IV.A.6 Production of Hydrogen by Biomass Reforming

David L. King (Primary Contact), Yong Wang, James Cao, Gordon Xia, Hyun-Seog Roh,
and Alexander Platon
Pacific Northwest National Laboratory
P.O. Box 999
Richland, WA 99354
Phone: (509) 375-3908; Fax: (509) 375-2186; E-mail: david.king@pnl.gov

DOE Technology Development Manager: Mark Paster
Phone: (202) 586-2821; Fax: (202) 586-9811; E-mail: Mark.Paster@ee.doe.gov

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Objectives

The objective is to develop a cost effective and feedstock flexible technology for the conversion of biomass feedstocks to hydrogen that meets the DOE cost targets. Target feedstocks include:

- Ethanol
- Sugar, sugar alcohols (xylitol, sorbitol, glucose)
- Less refined starting materials such as cellulose, hemicellulose

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. Fuel Processor Capital Costs
- D. Feedstock Issues
- E. Carbon Dioxide Emissions

Technical Targets

The goal of this project is to develop a cost effective and feedstock flexible technology for reforming of biomass feedstocks. The synergistic improvement in reforming catalysts and reaction engineering will help the reforming technology development that meets the following DOE 2010 targets for distributed production of hydrogen from bio-derived renewable liquids:

- Cost: $3.60/gge
- Total Energy Efficiency: 66%

Approach

Aqueous phase reforming

- Prepare candidate catalysts identified from high throughput screening and other leads.
- Construct fixed bed and slurry batch reactors to measure activity and product selectivity of most promising catalyst systems.
- Compare catalyst performance in fixed bed and batch reactors.

- Develop feedstock structure/reactivity relationships.
- Determine catalyst life and stability.
- Determine potential benefits of microchannel reactors and select best reactor technology.

Ethanol reforming

- Optimize catalyst compositions, supports, and pretreatment to reduce the selectivity to methane while improving the activity.
- Identify the potential challenges associated with low temperature reforming, and develop relevant strategies by synergistically improving catalyst, reaction engineering, and process conditions.
- Determine catalyst life and stability.
- Evaluate the potential advantages of novel reaction engineering, i.e., microchannel reactor, for process intensification.

Accomplishments

- Hydrogen productivity as high as 141 l H_2/l catalyst/hr was achieved with a more concentrated sorbitol feed (10%) and at a higher temperature of 265°C using a baseline 3% Pt/Al_2O_3 catalyst. It was also found that higher feed concentration and temperature slightly lowers the hydrogen selectivity.
- It was discovered that some reaction intermediates from aqueous phase sorbitol reforming are significantly more active and show higher hydrogen selectivity than sorbitol itself. Thus, hydrogen productivity can be improved by a factor of 2.5 if sorbitol can first be selectively converted to glycerol or propylene glycol.
- Comparison of fixed bed vs. slurry batch reactor tests were conducted which suggests the importance of a reaction engineering component in selecting and optimizing the reactor configuration for aqueous phase reforming.
- A highly active and selective Rh/CeO_2-ZrO_2 ethanol steam reforming catalyst was developed as demonstrated by high conversion and below equilibrium methane selectivity at a gas hourly space velocity (GHSV) >100,000 hr^{-1} and a low temperature of 350°C.
- It was discovered that this active and selective Rh-based lower temperature ethanol steam reforming exhibits relatively rapid catalyst deactivation. Additional effort is needed to better understand the deactivation mechanism and to develop strategies to mitigate the catalyst deactivation problem including catalyst modification and operating conditions.

Future Directions

Aqueous phase reformation

- Develop a structure-reactivity relationship to evaluate potential advantages of converting sorbitol to more active and selective intermediates.
- Explore approaches to directly use glucose rather than sorbitol as a feed.
- Explore less pure feedstocks such as hemicellulose.
- Evaluate best reactor types to minimize heat and mass transfer effects.

Ethanol reformation

- Continue catalyst development for improved longevity (>100h at steady state performance).
- Evaluate and compare ethanol reforming in both vapor and aqueous phases for reactor productivity and catalyst longevity.
- Develop novel reaction engineering to improve thermal efficiency and to potentially integrate with the water gas shift (WGS) step.

