of small amounts of Cu in the scrap iron that was dissolved (0.005 wt.%) were decisive for high catalytic activity (V-13). Initially soda and ammonia were used as precipitating agents but when it was learned that deviations of only as little as 0.1wt% K_2CO_3 (relative to Fe) could be a significant factor in the activity of the catalyst, precipitations were thereafter conducted with ammonia. This removed the uncertainty of the promotion by sodium carbonate, which is strongly retained by the iron hydroxide after washing. It was found that, in spite of the possibility of the formation of soluble ammonia-copper complexes, solutions containing up to 0.1 wt.% Cu could be precipitated with ammonia because of the highly surface-active ferric hydroxide retained a sufficient amount of the Cu (V-12). The use of ammonia, rather that soda, for precipitation permits washing to be effected with 40% less wash water. Better catalyst control was possible with continuous precipitation, in contrast to batch preparations. The use of a short residence time in the precipitation reactor and effecting filtration and washing quickly to prevent changes in the gel were desirable. The activity, selectivity, efficiency, lifetime, and the protection against carbon deposits are reported to be increased considerably if the ferric oxide catalyst is subjected to annealing at 250 to 350°C with air or oxygen following drying (V-12). Annealing was attributed to the formation of short-period lattice defects which decrease the crystallite size (V-14) and to shift the pore-frequency maximum to larger pore diameters (V-15).

Kölbel and Ralek (V-12) report that the ferric iron must be converted to the metallic bonding state before the catalyst can be put to use. Iron-carbon inclusion structures such as carbides have bonding states similar to that of metallic iron. The bonding state is obtained by: (1) treatment with CO, (2) with a CO/H_2 mixture, or (3) by consecutive treatment with CO and then H_2.

The reactor containing the catalyst/wax mixture was brought to a temperature 15 to 30°C above the final operating temperature as quickly as possible (V-12). The suspension was vigorously agitated with an inert gas (N_2, CO_2) at the final operating pressure (8 to 15 bar). When the desired temperature is reached, the system is suddenly switched from inert gas to synthesis gas ($H_2/CO = 0.67$ to 0.77; GHSV = 2,000). A "formation wave" sets in during the first few minutes and results initially in a high conversion of CO, indicated by the high CO_2 concentration in the exit gas stream, but this decreases in a short time, and then begins to slowly rise again. Eventually the CO_2 in the exit gas reaches a maximum and then decreases asymptotically to approach a limiting value. The process requires several hours to complete. The formation (activation) temperature depends on the activity of the catalyst as well as the product spectrum for which the catalyst was prepared. If the formation temperature is too high there is danger of "supercarbonization"; if it is too low the formation does not get started. In both cases, the catalyst activity is low.

V.3. U.S. BUREAU OF MINES WORK

The work on induction at the Bureau of Mines has been summarized in a number of publications (e.g., refs. V-16 - V-21). Schultz et al. (V-22) made a detailed comparison of the induction of a precipitated-iron catalyst and a fused-iron catalyst. The fused-iron catalyst was reduced in hydrogen and then converted to cementite by direct carburization using three methods. In the first method, the reduced catalyst was converted with CO so that 2/3rds of the iron was converted to Hägg carbide and helium was then passed over the mixture of Hägg carbide and iron for 2 hours at 475°C. The second approach involved treatment of the reduced catalyst with H_2:CO = 2:1 at a space velocity of 2,500 hr^{-1} at 310°C for 6 hours and then cooled in this gas mixture. In the third approach, pure methane was passed over the reduced catalyst at an hourly space velocity of 1,000 at 500°C for 4 hours and then cooled to room temperature in a flow of methane. Two procedures were used for the induction of the fused-iron catalyst to produce Hägg carbide. The first utilized the treatment of the reduced catalyst with CO at an hourly space velocity of 100 and progressively increasing the temperature from 150 to 350°C so as to maintain CO_2 content in the exit gas at about 20%. After about 20 hours sufficient carbon had been incorporated to correspond to Fe_2C. They reported that this procedure, if the freshly reduced catalyst was carbided at 325-350°C, would produce cementite, elemental carbon and magnetite in addition to the Hägg carbide. The second approach involved carbiding with a mixture comprised of H_2:CO = 1:4, with the temperature increased by steps, 12 hours at 200°C, 12 hours at 250°C and then 12 hours at 275°C.

Precipitated catalysts were inducted, without prior reduction, using a mixture of H_2:CO = 2:1 at an hourly space velocity of 2,500 at 310° and atmospheric pressure for 6 hours. This procedure produced predominantly Hägg carbide with an appreciable quantity of elemental carbon. Another procedure involved treating the unreduced catalyst with CO at an hourly space velocity of 100 and progressively increasing the temperature from 150 to 350°C so as to maintain CO_2 content in the exit gas at about 20%. Although the temperature required to maintain the 20% CO_2 in the exit gas did not exceed 250°C, an appreciable amount of carbides was not found in the catalyst. Treatment of the reduced catalyst by this procedure, with the temperature being increased from 185 to 300°C as required during 13 hours, produced largely Hägg carbide.

