

IV. DEVELOPMENT OF IMPROVED IRON-SILICA CATALYSTS

Introduction

Supported catalyst systems with high support-to-metal ratios have not been overly effective in yielding good Fischer-Tropsch synthesis performance. In the slurry phase process, supported catalysts reduce the bulk concentration of metal and thus may hinder mass transfer of gas to liquid as solids loadings are increased to maintain metal concentrations. On the other hand, supported systems may actually increase the concentration of active metal sites by maintaining higher metal dispersions. The nature of the support is also important, since acidic sites on the support can render basic promoters like potassium ineffective, preventing interaction between promoter and metal. Previous work at the SASOL (Dry, 1981) in fixed bed reactors, examined the effects of promoters and supports on the performance of Ruhrchemie-type precipitated Fe catalysts. In one set of experiments, a series of Fe/Cu/K₂O precipitates were prepared using Cr₂O₃, MgO, Al₂O₃ or ZnO in place of the silica. None of these catalysts was as active as the standard SiO₂ containing material. An unsupported composition was also less active. Compositions containing both SiO₂ and a second support material also showed lower performance. Of all the supports, small amounts of added Al₂O₃ resulted in the lowest wax selectivity without excessive deactivation. This concept could be used to control selectivity to some extent.

A brief examination of precipitated iron catalysts containing silica or alumina as binder/support has been made in our laboratory at TAMU as a part of the DOE Contract DE-AC22-85PC80011 (Bukur et al., 1989b, 1990b). Six catalysts were employed in this study: an unsupported iron/copper/potassium catalyst (100 Fe/5 Cu/4.2 K in parts per weight), three silica-supported catalysts (100 Fe/5 Cu/4.2 K/xSiO₂, where x=8, 24 and 100), and two alumina-supported catalysts (100 Fe/5 Cu/4.2 K/xAl₂O₃, where x=8 and 24). The major findings from catalytic tests in fixed bed reactors are summarized below.

Addition of silica or alumina to the precipitated unsupported iron catalyst (100 Fe/5 Cu/4.2 K) influenced catalyst activity, stability, and selectivity during Fischer-Tropsch synthesis. Changes in catalyst performance became pronounced only at sufficiently high binder (support) concentrations and may be attributed to interactions between support and potassium and/or between metal and support.

The specific FTS activity decreased with increasing support content which may be ascribed to lower degree of iron reduction following the catalyst pretreatment with CO and to the reduction in the effective potassium content of the catalyst. However, the catalyst stability improved with addition of silica either because of stabilization of iron crystallites during synthesis or due to a decrease in the carbon deposition rate resulting from partial neutralization of potassium promoter by acidic sites on silica (i.e. reduction in surface basicity). It was also found that the WGS activity decreased with increasing silica content of the catalyst (catalysts with 24 and 100 g of SiO₂ per 100 g of Fe). This is attributed to reduction in surface basicity and decreased Fe/K contact due to the high catalyst surface area.

Product selectivities also changed markedly with increasing silica content of the catalyst, whereas no significant changes were observed with the two alumina-containing catalysts. The total olefin content and the fraction of branched hydrocarbons both decreased, whereas the fraction of internal olefins increased with an increase in the silica content of the catalyst. These observations reflect the expected trends arising from the reduction of surface basicity of the catalyst with increasing silica content and are in agreement with results obtained in previous studies with similar catalysts (Dry, 1981; Egiebor and Cooper, 1985)

Two of the three silica containing catalysts synthesized at TAMU (8 and 24 parts of SiO₂) and the Ruhrchemie catalyst (100 Fe/5 Cu/4.2 K/25 SiO₂) were also evaluated at a fixed set of process conditions over relatively long periods of time on stream (250-

480 hours) to determine their activity and selectivity maintenance, and the rate of deactivation (Bukur et al., 1989b).

The initial activity of the catalyst containing 8 parts of SiO₂ was much higher than that of the other two catalysts, but after 120 hours on stream it declined rapidly with time on stream. The catalyst containing 24 parts of SiO₂ was remarkably stable over 480 hours on stream. Its activity declined by 5.6% only over a 400 hour period and was about 20% higher than that of the commercial Ruhrchemie catalyst. The hydrocarbon product distributions obtained in the tests with the Ruhrchemie catalyst, and the catalyst containing 24 parts of SiO₂ were very similar with either H₂/CO=1.0 or H₂/CO=0.67 synthesis gas feed ratios. The catalyst containing 8 parts of SiO₂ produced less light hydrocarbons but its stability needs to be improved.

These promising results with silica containing catalysts warrant more detailed studies to develop catalysts suitable for commercial use. Further improvements can be achieved by judicious choice of silica content, which has significant effect on catalyst activity and stability, and promoter levels (particularly potassium) which have significant effect on product selectivity. Results from tests of baseline catalysts and catalysts synthesized at TAMU in stirred tank slurry reactors are described and discussed in the following sections of this report.