify purification needs with the raw feed material, as needed.

FY 2010 Publications and Presentations

1. Ayman M. Karim, Yu Su, Junming sun, Cheng Yang, James J. Strohm, David L. King, Yong Wang. *A Comparative Study between Co and Rh for Steam Reforming of Ethanol*. Applied Catalysis B: Environmental (2010), 96, 441-448.
2. King, David L., Liang Zhang, Gordon Xia, Ayman M. Karim, David J. Heldebrant, Xianqin Wang, Tom Peterson, Yong Wang. *Aqueous phase reforming of glycerol for hydrogen production over Pt-Re supported on carbon*. Applied Catalysis B: Environmental (2010), in press.
3. Ayman M. Karim, Yu Su, Mark Engelhard, David L. King, and Yong Wang. *Catalytic roles of Co and Co²⁺ during steam reforming of ethanol on Co/MgO catalysts*. Submitted to the Journal of Catalysis.
4. Ayman Karim, Yu Su, Junming Sun, Vanessa Lebarbier, James Strohm, David King and Yong Wang. *On the Role of Co⁰ and Co²⁺ in Steam Reforming of Ethanol*. Presented at the 239th meeting of the ACS, San Francisco, March 2010.
5. Liang Zhang, Yong Yang, Gordon Xia, David Heldebrant, David L. King, Yong Wang. *Investigation of Pt-Re Interaction in PtRe/C Catalyst for Production of Hydrogen and Biofuels from Bioliquids*. Oral presentation at the ACS Annual Meeting, Washington, D.C., Aug 2009.
6. Karim AM, J Sun, VMC Lebarbier, Y Su, MH Engelhard, DL King, and Y Wang. *Effect of Cobalt Oxidation State on Ethanol Steam Reforming*. Oral presentation at the Annual meeting of the Pacific Coast Catalysis Society, Seattle, WA, March 2010.
7. Liang Zhang, Yong Yang, Gordon Xia, David Heldebrant, David L. King, Yong Wang. *Pt-Re Interaction in PtRe/C Catalyst under Hydrothermal Environment for Production of Hydrogen and Biofuels through Aqueous Phase Reforming*. Oral presentation at the Annual Meeting of the Pacific Coast Catalysis Society, Seattle, WA, March 2010.
8. Liang Zhang, Ayman Karim, Yong Yang, Gordon Xia, David Heldebrant, David L. King, Yong Wang. *Pt-Re Interaction under Hydrothermal Conditions and Its Effect on Aqueous Phase Reforming Reaction Pathways*. Poster presentation at the Gordon Conference on Catalysis, New London, NH, June 26-July 2, 2010.
9. Liang Zhang, David L. King, Yong Wang, Lawrence F. Allard. *Morphological and Electronic Structure of Pt-Re Nanoparticles Supported on Carbon for Aqueous Phase Reforming of Bioliquids*. Oral presentation at the Microscopy & Microanalysis Annual Meeting, Portland, OR, Aug 2010.