

## EXECUTIVE SUMMARY

The Fischer-Tropsch synthesis (FTS) reaction is the established technology for the production of liquid fuels from coal by an indirect route using coal-derived syngas ( $\text{CO} + \text{H}_2$ ). Modern FTS catalysts are potassium- and copper-promoted iron preparations. These catalysts exhibit moderate activity with carbon monoxide-rich feedstocks such as the syngas produced by advanced coal gasification processes. However, the relatively large yields of by-product methane and high-molecular-weight hydrocarbon waxes detract from the production of desired liquid products in the  $\text{C}_5$ - $\text{C}_{16}$  range needed for motor and aviation fuel.

The goal of this program was to decrease undesirable portions of the FTS hydrocarbon yield by altering the Schultz-Flory polymerization product distribution through design and formulation of improved catalysts. Two approaches were taken: (1) reducing the yield of high-molecular-weight hydrocarbon waxes by using highly dispersed catalysts produced from surface-confined multiatomic clusters on acid supports and (2) suppressing methane production by uniformly pretreating active, selective conventional FTS catalysts with submonolayer levels of sulfur.

The objective of the first approach was to produce non-ASF distributions from the FTS reaction by developing ruthenium cluster catalysts that produce "living polymers" and at the same time limit chain growth so that the majority of products fall within the normal motor fuel range ( $\text{C}_6$  through  $\text{C}_{15}$ ). We also hoped to achieve this goal by using Ru catalysts and supporting them within zeolites at high pressures to give the "living polymers" and to further limit chain growth and stabilize the catalyst metal particle size. In all cases, the metal particle size was to be maintained in the highly dispersed state by strongly anchoring the cluster catalyst precursors to the supports using strong covalent bonds.

Nine supported atomic and multiatomic ruthenium catalysts were prepared via organometallic reactions of tetra- and hexaruthenium hydridocarbonyls and allyl monoruthenium carbonyl complexes with acid sites on three support materials: alumina, sodium Y zeolite, and molecular sieve (Linde 5A). FTS performance was measured for each catalyst in a fixed-bed microreactor under the following reaction conditions: 523 K, 1:1 and 2:1  $H_2:CO$ , and 100 kPa. The activity of these catalysts varied from 2.3 to 21 nanomoles of product per second per gram of catalyst (nmol/s/g cat.). Conventional ruthenium on alumina had activity of 11.5 nmol/s/g cat. under these conditions. The tetraruthenium cluster catalyst supported on alumina had the highest FTS activity but had a methane selectivity of 61%. The hexaruthenium cluster catalyst supported on sodium-Y zeolite had the lowest methane selectivity (36%) and the highest olefin selectivity (ethylene/ethane > 20). The Schulz-Flory-Anderson product distribution and chain growth factors for all ruthenium cluster catalysts through  $C_8$  were nearly independent of support type and cluster size.

Substantial changes in selectivity of potassium-promoted fused iron catalysts were found following treatment to uniformly chemisorb submonolayer quantities of sulfur. After reduction and passivation by accumulation of a surface layer of carbon and chemisorbed CO, approximately 40% of a monolayer of sulfur was slowly adsorbed at 473 K on the fused iron catalyst. The passivating layer was removed and the sulfur locally dispersed by heating to 1000 K in hydrogen. The treated catalyst had a three-fold reduction in methane selectivity relative to the untreated reduced fused iron in 2:1  $H_2:CO$  syngas at 573 K and 100 kPa. The  $C_2$  olefin selectivity approached 100% ( $C_2H_4/C_2H_6 > 20$ ). The sulfur treatment decreased the  $C_{2+}$  production rate at 573 K to only about half the rate of the untreated catalyst per unit area and was comparable to the stationary-stable activity of the fused iron at 523 K.

