

II.A.1 Biomass-Derived Liquids Distributed (Aqueous Phase) Reforming

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understanding the causes of catalyst deactivation. This improved understanding is aimed at reducing operating costs, which will lower cost of hydrogen production. The following are our technical targets:

- Cost: \$3.80/gge in 2012 and \$3.00 in 2017 (\$3.00/kg H₂)
- Catalyst life: 100 h without loss of selectivity

FY 2011 Accomplishments

- Completed a series of acidity characterization studies with Pt-Re catalysts. Verified that the amount of acid sites as measured by ammonia temperature programmed desorption (NH₃TPD) correlated with the amount of Re added to the catalyst, making clear the role of Re in the generation of acid sites on the catalyst surface.
- Showed the presence of Bronsted acid sites on Pt-Re/SiO₂ catalysts after exposure to water vapor by infrared studies and pyridine adsorption. This sheds more light on the character of the acidity with this particular metal combination.
- A cell was constructed to allow measurements of the Pt-Re/C catalyst under operating conditions in X-ray absorption experiments, to be carried out at the Brookhaven National Laboratory Synchrotron source. Preliminary experiments (not in situ) were carried out, demonstrating operability of the system and indicating areas for upgrading the hardware.
- APR studies of aqueous-soluble bio-oil components were carried out with the Pt-Re/C catalyst. We showed successful reforming of most oxygenated species, but also identified difficulty in reforming acetic acid, which is a component present in significant concentration.
- H2A analysis indicates that the DOE H₂ production target of \$3.00/kg H₂ can be achieved, but only with virtually complete reforming of all the components present in the bio-oil to H₂ and CO₂.

Fiscal Year (FY) 2011 Objectives

- Evaluate and develop bio-derived liquids aqueous phase reforming (APR) technology for hydrogen production, with a specific focus on aqueous-soluble bio-oil, 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, we have been focusing on identifying the specific role of the different catalyst components, delineating the mechanistic pathways leading to desired and undesired products, and



Introduction

The conversion of biomass-derived liquids to hydrogen is attractive because of the near carbon-neutral footprint it provides, and availability of such feedstocks in many regions of the U.S. We have previously targeted sugars and sugar alcohols, along with other polyols such as glycerol, as feedstocks. In FY 2011, we made a transition to bio-oil as a feedstock, specifically water-soluble bio-oil which contains a large fraction of oxygen-containing functionality, but is overall a more complex mixture that can be expected to raise some new challenges. Much of our catalyst development

work in the APR area has focused on understanding the correlation between catalyst function and performance. Our primary catalyst system has comprised Pt-Re/C, which is a highly active catalyst. We continued work with this same catalyst as we changed feedstock.

Approach

For the APR of bio-oil, we used our standard testing conditions of relatively low temperatures (225-265°C) and sufficient pressure (about 30 bar) to maintain the system in the liquid phase. We started by first identifying and assembling a slate of representative components known to be present in the aqueous-soluble bio-oil, and testing them individually for performance. We then combined these individual components into a single feed, and again compared performance, giving us insight into whether there might be interactions between components that could not be predicted from the individual component studies. This would provide us with guidance regarding what kind of modifications might be required for our catalyst.

For catalyst characterization, we focused primarily on identifying and quantifying the acidity that is developed with the Pt-Re/C catalyst, a result of Pt-Re interactions under both reduced and aqueous phase conditions. This provided insights into the nature of the acidity and how to develop approaches to mitigate the effects of this acidity, including the possibility of complete catalyst modification/substitution.

Results

Our original list of representative compounds was selected based on a literature report from the Huber group [1]. This list is provided in Figure 1. Subsequently, we found that furfural and guaiacol, two of the identified components, were insoluble in water at ambient temperature at the concentrations

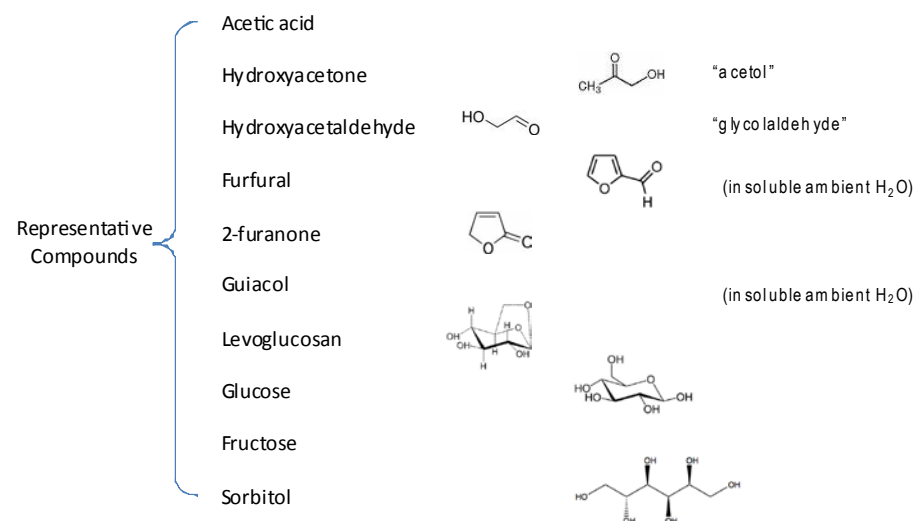


FIGURE 1. Initial List of Representative Compounds for Study of Bio-Oil APR

necessary for APR studies. We later made substitutions for these compounds: furfuryl alcohol for furfural, and p-methoxyphenol for guaiacos, but these two components were not present in our first pass screening studies.

