

### III. PRETREATMENT EFFECT RESEARCH

#### Introduction

The most common catalysts for CO hydrogenation are group VIII elements: cobalt, nickel, ruthenium and iron. Before synthesis, a catalyst precursor is subjected to a pretreatment, the purpose of which is to bring the catalyst into an active form for synthesis. Cobalt, nickel, and ruthenium are almost always reduced in flowing H<sub>2</sub> at 200-450°C to the zero-valent metallic state. During the synthesis, under a variety of process conditions, these catalysts remain in the zero-valent state (Anderson, 1956). However, the purpose of pretreatment for iron catalysts is not so clear. Reduction with H<sub>2</sub> may lead to the zero-valent state, but during the synthesis, the metallic iron is rapidly converted to a carbide phase (Amelse et al., 1978; Raupp and Delgass, 1979b). At high syngas conversions, the reaction mixture becomes more oxidizing (relatively high H<sub>2</sub>O/H<sub>2</sub> and CO<sub>2</sub>/CO ratios) and magnetite (Fe<sub>3</sub>O<sub>4</sub>) is also formed (Anderson, 1956; Dry, 1981; Satterfield et al., 1986). Other pretreatments have also been employed, such as CO reduction (activation), synthesis gas treatment (induction), and/or H<sub>2</sub> reduction followed by CO or vice versa. These activations often yield a better catalyst than that obtained by H<sub>2</sub> reduction, but the catalyst composition still changes during synthesis.

There is a large number of studies in literature dealing with the issue of the role of iron phases in the FT synthesis. Typically, these studies were conducted with model catalyst systems (e.g. iron supported on alumina, silica and other supports), at atmospheric pressure, with H<sub>2</sub> rich syngas mixtures (H<sub>2</sub>/CO = 3 or higher), over short periods of time (several hours on stream) and at low (differential) conversions. In the majority of these studies calcined catalyst precursor was completely reduced with H<sub>2</sub> prior to exposure to synthesis gas, and conversion of metallic iron to iron carbide

phases was followed as a function of time (usually by Mössbauer effect spectroscopy - MES), while changes in gas phase composition were monitored with an on-line GC or a mass spectrometer. In some of these studies a precarbided (e.g. Matsumoto and Bennett, 1978, Butt, 1990) and oxidized (e.g. Dwyer and Somorjai, 1978; Raymond et al., 1982; Butt, 1990) catalysts were used. In studies where the catalyst precursor was completely reduced prior to FT synthesis it was found that rate of FT synthesis as a function of time on stream passes through a maximum. Several models have been proposed to explain this type of behavior, and the two which are most frequently cited are: the carbide model (Amelse et al., 1978; Raupp and Delgass, 1979a,b) and the competition model (Niemantsverdriet and van der Kraan, 1981). In the carbide model iron is not considered to be active for the FT synthesis, but the surface carbides with its underlying iron carbide bulk structure, whereas in the competition model iron atoms at the surface are considered as the active sites. In the latter model both bulk carbidation and FT synthesis (hydrocarbon formation) have a common surface carbidic precursor. In addition to these two postulates concerning the nature of the active phase, Teichner and co-workers proposed that magnetite ( $\text{Fe}_3\text{O}_4$ ) is the active phase in FT synthesis (Raymond et al., 1982, Blanchard et al., 1982). According to them, the oxide phase is more difficult to carburize and be covered by graphitic (inactive) carbon, and thus the catalyst remains in its active state during synthesis. The addition of support helps stabilize iron oxide and results in greater stability. The proposal that magnetite is the active phase for FT synthesis was questioned by Dictor and Bell (1986). However, results from recent studies by Soled et al. (1990), and Butt and co-workers (Kuivila et al., 1989; Butt, 1990) lend support to this proposal. In these studies magnetite was the only phase present in the working active catalyst. Furthermore, X-ray photoelectron spectroscopy (XPS) results strongly suggest that magnetite is active for FT synthesis (Kuivila et al., 1989).

There have been only a few systematic studies on the effect of activation parameters on subsequent catalyst activity, selectivity and stability during the synthesis. The early work was reviewed by Anderson (1956, 1984) and the key findings were summarized by Bukur et al. (1989a, b). Recently, we have completed a comprehensive study of pretreatment effects with an unsupported doubly promoted precipitated iron catalyst with nominal composition 100 Fe/ 3 Cu / 0.2 K (Bukur et al., 1989a). Major findings from this study are described below.

Eleven different pretreatment procedures were employed to study effects of: temperature (250-310°C), duration (8 vs. 24 hours), pressure (0.1 vs. 1.48 MPa, with CO only) and type of reductant (CO, H<sub>2</sub> and H<sub>2</sub>/CO = 0.68 at 280°C, 0.1 MPa for 24 h) on performance of 100 Fe/ 3 Cu/ 0.2 K catalyst in a fixed bed reactor. Flow rate of reductant was 3 NI / g-cat/ h in all pretreatments. Following activation the catalyst was tested at 250°C, 1.48 MPa (200 psig), 2 NI / g-cat/ h using syngas with H<sub>2</sub> to CO molar feed ratio of about 1. Results showed that activation parameters have significant effect on catalyst activity, stability (deactivation) and selectivity during the FT synthesis. Activations with CO or syngas minimize production of gaseous hydrocarbons and produce more liquid and high molecular weight hydrocarbons (wax), relative to reductions with pure H<sub>2</sub>. However, these treatments usually lead to faster deactivation during the synthesis. Good stability can be achieved with a proper combination of activation parameters (temperature and duration). Reductions with hydrogen result in a constant or gradually increasing activity over 120 h of FT synthesis. The same trends were observed in tests with a variety of precipitated iron catalysts (Bukur et al., 1989b, 1990a) after hydrogen reductions. The catalyst activity can be improved by performing reduction at relatively low temperatures (220 - 240°C). In a stirred tank slurry reactor test SB - 0458 with a precipitated catalyst having nominal composition 100 Fe/0.3 Cu/0.5 K, we were able to achieve : (1) no loss in activity over 460 h period; and (2)

desirable hydrocarbon selectivity (low methane and C<sub>2</sub> - C<sub>4</sub> selectivities and high yield of C<sub>12+</sub> products), by using hydrogen reduction (Bukur et al., 1989b).

Although, it has been shown that activation parameters have significant effect on subsequent catalyst activity, selectivity and stability, the underlying reasons for differences in catalytic behaviors during FT synthesis are still unknown. Detailed catalyst characterization studies are needed to help explain catalytic results and provide basis for development of improved catalysts.

In order to gain better understanding of the role of pretreatment on catalyst performance during FT synthesis, we have examined the effect of various pretreatment conditions (reductant type, flow rate, temperature and duration of pretreatment) with three precipitated iron catalysts with nominal compositions: 100 Fe/0.3 Cu/0.8 K, 100 Fe/5 Cu/4.2 K/25 SiO<sub>2</sub> (Ruhrchemie catalyst which was used initially at SASOL in their commercial fixed bed reactors) and 100 Fe/5 Cu/4.2 K/16 SiO<sub>2</sub>. The catalysts were tested in fixed bed and stirred tank slurry reactors. Catalyst samples before and after the pretreatment were characterized by a variety of physico-chemical and instrumental techniques, such as: BET surface area and pore size distribution, X-ray powder diffraction (XRPD), Mössbauer effect spectroscopy (MES) and/or transmission electron microscopy (TEM). Catalyst samples withdrawn from the reactor during STSR tests and/or after FBR and STSR tests were characterized by XRPD and/or MES to determine bulk phases in the working catalyst. Results from these characterization and reaction studies are described in the following sections of this report.