Introduction

Biomass-derived feedstocks that can potentially be converted into hydrogen include ethanol, sugars, sugar alcohols, polyols, and less refined hemicellulose or cellulose. Catalytic conversion of these biomass feedstocks provides a means for hydrogen production through a renewable source. In general, the feedstocks with larger size molecules such as sugar or sugar alcohols are less thermally stable and more amenable to low temperature aqueous phase reforming. Ethanol, on the other hand, is thermally more stable and may take the advantage of reforming in a gas phase that allows higher space time yield due to the use of more concentrated feedstocks and relatively higher reforming temperatures. Because of the relatively high cost of biomass feedstocks compared to fossil fuels, biomass conversion processes must be highly efficient in terms of high productivity and hydrogen selectivity. The major objective of this project is to research the options of aqueous and gas phase reforming and develop feedstock flexible reformers for distributed hydrogen production. These efforts will lead to the improvement in hydrogen productivity and selectivity and allow potential reduction of unit operation steps, which will help reduce the capital and operational costs and meet DOE 2010 cost targets for distributed hydrogen production.

Approach

For aqueous reforming, our approach has been to identify the most active catalysts and best reactor design for hydrogen production from a potentially cheap feedstock, sorbitol. We are currently using high purity sorbitol, but envision moving to a less purified stream in the future, once the basic conversion chemistry is understood. Analytical capabilities and test reactors were developed for catalyst screening (batch reactor) and continuous operation (fixed bed reactor). Catalyst performance was compared in both fixed bed and slurry type reactors to provide insight into the importance of transport phenomena on hydrogen productivity and selectivity. To gain more valuable information on the role of chemical structure of the starting material (for example number and proximity of C-OH groups) on reaction rate and hydrogen selectivity, we have also explored the performance of one typical catalyst,

Pt/Al_2O_3, toward related polyols that might be present either by intentional addition as starting materials or as plausible reaction intermediates. We have also carried out catalyst development work analyzing the effect of various catalyst supports as well as metal composition and concentration to improve hydrogen productivity.

For vapor phase steam reforming of ethanol, our approach has been to develop active and selective low temperature reforming catalysts which could facilitate efficient integration with the WGS reaction and membrane separation. Since methane formation is thermodynamically favored at low temperatures, the focus of catalyst development has been on achieving lower than equilibrium methane selectivity with Rh supported on metal oxides with high oxygen storage capacity such as zirconia-promoted CeO_2. Metal support interactions were also studied to reduce methane selectivity and to improve hydrogen selectivity. We also attempted to identify the potential challenges associated with low temperature reforming, and develop relevant strategies by synergistically improving catalyst, reaction engineering, and process conditions.

Results

In FY 2004, a combinatorial tool was used to screen a wide range of catalyst formulations so that candidate catalysts for aqueous phase reforming of xylitol can be identified. The combinatorial equipment was not designed for monitoring of gas phase products, nor was the system capable of operation above 200°C. It is, therefore, difficult to evaluate catalyst selectivities and long-term stabilities, as the data obtained primarily provided catalyst activity for xylitol conversion. For the next phase of work, we constructed both a batch reactor and a flow reactor test system at the beginning of FY 2005. Both reactor systems allow complete gas and liquid product analysis. The batch reactor system was set up to provide a quicker turn around on catalyst evaluation. It also allows us to evaluate the effects of mass transfer and back mixing on the hydrogen productivity and selectivity, and provides performance comparison with fixed bed and (future planned) microchannel reactors.

