II.A.7 Hydrogen Production from Biomass Reformation

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Objectives

- Develop a cost-effective and feedstock flexible method for the conversion of biomass feedstocks to hydrogen that meets the DOE cost targets. Target feedstocks include:
  - Ethanol
  - Sugars, sugar alcohols (xylitol, sorbitol, glucose)
  - Less refined starting materials such as cellulose, hemicellulose
- Provide technical and economic comparison with alternate biomass conversion approaches.

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:

- F. Feedstock Cost and Availability
- G. Efficiency of Gasification, Pyrolysis and Reforming Technology

Approach

- Aqueous phase gasification
  - Select xylitol as model feedstock that is difficult to steam reform.
  - Evaluate catalyst candidates via combinatorial/high throughput screening approach.
  - Maximize activity toward useful gas phase products: syngas plus hydrocarbons.
  - Select best catalysts for further reactor studies.
- Microchannel steam reforming
  - Develop catalysts for the efficient steam reforming of ethanol.
  - Demonstrate advantage of microchannel vs. conventional steam reforming of ethanol.
  - Evaluate the feasibility of integrating water gas shift with ethanol steam reforming in microchannel reactors to improve the hydrogen space time yields.

Accomplishments

- Carried out two combinatorial screening runs to identify most active catalysts for the aqueous phase reformation of xylitol. Each combinatorial run comprised 96 separate catalytic tests, which included duplicates and “blank experiments” with no catalysts. Significant differences in catalysts were observed and quantified. Identified Ru as the most active catalyst and titania-rutile as the most active support.

- Evaluated the effects of metals and supports on the activity and selectivity of ethanol steam reforming. A CeO_2-ZrO_2 support favors selectivity to hydrogen while avoiding ethylene formation. Addition of Pt to a Rh catalyst supported on CeO_2-ZrO_2 showed higher CH_4 and CO_2 selectivity. Minimization of methane formation while achieving significantly high activity towards ethanol steam reforming at low temperature was identified as a major challenge in reforming ethanol.
- Demonstrated that H_2 productivity at low temperatures can be enhanced using a microchannel reactor due to efficient heat transfer.

Future Directions

- Test Ru/TiO_2 and other catalysts identified from combinatorial screening experiments for xylitol conversion in slurry and fixed bed reactors. Evaluate activity, activity maintenance, and gas phase product selectivity.
- Continue microchannel steam reforming studies of ethanol with a focus on minimizing CH_4 product.
- Demonstrate combined process incorporating aqueous phase reforming with secondary microchannel reforming to maximize H_2 productivity from sugars and sugar alcohols.

Introduction

Catalytic conversion of biomass feedstocks such as sugars and alcohols provides a means for production of hydrogen through a renewable source. Because of the relatively high cost of biomass compared to fossil fuels, biomass conversion processes must be highly efficient, requiring high reactor productivity and high product selectivity. Biomass feedstocks tend to form carbonaceous residues during their conversion to gaseous products, leading to a reduction in hydrogen yield.

Aqueous phase reformation (gasification) and moderate temperature steam reforming provide alternatives to conventional high temperature gasification and pyrolysis approaches for the production of hydrogen from biomass. Aqueous phase reforming allows a broad range of biomass feedstocks to be processed, but in order to obtain high productivity, the selectivity toward hydrogen may be compromised. Conventional fixed bed steam reforming is an effective approach to hydrogen production but is limited in feedstock choice due to the difficulty in volatilizing sugars, sugar alcohols, and other biomass products. The combination of these two technologies could provide a novel approach to high productivity and hydrogen selectivity.

