

Conversion of biomass-derived syngas to alcohols and C₂ oxygenates using supported Rh catalysts in a microchannel reactor

Jianli Hu^{*}, Yong Wang, Chunshe Cao, Douglas C. Elliott, Don J. Stevens, James F. White

Pacific Northwest National Laboratory, 902 Battelle Boulevard, Richland, WA 99352, United States

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Abstract

The capability of a microchannel reactor for synthesis of alcohols and C₂⁺ oxygenates from biomass-derived syngas was explored. Supported Rh catalysts were selected to integrate with a microchannel reactor for this study. The focus of the present research was to investigate the impact of reaction variables, including temperature, pressure, H₂/CO ratio, and activation procedures, on the activity and product selectivity of supported Rh catalysts. It was observed that the formation of undesired product, methane, can be suppressed under conditions of low temperature, high pressure, and low H₂/CO ratio. Interestingly, different catalysts responded differently to reduction–oxidation cycle (RedOx) treatment. A hybrid catalyst system containing CuZnAl and Rh-Mn/SiO₂ exhibited continued increase in activity after RedOx treatment. When Rh-Mn/SiO₂ catalyst was coated on a FeCrAlY metallic felt substrate and subsequently integrated into a microchannel reactor, a significant enhancement in specific activity was obtained, which highlights strong process intensification potential for commercial application.

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1. Introduction

With the continued climbing of crude oil price, research on alternative energy resources becomes more and more important. Biomass feedstocks, such as agriculture and forestry residues, play an important role in developing alternatives to fossil fuels [1]. While there are several methods of generating energy from biomass, gasification, in which a hydrogen–carbon monoxide gas mixture (syngas) is produced, offers several advantages. Just like petroleum products, syngas can be converted to useful chemicals and fuels via different synthetic routes including methanol synthesis, higher alcohol synthesis, Fischer-Tropsch synthesis, etc. However, an obstacle to converting biomass-derived syngas, at an economical scale, has been the decentralized nature of biomass operations. Petroleum, coal, and natural gas are high energy density materials and thus amenable to centralized, large-scale processing plants. However, biomass feedstocks with their inherently lower energy density are and will continue to be processed in geographically decentralized plants

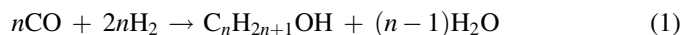
and gasification facilities. It is reported that if conventional processing technology is adopted for biomass gasification, a minimum scale of 2500 t/d would be required for production economically comparable to conventional LPG fuel [2]. Since it is difficult to supply and deliver enough biomass to satisfy this criterion using conventional technology, a more compact and efficient portable process is needed. This new process would operate under the lower limit of industrial process conditions, but with a high space time yield. It would also be compatible with both current and future bio-refinery, that is, forest product mills and corn processing facilities.

The purpose of the present research discussed here is to develop such a process capable of converting syngas generated from gasification of dispersed biomass resources. In this paper, we explore possibility of converting biomass-derived syngas to methanol, ethanol, and C₂⁺ oxygenates, but preferably with high selectivity to ethanol, a product of greater value. Among the choice of supported metal catalysts, Rh appears to be the most adaptable of the elements in the transition series in terms of its properties for catalysis, particularly for syngas conversion [3–6]. Rh supported on silica and/or vanadium tends to yield alcohol synthesis catalysts with high selectivity towards ethanol [7–9]. General

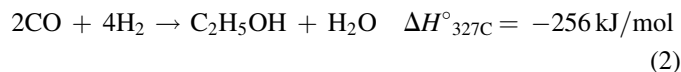
^{*} Corresponding author. Tel.: +1 509 376 0427; fax: +1 509 376 5106.

E-mail address: Jianli.Hu@pnl.gov (J. Hu).

alcohol synthesis is described by Eq. (1), stoichiometrical requirement of H₂/CO ratio equals 2.



For ethanol synthesis, the reaction is described by Eq. (2), which is highly exothermic.



Considering the exothermic nature of alcohol synthesis and the small to moderate expected scale of production, we explored the feasibility of utilizing a microchannel reactor for alcohol synthesis with parallel exploration of supported Rh catalysts. It is known that microchannel reactors have the advantage of improved heat and mass transfer, which allow greater process intensification [10,11]. That is, microchannel reaction systems can be much smaller than conventional devices and still deliver high space time product yields.