A 10 wt% sorbitol aqueous solution was chosen as the feed for the catalyst evaluations. Sorbitol was selected in concordance with DOE programmatic objectives. It can be readily obtained with >90% selectivity from glucose hydrogenation and does not have the homogeneous thermal degradation issues associated with glucose, thus allowing for detailed catalyst and reaction engineering evaluations. Pt/alumina is one of three promising catalysts identified from the combinatorial screening, and is also the most suitable catalyst for sorbitol conversion as reported by Dumesic's group in open literature [1]. It was therefore used for the shakedown tests in both flow and batch reactors. Under similar reaction conditions, a 3%Pt/alumina catalyst prepared in our laboratory matches the best performance published by Dumesic et al. [2] on the similar catalyst in a flow reactor (see Table 1) at both 225 and 265°C. A 10 wt% feed concentration was used in our studies vs. 1 wt% in Dumesic's work, but it has been reported that hydrogen productivity is insensitive to the sorbitol feed concentration. As also seen in Table 1, a hydrogen productivity as high as of 141 l H_2/l catalyst/hr was achieved with a more concentrated sorbitol feed (10%) and at a higher temperature of 265°C. These results validated our testing and analytic protocols, and allow for further catalyst and reaction engineering studies. To further study the effects of mass transport on hydrogen selectivity, the performance of sorbitol conversion in both a fixed bed reactor and a batch reactor was compared on the 3%Pt/alumina catalyst. A lower hydrogen productivity and selectivity was observed in the fixed bed reactor where backmixing could be an issue.

Table 1. Aqueous Phase Reforming of Sorbitol in Continuous Plug Flow Reactor

	Run #1	**Literature**	**Run #2**	**Literature**	**Run #3**
Catalyt	3%Pt/Al$_2$O$_3$	3%Pt/Al$_2$O$_3$	3%Pt/Al$_2$O$_3$	3%Pt/Al$_2$O$_3$	3%Pt/Al$_2$O$_3$
Liquid feed	10% Sorbitol	1% Sorbitol	10% Sorbitol	1% Sorbitol	10% Sorbitol
T	225	225	265	265	225
P	471	425	835	812	475
WHSV (gSorbitol/gcat/hr)	0.08	0.008	0.08	0.008	0.14
Contact time (min)	70	94	70	94	42
Sorbitol Conversion	88.3%		99.88%		74.2%
% Carbon in gas-phase effluent	58.3%	61.0%	95,7%	90.0%	40.6%
% Carbon in liquid-phase effluent	41.7%	39.0%	4.3%	12.0%	59.4%
H$_2$ productivity (l/l catalyst/hr)	91.3		140.9		86.0
Gas Phase composition (mol%)					
H$_2$	58.9%	61.0%	57.0%	54.0%	49.2%
CO$_2$	35.5%	35.5%	33.8%	36.0%	47.9%
C$_2$	0.9%	0.7%	2.2%	2.3%	0.7%
CH$_4$	4.7%	2.5%	7.2%	6.0%	2.2%
H$_2$/CO$_2$	1.66	1.74	1.69	1.50	1.03
H$_2$ selectivity	64.8%	66.0%	58.3%	46.0%	44.1%
Alkane selectivity	15.4%	15.0%	25.2%	32.0%	7.0%
H$_2$/CH$_4$	12.5	24.4	8.1	9.0	22.8

Primary liquid phase product include: propylene glycol, glycerol, ethanol, ethylene glycol, butane-diols, propanols

This result indicates that reaction engineering may play an important role in improving hydrogen productivity and selectivity.

Based on studies of hydrothermal stability of catalyst supports, alumina supports are unlikely to demonstrate required stability over extended periods of operation in the aqueous phase, whereas carbon and titania (rutile phase) should have the requisite stability. These two supports, in combination with the two active metals Pt and Ru identified from the combinatorial screening effort, were further evaluated in the batch runs and the results are summarized in Table 2.

Table 2. Batch Reactor Catalyst Screening

Catalyst	5% Ru/Tio$_2$	5% Pt/C	3% Pt/Al$_2$O$_3$
Gas Product (mmol)	60.68	117.56	48.55
H$_2$ Selectivity	23.7%	16.85%	39.39%
Alkane Selectivity	17.8%	19.91%	9.08%
H$_2$/CO$_2$	0.68	0.46	0.94

Both Pt/C and Ru/TiO$_2$ show higher gas productivity than 3%Pt/alumina, but they also show higher selectivities to alkanes and lower H$_2$/CO$_2$ ratios. This is not surprising for Ru based catalysts since Ru is known to be active for CO methanation. The poor selectivities with Pt/C catalyst are likely due to the presence of microporosity in the carbon support, leading to more severe internal mass transfer limitations and facilitating the sequential methanation reactions. Further catalyst improvement will be conducted in modifying Ru selectivity to decrease methanation, increasing Pt activity with promoters, and evaluating carbon supports with greater macroporosity and less internal mass transfer limitations.