Approach

For aqueous phase gasification, our approach has been to identify the most active catalysts for the conversion of xylitol (a representative feedstock) to gaseous products. These gaseous products, which could contain large quantities of methane and higher hydrocarbons as well as hydrogen, will be converted by a second stage microchannel steam reforming reactor operating at elevated temperatures to provide a high hydrogen content synthesis gas. Catalyst activity and reactor productivity are potential concerns in aqueous reforming due to the relatively low temperatures of conversion (<275°C). In order to accelerate the discovery of high activity catalysts, our approach was to carry out preliminary experiments using a combinatorial synthesis-high throughput screening apparatus. These experiments determined activity by loss of starting material, without separate analysis of the gas phase product composition.

For the microchannel steam reformer work, studies have focused on the ability to produce hydrogen in high yield from ethanol, a candidate feedstock that could benefit from a high activity steam reforming approach. These feedstocks are readily available in low cost and can in principle be reformed at relatively low temperatures (by steam reforming standards: ~400°C). However, selectivity to the desired H_2 and CO can be compromised by the formation of methane, which would require higher

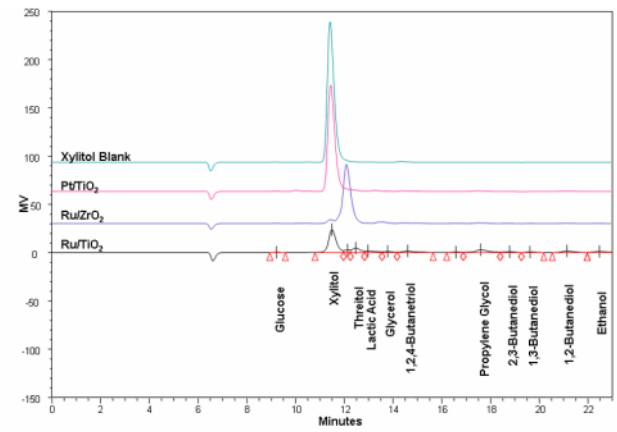

Figure 1. High-Throughput Screening Tests Showing the Effect of Catalytic Metal and Catalyst Support on Xylitol Conversion

temperatures for its reformation. The approach has been to identify conditions and catalysts that can maximize hydrogen production and minimize methane formation.

Results

For the aqueous phase gasification catalyst screening, two sets of 96 experiments were carried out via high throughput synthesis and screening. Several of the experiments within the set of 96 were duplicates or blanks without catalyst. The second set of 96 experiments explored additional variables and provided verification of initial round results. The primary variables were the active catalytic metal; the support; and whether the solution pH was acidic, basic, or neutral. All experiments employed a 5 wt.% concentration of xylitol in water, 5 wt.% catalyst charge of catalyst relative to solution, and 3 wt.% loading of metal on the support. Experiment duration was 4 hours at 200°C. Table 1 summarizes a small subset of the data, highlighting important results and differences among catalytic materials. Figure 1 shows the chromatographic traces of 4 of those experiments, demonstrating more clearly the activity and selectivity differences that can be observed for different combinations of metal and support. The top trace is the xylitol blank. By comparison, it can be seen that the Pt/TiO_2 sample shows relatively low conversion, whereas Ru/TiO_2 shows significant xylitol conversion. By changing the Ru support from TiO_2 to ZrO_2, the xylitol appears to convert to an alternate product, identified as an ether product formed by cyclization of the xylitol with loss of water. This illustrates that the support as well as the metal is important in dictating final products.

Steam reforming studies of ethanol focused on the identification of highly active and selective steam reforming catalysts and the demonstration of the advantages of microchannel reactors over conventional micro fixed bed reactors. A thorough literature search of the ethanol steam reforming literature indicates that the Rh based catalysts are most active, and ethanol steam reforming mechanisms are complex (1-4). Therefore, Rh based catalysts modified by promoters on various supports were initially targeted for the catalyst development effort. Supported Rh catalysts can achieve nearly 100% ethanol conversion at 450°C at a weight hourly space velocity (WHSV) of 85,320 cc/g cat/hr (Table 2). It was observed that the support has a significant effect on the product distribution in the temperature range between 350 and 550°C. Ethylene formation

