

Synthesis of Ethanol, DME and Hydrocarbon Fuels from Biomass Derived Syngas: Catalysts and Microchannel Reactor

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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 and Fischer-Tropsch synthesis, etc.

This paper presents the capability of a catalytic microchannel reactor in direct synthesis of dimethylether (DME), selective ethanol synthesis and Fischer-Tropsch Synthesis. In DME synthesis, the reactor was operated in conjunction with a hybrid catalyst system consisting of methanol synthesis and dehydration catalysts, and the influence of reaction parameters on syngas conversion was investigated. Using the microchannel reactor, it was possible to achieve a space time yield almost three times higher than commercially demonstrated performance results, which highlights strong process intensification potential for commercial application. In ethanol synthesis, supported Rh catalysts were selected to integrate with a microchannel. 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. In F-T synthesis, we have developed a unique structured catalyst system suitable for the deployment in microchannel reactor applications. By tailoring the mass transfer limitations, we have demonstrated that this engineered catalyst produces hydrocarbons with narrower carbon distributions (mainly less than C₂₅) than a conventional particulate catalyst at similar conversion and methane selectivity. In the microchannel reactor, heat generated from synthesis reactions can be removed at a speed almost six times faster than in the slurry reactor.

Materials and Methods

A hybrid catalyst system, consisting of methanol synthesis catalyst, F51-8PPT (Kataco Corporation) and dehydration catalysts, ZSM-5 zeolite or acidic Al₂O₃ was placed in microchannel reactor[2]. 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 wt% and 1.5 wt%, respectively[3]. F-T catalysts were

synthesized in PNNL's laboratory. Five sequential impregnations were used to obtain final formulated catalyst with 30wt%Co and 4.5wt%Re on alumina[4].

Results and Discussion

Results shown in Figure 1 illustrates that, after RedOx treatment, CO conversion continues to increase and does not level off until after 200 hours operation. Meanwhile, CO₂ selectivity exhibits an upward trend and levels off after 200 hours time on stream. The formation of CO₂ is expected which is mainly attributed to the well known water gas shift function of Cu-based catalyst. As the run proceeds, methane selectivity decreases from 20% to 10%. On the absolute basis, selectivity to methane on the hybrid catalyst is much lower than on supported Rh catalyst alone. Implications from these findings are the possibility of further improving the performance of such a catalyst system by varying the ratio and the interaction of the two different catalysts.

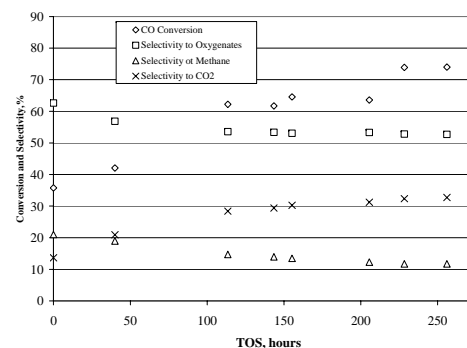


Figure 1. Effect of RedOx treatment on the performance of hybrid catalyst system for the synthesis of oxygenates.(CuZnAl and Rh-Mn/SiO₂ mixed at ratio of 1:2, P=5.4 MPa, GHSV=3750 h⁻¹, T=280°C)

Significance

The unique design of the microchannel reactor enables highly exothermic CO hydrogenation reaction to be operated in an isothermal mode to achieve high productivity. Integration of structured catalyst in a microchannel reactor allows syngas to be converted to alcohols at high throughput to obtain high space time product yield and improved product selectivity.

References

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