In the course of investigating catalyst and support effects, we analyzed the products of reaction from sorbitol aqueous phase reformation. We detected a number of polyol-containing species at various concentrations in the product at relatively low conversion of sorbitol. This included C$_3$ species such as propylene glycol, 1,3 propanediol, and glycerol. To further understand how these intermediates affect the hydrogen productivity and selectivity in sorbitol conversion, we performed further tests on the reactivity of individual C$_3$ species. Sorbitol and ethanol were also included for comparison purposes. The tests were conducted on the 3%Pt/alumina catalyst because of its good performance and the wealth of data accumulated while we continue to investigate alternate supports with better hydrothermal stability. As shown in Figure 1, the rate of conversion as well as selectivity toward hydrogen was different for each of these species. Specifically, the rates of conversion of propylene glycol, 1,3-propanediol, and glycerol were all faster than the rate of conversion of the parent sorbitol molecule. The hydrogen productivity from propylene glycol and glycerol was more than a factor of 2 higher than the parent sorbitol. Ethanol, 1-propanol, and 1,3 propanediol on the other hand exhibited higher selectivity to alkanes than did sorbitol. The importance of understanding the relative reactivity of species such as the C$_3$ polyols described above is that it may prove useful to carry out an intentional pre-hydrogenolysis of sorbitol to smaller chain polyols such as propylene glycol and glycerol, which would have higher reactivity for the aqueous phase reforming reaction and selectivity to hydrogen than sorbitol. Although there will be a higher process cost to carry out a hydrogenation step, there is no net loss of hydrogen and ultimately a gain if the selectivity from aqueous phase reforming of the smaller molecules toward hydrogen is greater.

The objective of ethanol steam reforming is to develop highly active and selective ethanol steam reforming catalysts and the enabling reactor technology so that the ethanol reforming can be conducted at low temperatures (<500ºC). In FY 2004, we evaluated the effects of metal and support on ethanol steam reforming, and identified Rh/CeO$_2$-ZrO$_2$ as a potential candidate for low temperature ethanol steam reforming (<500ºC). In early FY 2005, the metal loading, Ce/Zr ratio and pretreatment conditions of the Rh/CeO$_2$-ZrO$_2$ catalysts were studied. The aim was to increase the interaction between CeO$_2$ and Rh, so that (under a postulated reaction mechanism) the oxygen atom provided by the ceria is efficiently supplied to CH$_3$ radical after C-C cleavage, facilitating its conversion to hydrogen and CO. It was demonstrated that a Ce/Zr ratio of 4 and the CeO$_2$-ZrO$_2$ support as-
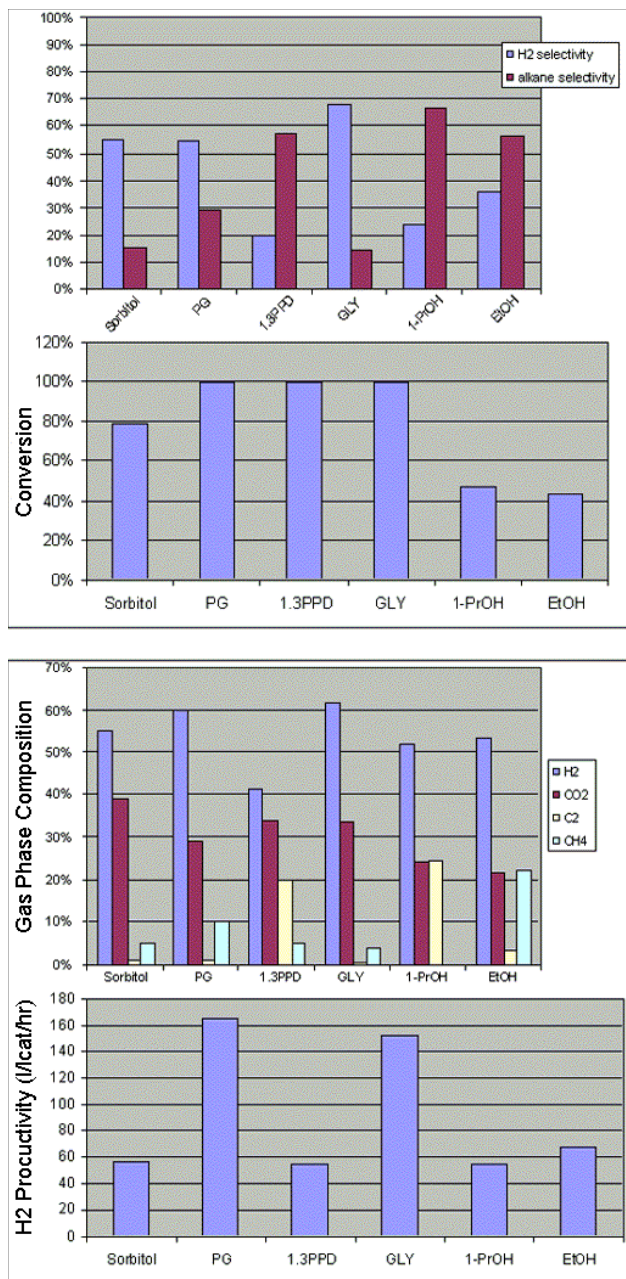
Figure 1. Reactivity of Sorbitol and C_3 Feedstocks Over 3% Pt/Al$_2$O$_3$ Catalyst

