HYDROGEN PRODUCTION FROM BIOMASS FEEDSTOCKS

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Introduction

Hydrogen attracts significant research interests because it is a clean fuel emitting only water without formation of greenhouse gases. Commercially, hydrogen has been produced from catalytic steam reforming of fossil fuels, for example, methane.[1] To reduce greenhouse gas emissions, the hydrogen should be derived from renewable energy sources such as bio-ethanol.[2-4] As a consequence, ethanol steam reforming has been studied, which gives potential alternative to hydrogen production.[4,5] For the purpose of H_2 production as a fuel in molten carbonate fuel cell (MCFC), ethanol steam reforming has been studied at the temperature range of 600 – 700°C, which is the operating temperature of anode in MCFC.[6-8] As for a steam/ethanol ratio, most researchers employ more than 8 to avoid carbon formation.[7-9]

In this paper, we have tested various supported Rh catalysts and the effects of metal composition, promoter, and support on the selectivity to intermediates, hydrogen, and CO/CO_2 were evaluated. For comparison, micro-channel reactor was employed at low temperatures (350 – 500°C) with a stoichiometric feed ratio ($H_2O/EtOH$ = 3.0) to examine the benefits of efficient heat and mass transport comparing with conventional quartz tube reactor.

Experimental

Support materials employed in this study were γ-Al_2O_3 (99%, SASOL), ZrO_2 (99%, MEL Chemicals), and CeO_2-ZrO_2 (CeO_2: 17.5%, MEL Chemicals). The supports were pre-calcined at 800°C for 6 h in air. Supported Rh catalysts were prepared by the incipient wetness method using its nitrate source. In some cases, Pt was co-impregnated with Rh. The catalyst samples were calcined at 600°C for 6 h in air.

Catalytic activity measurements were conducted in a fixed-bed micro-tubular quartz reactor with an inner diameter of 4 mm at atmospheric pressure. Special cares were taken to eliminate the potential mass and transport limitations. SiC was employed as a diluent in a micro-tubular quartz reactor, otherwise stated. For comparison, catalytic performance was also tested in a micro-channel single reactor having a gap of 0.75 mm, which is a much shorter transport distance as compared to that in a micro-tubular reactor. Thermocouples were placed strategically throughout the reformer system. Prior to each catalytic measurement, the catalyst was reduced in H_2/N_2 (10% H_2 in vol.) at 350°C for 1 h. A stoichiometric steam to ethanol ratio of 3 and a weight hourly space velocity (WHSV) of 75,660 cm^3/g cat/hr were used in all experiments. The mixture of ethanol and water was fed using a syringe pump and was vaporized at 250°C in the vaporizer.[10] The reformate was chilled, passed through a ice-trap to condensate residual water and ethanol, and then flowed to the on-line gas chromatograph (GC) for analysis. The GC was a micro-GC (Agilent) and GC columns used in this study were Molesieve 5A and PoraPlot Q.

Results and Discussion

A thorough literature search on ethanol steam reforming indicates that the Rh based catalysts are most active, and ethanol steam reforming mechanisms are complex.[4,5,7-9] Cavallaro assumes that the ethanol is converted during the first stage into ethylene by dehydration or into acetaldehyde by dehydrogenation.[11] The acetaldehyde easily undergoes decarbonylation to form CH_4 and CO.

First, we studied the effect of support on product distribution. Ethanol conversion is relatively independent on Rh loading (over 3wt%) while methane selectivity increases with Rh loading. It is most likely that acidic supports favor the ethylene formation over methane formation. The ethylene selectivity over Rh/Al_2O_3 catalysts with various Rh loading is summarized in Table 1.

Table 1. Ethylene Selectivity with Temperature over Rh/Al_2O_3 Catalysts

Temp. (°C)	1%Rh	3%Rh	6%Rh	10%Rh
500	0.73	0.69	0.59	0.46
550	0.46	0.45	0.34	0.22
600	0.14	0.12	0.00	0.00
650	0.00	0.00	0.00	0.00

1%Rh catalyst showed higher than 70% ethylene selectivity at 500°C. The ethylene selectivity decreases with reaction temperature due to the fact that ethylene steam reforming is favorable at higher temperatures. It is also clear that the ethylene selectivity decreases with Rh loading. This is possibly due to the fact that the portion of Al_2O_3 in the catalyst decreases with Rh loading. In addition, the effects of support were also studied. 10%Rh/ZrO_2 showed 12% ethylene selectivity at 500°C, while 10%Rh/CeO_2-ZrO_2 exhibited no ethylene formation at the same condition. Instead, 10%Rh/CeO_2-ZrO_2 showed 43% CH_4 selectivity. Under the same condition, the selectivities to CH_4 over 10%Rh/ZrO_2 and 10% Rh/Al_2O_3 were 15% and 3%, respectively.