Table 1. High Throughput Screening Test Results for Xylitol Conversion

Support	Metal	pH	Xylitol Conversion %	Selectivity to gas phase products, %
TiO_2	Ru	neutral	82.2	100.0
TiO_2	Ru	neutral	82.9	98.3
ZrO_2	Ru	neutral	97.4	48.7
SiO_2	Ru	neutran	51.0	68.7
SiO_2	Ru	basic	60.2	68.0
SiO_2	Ru	acidic	50.1	64.5
Carbon	Ru	neutral	49.2	100.0
TiO_2	Pt	neutral	2.2	100.0
SiO_2	Pt	neutral	44.2	41.8
SiO_2	Pt	basic	46.4	54.2
SiO_2	Pt	acidic	43.8	60.7
TiO_2	Rh	neutral	22.8	82.9
ZrO_2	Au	neutral	72.4	21.5
SiO_2	Pd	acidic	35.4	40.2

Table 2. Comparison of Catalyst Activity and Selectivity at 450°C, WHSV = 85,320 cc/g cat/hr, H_2O/EtOH/N_2 = 8.0/1.0/3.5

	1% Rh/$CeZrO_2$	1% Rh/MgO-Al_2O_3	1% Rh/Al_2O_3
Conversion, %	100	74	98
CH_4 selectivity, %	31	29	3
CO_2 selectivity, %	52	10	2
Ethylene selectivity, %	0	10	68
Mole H_2/mole ethanol fed	3.514	1.750	1.165

via ethanol dehydration is favored by -Al_2O_3 over methane formation due to the acidic nature of the alumina surface. Ethylene formation is less desirable due to the potential for subsequent coke formation. The ethylene selectivity over 1% Rh/-Al_2O_3 was about 70% at 450°C, resulting in low hydrogen productivity. MgO-modified Al_2O_3 suppressed ethylene formation, as MgO neutralizes the acidity and provides a basic surface property. As a result, 1% Rh/MgO-Al_2O_3 exhibited higher H_2 productivity as determined by H_2 produced / ethanol (EtOH) fed. A CeO_2-ZrO_2 support provided the highest hydrogen productivity (H_2 produced / EtOH fed) due to enhanced water gas shift activity. The effects of Pt promotion of Rh were also evaluated, and Table 3 summarizes the result of 3% Pt addition to the 3% Rh/CeO_2-ZrO_2 catalyst at 450°C. The addition of Pt to Rh results in greater ethanol conversion. In addition, Pt plays a role in decreasing CO selectivity and enhancing the formation of both CH_4 and CO_2. The increased CH_4 selectivity is possibly due to the increased decarbonylation of the intermediate CH_3CHO (acetaldehyde) product. The increase in CO_2 selectivity is mainly due to the effect of CeO_2 in facilitating the water gas shift reaction.

In order to demonstrate the potential advantages of microchannel reactors, a 3% Rh-3% Pt/CeO_2-ZrO_2 catalyst was compared in both a microchannel reactor and a conventional micro-tubular reactor. The microchannel reactor had a gap of 0.75 mm, providing a much shorter transport distance as compared to that in a micro-tubular reactor with an

Table 3. Promotion Effect of Pt on 3% Rh/CeO_2-ZrO_2 Catalyst at 450°C

Catalyst	X_{EtOH}%	S_{CO}%	S_{CO2}%	S_{CH4}%
3% Rh-3% Pt	100	8	38	53
3% Rh	74	57	12	30

inner diameter of 4 mm. To demonstrate the benefits of the microchannel reactor, the catalyst packed in the microchannel reactor was not diluted with inert materials. In the case of the micro-tubular quartz reactor, catalyst tests were executed both with and without catalyst dilution. Catalyst dilution is used to determine whether there are heat transfer limitations in the catalyst bed. The comparison of reaction results at 400°C are summarized in Table 4.