synthesized without calcination prior to Rh impregnation gave complete ethanol conversion at a high weight hourly space velocity (WHSV; about 100,000 cc/g cat/hr) and exhibited higher than equilibrium hydrogen yield at 450ºC (see Table 3). The same catalyst also showed stable catalyst performance as evidenced by stable hydrogen productivity over a time on stream of about 1,000 minutes as shown in Figure 2 (legend "500/AS"

Table 3. Comparison of Product Yelds at 450°C

	Y_{H2}	Y_{CH4}	Y_{CO}	Y_{CO2}
1%Rh/Ce-ZrO$_2$	3.50	0.63	0.33	1.05
Thermodynamic equilibrium	2.40	0.89	0.05	1.06
1%Rh/Al$_2$O$_3$	1.17	0.06	0.48	0.03

Reaction conditions:
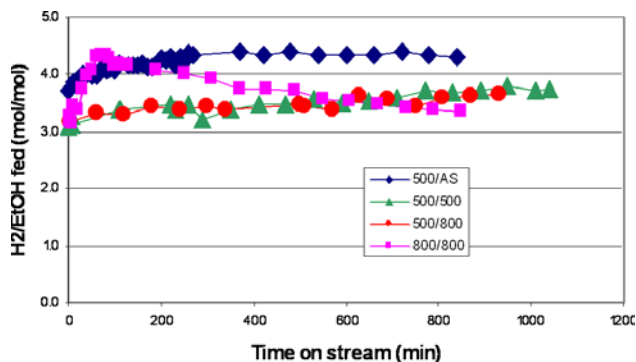WHSV = 85,320 cm3/gh, H2O/EtOH/N2 = 8.0/1.0/3.5

Figure 2. Effect of Calcination Temperature on Hydrogen Yield at 450ºC

denotes the CeO$_2$-ZrO$_2$ support was synthesized as-is without calcination, and the catalyst after impregnating with Rh was finally calcined at 500ºC). However, true stability of the catalyst is not easily determined if conversion of ethanol is 100%, because excess catalyst activity may be present to mask any deactivation actually occurring.