2. Experimental

2.1. Methods of catalyst preparation and activation

Catalyst formulation selection is based on literature reported information [5,6]. The SiO₂ was supplied by Davison, which had been pre-calcined in air at 550 °C (BET surface area = 400 m²/g). A rhodium nitrate solution containing 10% Rh metal purchased from Engelhard was used as precursor. Although Rh/SiO₂ itself can catalyze syngas conversion to ethanol, the use of appropriate promoters (e.g. Mn, V, etc.) is essential for the improvement of the activity and selectivity. Mn(NO₃)₂ (99%) and NH₄VO₃ (>98%) were obtained from Aldrich and used as precursors for Mn and V, respectively. Rh-Mn/SiO₂ catalyst was prepared by co-impregnating Rh and Mn precursors on SiO₂ support using incipient wetness technique. Final concentration of Rh and Mn were controlled at level of 6 and 1.5 wt%, respectively. After impregnation, all catalysts were subject to air calcination at 350 °C for 3 h. A methanol synthesis catalyst, F51-8PPT (Katalco Corporation) was modified by impregnating 3% Cs using incipient wetness technique. This catalyst was used as a comparison higher alcohol synthesis catalyst. Most of catalysts were tested in powdered form and only Rh-Mn/SiO₂ was tested in structured monolith type configuration. When tested in the powder form, fine particle powder catalysts were pelletized, crushed, and sieved into 70–100 mesh before placed into microchannel reactor. The purpose was to minimize pressure drop. Structured Rh-Mn/SiO₂ catalyst was prepared by wash coating technique. Powdered Rh-Mn/SiO₂ catalyst was ball-milled with water as a medium for 24 h, after which the ball-milled catalyst slurry was wash coated on FeCrAlY metallic felt. Characterization by SEM showed that the catalyst particle size on the structured catalyst varied between 0.5 and 2 μm. After wash-coating to desired weight gain, the felt catalyst

(structured catalyst) was installed into a microchannel reactor equipped with active cooling functions.

All the catalysts were reduced with flowing 10% hydrogen in Helium in the 220–350 °C temperature range under atmospheric pressure. A special catalyst treatment procedure was developed where catalysts were treated by reduction–oxidation cycles (RedOx). During the RedOx treatment, catalyst is reduced first by 10% hydrogen at 350 °C for 12 h, then cooled to room temperature. After reactor was purged by nitrogen, 2% oxygen in Helium was introduced and reactor temperature was increased to 250 °C at ramping rate of 1 °C/min. The duration of oxidation is 2 h, after which reactor was cooled to room temperature under Helium gas flow. The above reduction and oxidation procedure was repeated once, and the catalyst was finally reduced by 10% hydrogen in Helium before feed gas mixture was introduced.

2.2. Microchannel reactor and operation

The experiments were carried out in a microchannel reactor (316 stainless steel), with the channel dimensions of 5.08 cm × 0.94 cm × 0.15 cm. The microchannel reactor was configured for high pressure down flow mode. The schematic diagram of the reactor system and microchannel reactor assembly was similar to those described in reference [12]. To minimize methanation reaction in the stainless steel reactor, silica (SiO₂) coated stainless steel tubing was used in the high-temperature preheating zone. Experiments were conducted at temperatures from 260 to 300 °C and pressure from 2 to 5.4 MPa. All the experiments were carried out under isothermal conditions as indicated by the uniform temperature distribution along catalyst bed.

A mixture of N₂/H₂ was fed during startup to establish steady-state flow and to heat the reactor to the desired temperature. When the catalyst bed temperature reached the target, premixed syngas at the desired ratio was fed into the reactor. The typical feed composition was CO:H₂:CO₂:Ar = 30:62:4:4. The presence of Ar served as the internal standard for conversion and selectivity calculation purposes. For each run using powdered catalyst, 0.20 g of catalyst were loaded into the reactor, and the volume was measured. Total feed flow rate was set to achieve the desired gas hourly space velocity (GHSV), which is measure by reactor channel volume. The reaction products were analyzed by on-line gas chromatography (HP 5890 GC) equipped with both TCD and FID detectors. GC column used was GS-Q 30 m manufactured by JW Scientific. Temperature program of 5 °C/min to 300 °C was chosen for the analysis. Liquid products were collected in a cold trap at –3 °C and were also analyzed by GC–mass spectrometry. Carbon monoxide conversion and product selectivity were calculated based on feed and product flow rates and carbon balance.

3. Results and discussion

It is well known that Rh/SiO₂ catalyst produce C₂-oxygenated compounds such as ethanol, acetaldehyde, and acetic acid from syngas with high selectivity. However, it is

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