Table 4. Promotion Effect of Pt on 3% Rh-3% Pt/CeO_2-ZrO_2 Catalyst at 400°C

Reactor	X_{EtOH}%	S_{CO}%	S_{CO2}%	S_{CH4}%	H_2/EtOH
Microchannel	99	33	25	40	2.10
Quartz (diluted)	97	44	11	44	1.65
Quartz (undiluted)	76	45	10	43	1.31

Comparing the results of the diluted quartz reactor with undiluted one, the former exhibited higher ethanol conversion than the latter, indeed suggesting the presence of heat transfer limitations in the undiluted bed. The product distributions are similar. As a result, the reactor hydrogen yield per unit ethanol fed with the diluted quartz reactor was higher than that of the undiluted one. At the same temperature, the ethanol conversion was 99% using the microchannel reactor, but less than 80% with the undiluted quartz reactor. This clearly shows the benefit of the microchannel reactor in ethanol steam reforming. Similar hydrogen productivity can be achieved in a microchannel reactor at a lower temperature. Lower temperature operation directly translates into potential energy savings. In addition, the CO selectivity was decreased by employing the microchannel reactor, resulting in higher CO_2

selectivity. The CH_4 selectivity provided by the microchannel reactor was also slightly lower than that from the quartz reactor with or without diluents. The reduced heat transfer distance benefits the endothermic ethanol steam reforming, and as a result, the microchannel reactor outperforms the micro-tubular reactor in terms of hydrogen productivity under identical reaction conditions. Hydrogen produced per mole ethanol fed is also dependent on the reactor type and reaction temperature, and the results are summarized in Table 5. The H_2/EtOH ratio typically increases with reaction temperature because ethanol steam reforming is thermodynamically favorable at higher temperatures. However, it is clear that the productivity of H_2 is strongly dependent upon the reactor type within the temperature range tested in this study. It should be noted that the productivity of H_2 at 450°C in the microchannel reactor is even higher than that at 500°C with the quartz reactor, regardless of the presence of diluents.

Table 5. H_2/EtOH as Function of Function of Reactor Type and Reaction Temperature over 3% Rh-3% Pt/CeO_2-ZrO_2 Catalyst

Reactor	350°C	400°C	450°C	500°C
Microchannel	1.25	2.10	2.64	2.64
Quartz (diluted)	0.92	1.65	1.86	2.32
Quartz (undiluted)	0.79	1.31	1.73	2.29

Conclusions

Aqueous phase gasification can provide an attractive alternative for generation of hydrogen from biomass feedstocks. A preliminary screening of candidate catalysts by use of combinatorial-high throughput screening methods indicates that ruthenium is the most active metal for production of gas phase products (CO, H_2, light hydrocarbons), and titania (TiO_2) the most effective support among those tested. Steam reforming of ethanol indicates two possible pathways, via ethylene and via acetaldehyde. The former is undesirable as it leads to coke formation. The latter can lead to formation of methane, which requires higher temperatures for hydrogen production via reforming. The catalytic challenge is to produce hydrogen while minimizing methane formation. Rh/CeO_2-ZrO_2 is an effective catalyst due to the high activity of Rh and the role of CeO_2-ZrO_2 in facilitating water gas shift. Addition of Pt to Rh/CeO_2-ZrO_2 catalyst increases undesirable methane formation. A microchannel reactor has been shown to provide higher ethanol conversion at lower temperature compared with a conventional packed bed reactor, as well as higher hydrogen selectivity.

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FY 2004 Publications/Presentations

1. "Hydrogen Production from Biomass Feedstocks" to be presented by Hyun-Seog Roh, David L. King, and Yong Wang in the 2004 ACS Fall Meeting in Philadelphia.

2. Hyun-Seog Roh, David L. King, and Yong Wang, "Hydrogen Production from Biomass Feedstocks," Prepr. - Am. Chem. Soc., Div. Pet. Chem., 49 [2] (2004).