

# Fischer-Tropsch Synthesis in a Microchannel Reactor: The Influence of Cobalt Loading and Support Properties on FTS Performance

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## Introduction

Oil resources in developed nations are rapidly being depleted. Conversion of synthesis gas into clean diesel fuel from stranded natural gas (GTL) and biomass (BTL) via a Fischer-Tropsch synthesis (FTS) process could provide an economical solution to the world's energy needs. However, conventional processes, fixed-bed and slurry phase, are not economically viable for the smaller plants required for processing stranded natural gas fields and biomass resources. On the other hand, a microchannel reactor for FTS offers the opportunity for a small, modular, less expensive and high efficiency facility.

Over the past several years Velocys has been engaged in not only the development of microchannel reactor technology for FTS, but also supported cobalt catalysts that provide the necessary level of C5+ productivity for an economically viable process. The influence of support properties and cobalt loading on C5+ selectivity has yielded some unexpected results for supported cobalt catalysts with metal loadings >40wt%. Various catalyst characterization tools have been used to explain the observed FTS results.

## Materials and Methods

Catalysts were prepared using both incipient wetness and molten salt techniques. Cobalt dispersion and TPR measurements were made using a Zeton-Altimira AMI-1 unit. N<sub>2</sub> pore volume results were obtained with a Micromeretics ASAP 2010 unit. Catalyst FTS performance results were achieved using a 316 SS single channel microreactor containing approximately 0.3 ml of catalyst. Samples were analyzed for CH<sub>4</sub>, CO, and CO<sub>2</sub>, and C<sub>2</sub>-C<sub>5</sub> hydrocarbons using an online Agilent micro GC equipped with a TCD detector.

## Results and Discussion

Previously, Moradi et al (1) reported that the FTS steady-state activity and C5<sup>+</sup> selectivity of 10 wt% Co/SiO<sub>2</sub> catalysts increased with zirconia loading; in agreement with the earlier results of Ali et al. (2). Moradi et al. also reported that with increasing zirconia loading the BET surface area of the catalyst decreased, thereby, explaining the increase in cobalt particle size as determined by XRD. TPR data revealed that with increasing zirconium loading the Co-silica interaction was replaced by a Co-zirconia interaction leading to a higher degree of cobalt reduction and an increase in the number of metallic Co sites.

In an effort to develop highly active catalysts for FTS in a microchannel reactor we have examined the effect of zirconium promotion for Co-Ru/SiO<sub>2</sub> catalysts with Co loading >40wt%. As illustrated in Table 1, we observed that with increasing zirconium loading a small increase in CO conversion, but also a decrease in C5<sup>+</sup> selectivity, contrary to what was reported by Moradi et al.

Table 1. FTS Catalyst Performance at 210°C, 310 psig, H<sub>2</sub>:CO=2:1, 290 ms contact time

Catalyst	TOS, hrs	CO Conv., %	CH <sub>4</sub> Sel, %	C5 <sup>+</sup> Sel, %
Co-Ru/SiO <sub>2</sub>	34.5 to 92.5	61.6 to 57.7	11.0-10.5	80.1 to 81.6
Co-Ru/3Zr-SiO <sub>2</sub>	35.3 to 93.4	64.0 to 61.8	11.6-10.7	78.6 to 80.3
Co-Ru/10Zr-SiO <sub>2</sub>	34.4 to 92.4	63.8 to 60.7	14.8-12.9	75.0 to 76.9

To understand why the observed results differ from those reported by Moradi et al., both physical and chemical properties of the catalysts were measured. The data suggest that neither the dispersion nor the reducibility of Co is significantly influenced by zirconium at Co metal loadings greater than 40wt%. The results do explain the observed nominal changes in catalyst activity with zirconia promotion. However, the more significant changes observed in C5<sup>+</sup> selectivity can be explained by changes in the physical properties of the support in agreement with previous publications (3-4). These results suggest that at Co loadings > 40%, promotion of SiO<sub>2</sub> with zirconia has a minimal impact on Co-support interaction.

## Significance

The results have facilitated continued efforts to improve catalyst activity and selectivity for Fischer Tropsch synthesis in microchannel reactors. Such efforts will lead to microchannel reactors with greater efficiency, further improving on the benefits in reactor size and economics for biomass and stranded natural gas applications.

## References

1. Moradi, G.R., Basir, M.M., Taeb, A., and Kiennemann, A. *Catalysis Comm.* 4, 27 (2003).
2. Ali, S., Chen, B., and Goodwin Jr., J.G. *J. Catal.* 157, 5 (1995).
3. Saib, A.M., Claeys, M., and Van Steen, E. *Catalysis Today* 71, 395 (2002).
4. Øyvind, b., Eri, S., Blekkan, E.A., Storåter, S., Wigum, H., Rytter, E., and Holmen, A. *J. Catal.* 248, 89 (2007).