Figure 2 provides a graphical comparison of the performance of the other components under APR testing conditions. Glycerol is added for comparison. Two feedstocks show poor H₂ selectivity (levoglucosan and fructose), and two showed virtually no selectivity (acetic acid and furanone). The poor selectivity of the first two we believe can be improved significantly through an adjustment in reaction conditions to lower flow rates and possibly carrying out the reaction at higher temperature. The performance of the latter two compounds is more problematic. Acetic acid is present in significant concentration, and we must find a way to increase the reactivity of the catalyst system or find an alternate catalyst system to handle acetic acid. Furanone is structurally more difficult in principle since both unsaturation and ring-opening must be contended with, and hydrogen is not initially present to remove the unsaturation. This may be alleviated by co-feeding hydrogen, and we expect furanone and similar molecules may only be tackled effectively by focusing on hydrogenolysis to form methane, rather than relying on catalytic conversions for hydrogen production. Furanone is present at significantly lower concentration than is acetic acid, thus it is only a very minor constituent. However, acetic acid is present at much higher concentrations, pointing to the primary importance in focusing on effective APR of acetic acid.

In Figure 3 we see the effect of acetic acid on the APR of glycerol. Both components were present at 10 wt% in the feed. It can be seen that the addition of acetic acid reduces the conversion of glycerol. Thus, it is not only that acetic acid is unreactive, but that it also inhibits the conversion of other feed molecules, presumably by strongly adsorbing on the catalyst surface and thereby making fewer active catalyst sites available. It can be seen that this is an effect specifically of the acetic acid and is not an effect of general acidity—addition of nitric acid has virtually no apparent effect on either activity or selectivity in the APR of glycerol.

In Figure 4 we show the results of characterization of the Pt-Re/C catalyst for surface acidity by ammonia TPD. This acidity has been responsible for generation of a significant byproduct alcohol and alkane production from glycerol to the detriment of H₂ production. It is clear that the acidity correlates with Re loading, although there is also some acidity present just with Pt/C. However, this acid strength

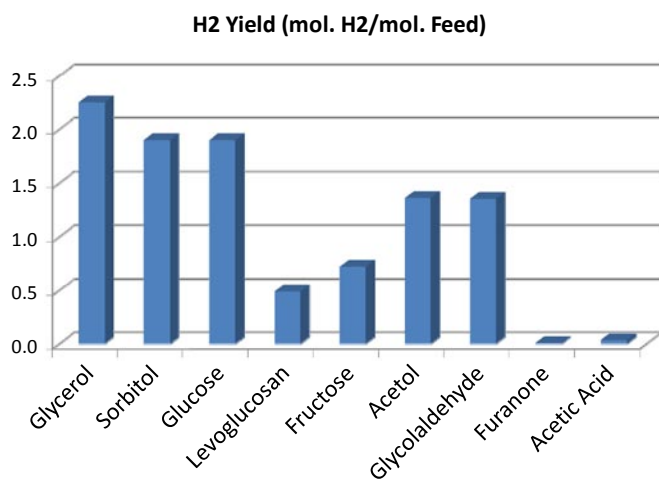


FIGURE 2. H₂ selectivity from the APR of representative bio-oil compounds with Pt-Re/C catalyst. Conditions: 225°C, 420 psig, 0.1 mL/min flow rate, all feeds present at the same molar concentration.

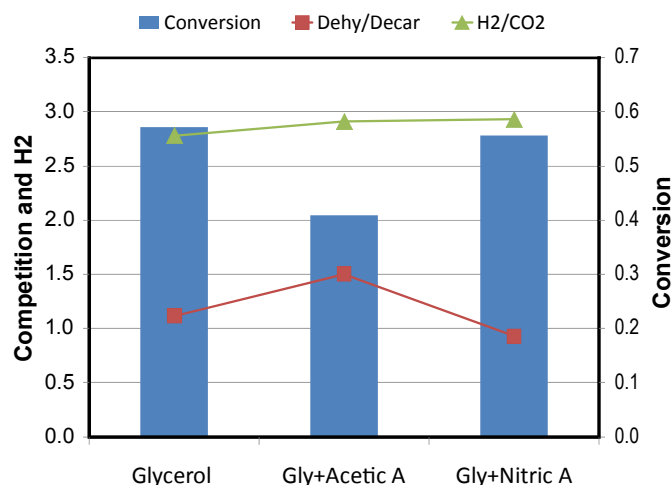


FIGURE 3. Effect of Acetic Acid and Dilute Nitric Acid on the APR of Glycerol with Pt-Re/C

(evidenced by a lower temperature peak) is significantly less than that obtained with the Pt-Re system. Finding methods to decrease or obviate this acidity is important to improve H₂ selectivity in APR. It is interesting to note that despite the surface acidity generated on the catalyst surface by Re, this is not sufficient to repel acetic acid, so that the acetic acid maintains an inhibitory effect on catalyst performance. This points to the possibility of the acid sites being distinct and different from the metal sites present on the catalyst.