Table 2 summarizes the effect of Pt promotion on 3%Rh/CeO_2-ZrO_2 catalyst at 450°C.

Table 2. 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%Rh3%Pt	1.00	0.08	0.38	0.53
3%Rh	0.74	0.57	0.12	0.30

The addition of Pt to Rh based catalysts results in enhanced ethanol conversion. In addition, Pt plays a role in decreasing CO selectivity and enhancing both the formation of CH_4 and CO_2. The increased CH_4 selectivity is possibly due to the enhanced decarbonylation of CH_3CHO.[11] The increase of CO_2 selectivity is mainly due to the beneficial effect of CeO_2 to increase water gas shift reaction.

In order to demonstrate the potential advantages of microchannel reactors, a 3%Rh3%Pt/CeO_2-ZrO_2 catalyst was compared in both a micro-channel reactor and a conventional micro-tubular reactor. Here, micro-channel reactor has a gap of 0.75 mm, which is a much shorter transport distance as compared to that in a micro-tubular reactor with an inner diameter of 4 mm. To demonstrate the benefits of micro-channel reactor, the catalyst packed in the micro-channel reactor was not diluted with inert materials. In the case of micro-tubular quartz reactor, catalyst tests were executed both with and without catalyst dilution. The comparison of reaction results at 400°C are summarized in Table 3. Comparing the results of diluted quartz reactor with undiluted one, the former exhibited higher ethanol conversion than the latter. This is due to the enhanced heat transfer in the presence of SiC as diluents. The product distribution is similar to each other. As a result, the

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hydrogen produced per ethanol fed of diluted quartz reactor is higher than that of undiluted one. At the same temperature, the ethanol conversion was 99% using micro-channel reactor but less than 80% with the undiluted quartz reactor. This clearly shows the benefit of micro-channel reactor in ethanol steam reforming. In another word, similar hydrogen productivity can be achieved in a microchannel reactor at a lower temperature. Lower temperature operations can directly translate into potential energy savings. In addition, the CO selectivity was decreased by employing micro-channel reactor resulting in high CO_2 selectivity.

Table 3. Comparison of Reaction Results on 3%Rh3%Pt/CeO_2-ZrO_2 Catalyst at 400°C

Reactor	X_{EtOH}	S_{CO}	S_{CO2}	S_{CH4}	H_2/EtOH
Micro-channel	0.99	0.33	0.25	0.40	2.10
Quartz (diluted)	0.97	0.44	0.11	0.44	1.65
Quartz (undiluted)	0.76	0.45	0.10	0.43	1.31

The CH_4 selectivity of micro-channel reactor was also slightly lower than those of quartz reactor with or without diluents. The reduced heat transfer distance was anticipated to be beneficial to the endothermic ethanol steam reforming.[10] Therefore, it is not surprising to see that the micro-channel reactor outperforms the micro-tubular reactor in terms of hydrogen productivity under the identical reaction conditions.

Table 4 shows the hydrogen produced per mole ethanol fed which are dependent on the reactor-type and reaction temperature.

Table 4. H_2/EtOH Depending on Reactor-Type with Reaction Temperature over 3%Rh3%Pt/CeO_2-ZrO_2 Catalyst

Reactor	350°C	400°C	450°C	500°C
Micro-channel	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

The H_2/EtOH 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 micro-channel reactor is even higher than that of 500°C with the quartz reactor regardless of the presence of diluents.

Conclusions

Ethanol steam reforming follows either dehydration to form ethylene or dehydrogenation to form CH_3CHO resulting in decarbonylation to form methane pathways. Acidic supports favor the ethylene formation over methane formation. Ethanol conversion is relatively independent on Rh loading (over 3wt%) while methane selectivity increases with Rh loading. Non acidic supports, such as CeO_2-ZrO_2, favors methane formation. Addition of Pt to Rh based catalysts increases both the formation of methane and CO_2 via water gas shift reaction. The micro-channel reactor outperforms the micro-tubular reactor in terms of hydrogen productivity under identical reaction conditions over 3%Rh3%Pt/CeO_2-ZrO_2 catalyst due to the reduced heat transfer distance, which is beneficial to the endothermic ethanol steam reforming.

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