Ethanol steam reforming can be carried out under high temperature conditions similar to that of methane steam reforming, which is energy intensive. However, our approach is to carry out the reforming at low temperatures, which is less energy intensive and is compatible with integration with a membrane. Since there is a C-C bond in ethanol, ethanol steam reforming faces an additional challenge of coke formation compared to methane steam reforming. To further evaluate the performance of the Rh/CeO$_2$-ZrO$_2$ catalyst, experiments were conducted at temperatures as low as 350°C and at a fairly high WHSV (480,000 cc/hr/g-cat) where initial conversion was below 100%. As shown in Figure 3, catalysts rapidly deactivated under these conditions, probably due to the formation of an ethylene intermediate that is a coke precursor. It was found

that the addition of alkali metals such as potassium decreases the deactivation rate but at the cost of a simultaneous decrease in the catalyst activity. This is exemplified in Figure 3, where one of the catalysts was prepared by impregnating 5% K on a CeO_2-ZrO_2 support before dispersing Rh, and it shows distinctly different behavior compared with potassium-free catalysts. Such a lower activity is likely due to poorer Rh dispersion as measured by hydrogen chemisorption measurement (see Table 4).

Table 4. Metal Dispersion of Rh/CeO_2-ZrO_2 Catalysts promoted with K

Material	% disp
2%Rh/Ce0.8Zr0.202 500/500	54.9
0.5%K/2%Rh/Ce0.8Zr0.202 500/500	42.4
2%Rh/K-Ce0.8Zr0.202 500/500	7.2

Further effort is focused on improving catalyst stability as affected by coke formation as well as catalyst activity by optimizing the alkali and metal dispersions.

In addition to catalyst development, a novel reaction engineering approach was attempted to improve heat transfer and thermal efficiency since ethanol steam reforming is highly endothermic. Specifically, integration of combustion and reformer was attempted in a microchannel reactor based on the guidance from flow sheet calculations that higher
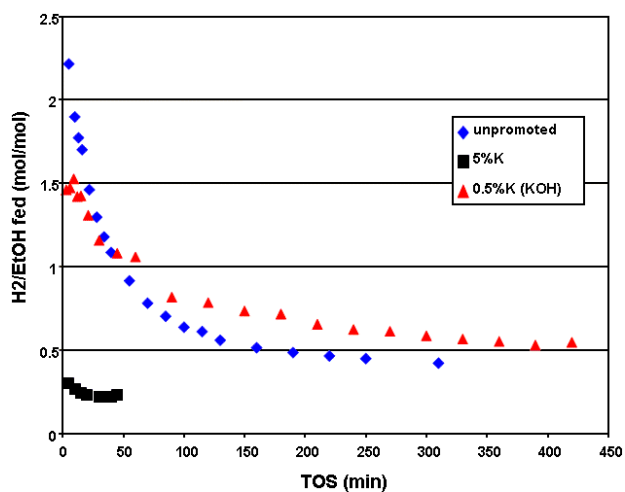
thermal efficiency could be achieved. To demonstrate the operation of integrated combustion with reforming, a first generation microchannel reactor with integrated catalytic combustion, reformer, and vaporizers was fabricated as shown in Figure 4 and was successfully tested. This first single-channel device for ethanol steam reforming has dimensions of ~5" by ~1" by ~0.6" and is constructed from stainless steel shims by diffusion bonding and welding. A power output of up to 40 We (power density of up 0.6 We/cc) was demonstrated (Figure 4). The major area needs for improvement from the first generation of
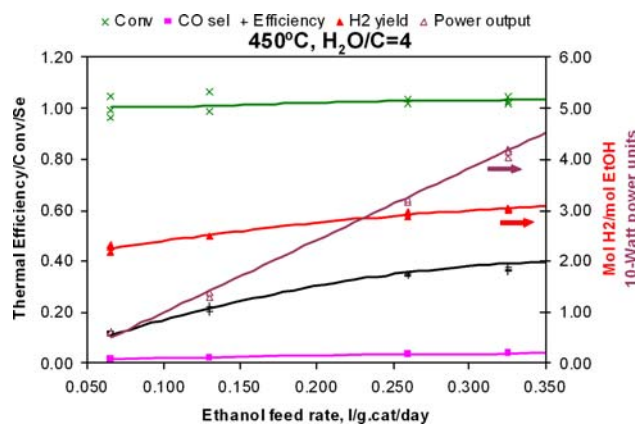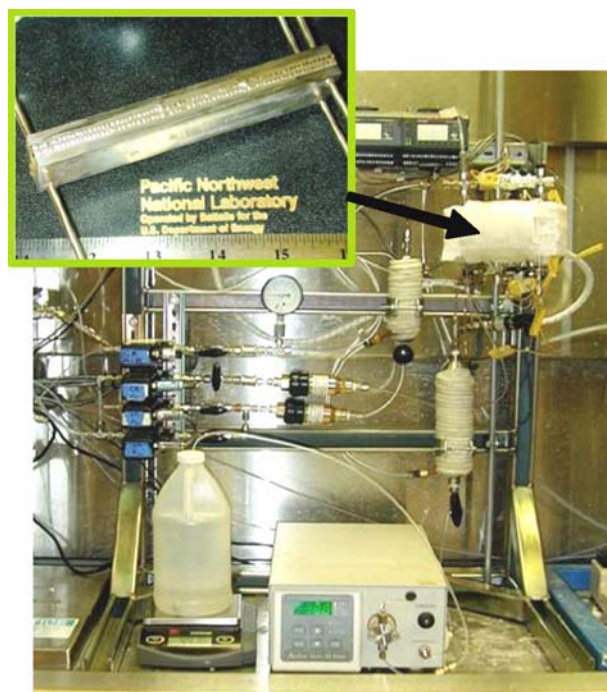