Conclusions and Future Directions

We have shifted feedstocks this FY from glycerol and sorbitol to aqueous fraction bio-oil. This shift was necessitated in order to work with cheaper biomass-derived

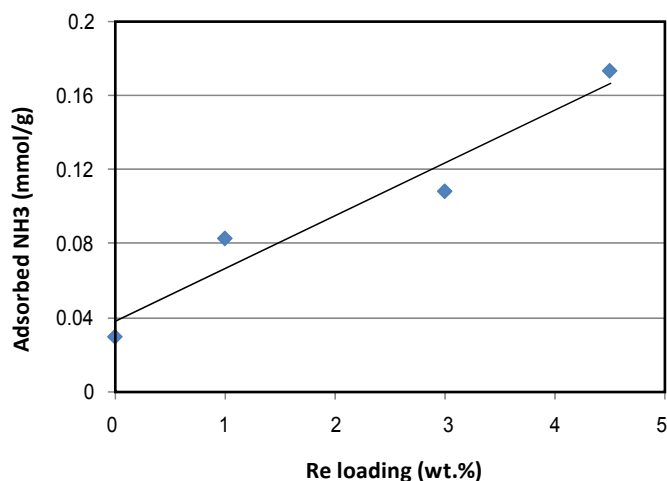


FIGURE 4. Correlation between Re Loading and Total Catalyst Surface Acidity as Measured by TPD of Ammonia

feedstocks that had a greater probability to meet the DOE target of \$3.00/gge in 2017. We developed a slate of representative bio-oil components and found that there are some significant challenges with this new feedstock, notably the low activity and apparent poisoning effect of acetic acid. In FY 2012, we will focus especially on catalyst development in order to improve the reactivity of bio-oil, especially dealing with the presence of acetic acid. One strategy that we intend to investigate is to increase the C-C bond breaking activity of our catalyst, for example by adding Ru to Pt/C, as well as evaluating alternate supports. One possibility is that in order to increase C-C cleavage activity we may also increase hydrogenolysis, leading to greater methane co-production. This might require co-feeding hydrogen. We believe that this may not be a negative outcome, since it will be possible to steam reform by-product methane (at higher temperature) using known technology. Such an approach would of course have to still meet the H₂ production cost targets, which will require H₂A analysis and verification.

FY 2011 Publications/Presentations

Publications

1. Ayman M. Karim, Yu Su, Mark H. Engelhard, David L. King, and Yong Wang. Catalytic Roles of Co⁰ and Co²⁺ during Steam Reforming of Ethanol on Co/MgO Catalysts. *ACS Catal.*, 2011, 1, 279–286.
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), 99, 206-215.
3. 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.

Presentations

1. David L. King, Liang Zhang, Ayman Karim, Yong Wang, Acidity of Bimetallic Catalyst under Hydrothermal Environment in Aqueous Phase Reforming of Bioliquids, presented at the 241st meeting of the American Chemical Society, Anaheim, CA March 2011.
2. Zhang L, AM Karim, G Xia, Y Yang, DJ Heldebrant, DL King, and Y Wang. Roles of Re in Pt-Re/C Catalysts for Production of Hydrogen through Aqueous Phase Reforming, presented at the Pacificchem, Honolulu, Dec. 2010.
3. Zhang L, AM Karim, G Xia, Y Yang, DJ Heldebrant, DL King, and Y Wang. Pt-Re Interaction in Pt-Re/C Catalysts under Hydrothermal Environment for Production of Hydrogen and Biofuels through Aqueous Phase Reforming, presented at the 240th ACS Meeting in Boston, MA, August 2010.
4. 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.
5. 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 orally at the 239th meeting of the American Chemical Society, San Francisco, CA, March 2010.
6. 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.
7. 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.
8. 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.
9. Liang Zhang, Ayman Karim, David L. King, Yong Wang. Pt-Re Interaction under Hydrothermal Environment in Aqueous Phase Reforming of Bioliquids for Hydrogen Production. Oral presentation at the AIChE Annual Meeting, Salt Lake City, UT, Nov.10, 2010.
10. Karim AM, Y Su, MH Engelhard, DL King, and Y Wang. In-situ XPS Analysis of Co and Co²⁺ During Steam Reforming of Ethanol on Supported Cobalt Catalysts, poster, 57th AVS National Symposium & Exhibition, Albuquerque, NM, October 2010.

References

1. T.P. Vispute and G. W. Huber, Green Chem., 2009, 11, 1433–1445.