A low-level sulfur-treated fused iron catalyst (20% monolayer sulfur coverage) was also prepared and tested for FTS activity and selectivity. This sulfur-treated catalyst showed almost a twofold reduction in methane

yield compared with clean fused iron catalyst. The sulfur-treated catalyst also demonstrated good stability, showing no sign of deactivation throughout a 24-h synthesis run. A similar examination was conducted for a fused iron catalyst with 80% of a monolayer of sulfur coverage. This catalyst had comparable FTS selectivity but an order of magnitude loss of activity relative to the low-level sulfur treated catalyst. These results indicate that the alkane production rate was roughly proportional to the cube of the density of the uncovered site, whereas the olefin production rate varied proportionately with the density of the uncovered site.

The medium-level sulfur-treated (50% monolayer sulfur coverage) iron and cobalt catalysts were tested for FTS activity, and the clean-fused iron catalyst was tested as a comparative standard for the fixed-bed reactor operated at high pressure (2 MPa). Of the four catalysts tested for FTS activity at high pressure, the medium-level sulfur-treated fused iron catalyst seems most promising, with a 50% reduction in methane yield, a narrower product distribution (chain growth probability factor,  $\alpha$ , was 20% less than that of the clean catalyst under the same reaction conditions), and a threefold increase in olefin selectivity. The sulfur-treated catalyst exhibited behavior at 2 MPa similar to that of the 100-kPa synthesis run; however, olefin selectivity decreased with increasing pressure or temperature.

The monoruthenium supported on molecular sieve and the tetra-ruthenium supported on sodium-Y zeolite had been chosen for slurry reactor study, and the conventional ruthenium supported on alumina and clean-fused iron catalysts was tested for comparison. Of the four catalysts tested for FTS synthesis at high pressure (6.9 MPa), only the conventional ruthenium catalyst exhibited a chain growth factor of 0.88 and a methane selectivity of 6.6%; these findings are typical of slurry reactor results reported under similar conditions. The other three catalysts tested showed chain growth factors from 0.44 to 0.57 and methane selectivity from 20% to 32%. We were not able to determine a chain growth probability factor for these catalysts in the wax range

because the field ionization mass spectrometry (FIMS) results were inconclusive.

A potassium and copper, doubly-promoted precipitated iron catalyst was prepared for evaluation of the effect of sulfur treatment on the methane selectivity and olefin-to-paraffin ratio of light hydrocarbons. Lack of reproducible surface area after reduction and difficulty in measuring metal surface areas complicated efforts to synthesize this catalyst with low sulfur coverage. The FTS activity and methane selectivity of the precipitated iron catalyst was inferior to that of the standard fused iron catalyst. High-level sulfur treatment resulted in a catalyst with greater activity and less suppression of methane than a similar treatment did for the fused iron catalyst, possibly because of nonuniform sulfur poisoning.

There are several technical advantages of direct synthesis of aromatic hydrocarbons with low  $H_2$  syngas. The key difficulty of this approach is deactivation of the FTS component because of carbon deposits. Since we observed that sulfur-treated fused iron resisted deactivation, we extended the scope of our project to include studies of aromatics production with dual-function catalysts.

The synthesis of aromatics was performed on several combinations of Fischer-Tropsch and sodium Y-zeolite catalysts in a fixed-bed reactor with  $H_2/CO$  ratio = 0.5, 2.0 MPa pressure, and a temperature range of 548 to 700 K. The medium-level sulfur-treated fused iron and sulfur-treated alumina-supported ruthenium were used as the FTS catalyst components and compared with results for the clean fused iron and clean ruthenium catalysts mixed with zeolite. The mixed catalyst containing sulfur-treated iron initially provided high yields of light oxygenates and aromatics with low yields of olefins, but the selectivity declined rapidly, especially with catalysts containing the more acidic low sodium zeolite components. The rapid decrease in aromatic and oxygenate yield and the increase in olefin yield was probably caused by carbon deposition on the surface of the zeolite component. The catalyst reactivity could be prolonged by using a higher zeolite/FTS catalyst ratio and by using zeolites with higher sodium weight loading.

These results with low  $H_2/CO$  syngas compare favorably with prior similar studies performed under less severe coking conditions.

Additional work with high silica-shape selective zeolite components to extend the catalyst active life is recommended at high syngas conversion using sulfur-treated iron catalysts.