

Technology Development for Iron and Cobalt Fischer-Tropsch Catalysts

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## Abstract

### CAER

The simple polymerization mechanism for the Fischer-Tropsch synthesis produces products which follows an Anderson-Schulz-Flory distribution. Thus, plotting the logarithm of the mole fraction versus carbon number will produce a straight line whose slope is related to  $\alpha$  which is determined by the chain termination and propagation probabilities. In contrast, the products from laboratory and large commercial plants exhibit a two-alpha plot. Vapor-liquid calculations show that product accumulation cannot be responsible for the two-alpha plot when the  $\alpha$  value is large enough to produce liquid products at the reaction temperature. Only in the case where  $\alpha$  is small and all products are in the vapor phase, allowing evaporation of the startup solvent and a “drying out” of the reactor can a product accumulation produce a two-alpha plot. Results of filtration successes and failures from runs with the CSTR are described.

### UC/B

Potassium K-edge X-ray absorption near edge structure (XANES) spectra of Fe-Zn-K-Cu oxides and their carbides showed that K was well dispersed on Fe or Zn oxides while K was present as  $K_2CO_3$  in the carburized samples. Fe K-edge XANES showed an absorption energy at 7.123 keV beyond the pre-edge (7.113 keV), indicating the presence of low oxidation state species like FeO besides the predominant  $Fe_2O_3$  species. *In-situ* Fe K-edge XANES of Fe-Zn-K-Cu oxides in CO showed that Fe carbides had an absorption energy at 7.112 keV. The extended X-ray absorption fine structure (EXAFS) spectra confirmed the Fe-Fe distance in carbides at 2.0 Å. *In-situ* Fe K-edge XAS spectra of Fe-Zn-K-Cu oxides in synthesis gas showed that Fe carbides were formed in the dominant bulk Fe oxides, and that the extent of carburization increased with increasing space velocity and with time on stream. The effects of K on secondary hydrogenation and isomerization reactions of primary  $\alpha$ -olefins and the effects of Cu on the activities for FTS and WGS reactions were examined on Fe-based catalysts. The results showed that Fe-Zn-Cu catalysts were active for secondary hydrogenation and isomerization reactions of  $\alpha$ -olefins. The introduction of K to these catalysts titrated these active sites. The addition of Cu increased FTS and WGS reaction rates. The promotion effects of Cu on these activities were less marked than those observed with K promotion. The addition of Cu to Fe-based catalysts had little effect on hydrocarbon production and olefin selectivity. The  $D_2$ - $H_2$  exchange studies showed that the  $H_2$  dissociation step was reversible and quasi-equilibrated in FTS.  $D_2O$  tracer studies showed that water dissociation proceeded slowly and was not quasi-equilibrated. Based on the kinetic data, a mechanism for the overall CO conversion reaction on Co/SiO<sub>2</sub> catalysts was proposed.

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