Figure 3. Ethanol Steam Reforming Activity at 350ºC, Steam/Ethanol=8, WHSV=480,000 cc/hr/g-cat

Figure 4. Preliminary Results from a Microchannel Reactor Test

microchannel reactor is to increase the lower than expected thermal efficiency, which may be due to thermal loss to the environment at a small scale, inefficient recuperation of the heat in the reformate, the high steam/carbon ratio used, and a large temperature gradient within the catalyst bed.

Conclusions

The following conclusions can be made for both aqueous phase and vapor phase reforming activities:

Aqueous phase reforming

- An increase in hydrogen productivity is observed at higher temperatures and with concentrated feedstocks at expense of hydrogen selectivity.
- C_3 reaction intermediates show higher product selectivity and hydrogen productivity compared with sorbitol, suggesting a possible approach involving pre-hydrogenolysis of sorbitol.
- Comparison of product selectivity from fixed bed vs. slurry batch reactor tests suggests the importance of a reactor engineering component.
- Microchannel technology is one potential approach to providing the necessary improvement in heat and mass transfer.

Ethanol reforming

- A Rh/CeO_2-ZrO_2 catalyst is active and selective toward hydrogen production at temperatures at or below $450^\circ C$.
- Low temperature methane selectivity is avoided (counter to thermodynamics) but catalyst deactivation is observed.
- Further catalyst development is necessary and ongoing.
- Novel reaction engineering provides the potential for efficient integration of unit operations.

FY 2005 Publications

1. H. Roh, Y. Wang, D. L. King, "Highly selective and active Rh based catalysts for ethanol steam reforming", to be submitted to *Topics in Catalysis* (invited publication)

2. H. Roh, Y. Wang, D. L. King, "Selective Production of H2 from Bio-Ethanol at Low Temperatures Over Rh/CeO_2-ZrO_2 Catalysts", Proc. of the 19th North American Catalysis Society Meeting, 2005 (in press).

3. H. Roh, D. L. King, and Y. Wang, "Hydrogen Production from Biomass Feedstocks", *Prepr. - Am. Chem. Soc., Div. Pet. Chem.*, 49 [2] 912-913 (2004).

FY 2005 Presentations

1. H. Roh, Y. Wang, D. L. King, "Hydrogen Production from Biomass", 228th ACS Meeting, Philadelphia, Aug. 22-26, 2004

2. D. L. King, "Bio-derived Liquid Reforming", presented to Hydrogen Production Tech Team, Jan. 13, 2005, NREL.

3. Y. Wang, H. Roh, A. Platon, D. L. King, "Selective Production of Hydrogen from Bio-Ethanol at Low Temperatures Over Rh/CeO_2-ZrO_2 Catalysts," accepted for oral presentation in 19th North American Catalysis Society Meeting, Philadelphia, May 21-25, 2005.

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1. R. R. Davda, J. W. Shabaker, G. W. Huber, R. D. Cortright, J. A. Dumesic. Appl.Catal. B: Enrironmental, 56 (2005) 171-186.

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