The precipitated catalyst was prepared for the above induction testing by precipitation from a hot aqueous solution of ferric nitrate (containing copper nitrate if used) by adding hot, aqueous sodium carbonate. The fused-iron catalyst was prepared by electrical fusion of iron oxide with the promoters.

The fused iron catalysts were D3001 (Fe,100:MgO,6.8:Si,0.9:Cr_2O_3,1.21:K_2O, 0.85) and D3008 (Fe,100:Al_2O_3,2.83:SiO_2,0.28:K_2O,1.39). For catalyst D3001, it appears that induction in CO only or a synthesis gas containing 80% CO produced a material with similar activity and stability but when the catalyst was used without an induction period it was less active and lost activity very rapidly (Figure V-5). When the

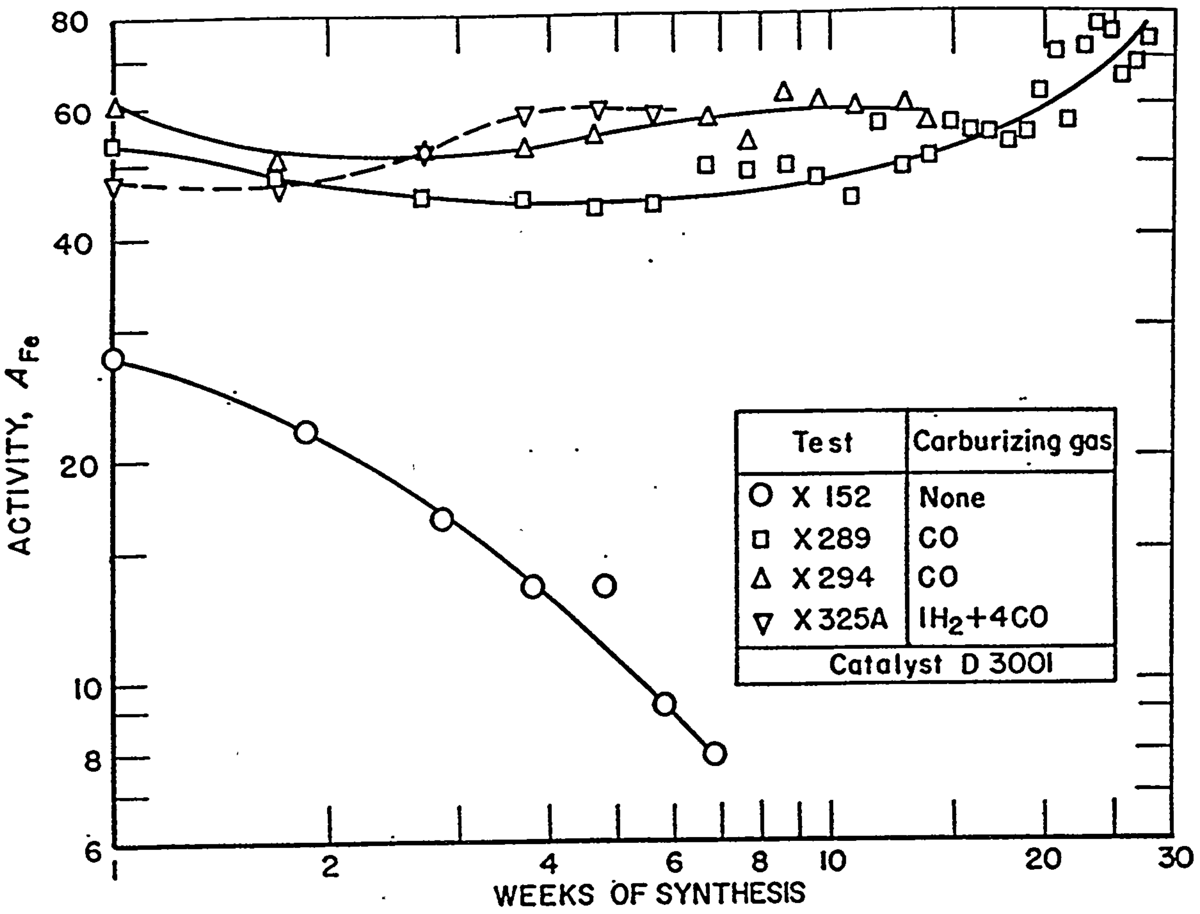

Figure V-5. Activity of reduced and carbided catalysts as a function of time for synthesis with $1H_2$ + 1CO gas at 7.8 atmospheres (from ref. V-22).

synthesis was conducted at 7.8 atm. the difference was much less when the synthesis was conducted at 21.4 atm. Starting with a catalyst containing essentially Hägg carbide, the catalyst was oxidized during synthesis with a mixture H_2:CO = 1:1 at 239°C and 11.1 atm as shown by the oxygen/iron ratio in Figure V-6; during this period the total carbon in the catalyst remained nearly constant but the fraction present as carbide decreased during the synthesis period. Similar results were obtained at other operating pressures; it appears that the oxidation occurs more rapidly and to a greater extent as the operating pressure is increased. Likewise, the oxidation occurs more rapidly and to a greater extent as the conversion is higher (Figure V-7). The activity and durability of this catalyst was also determined starting

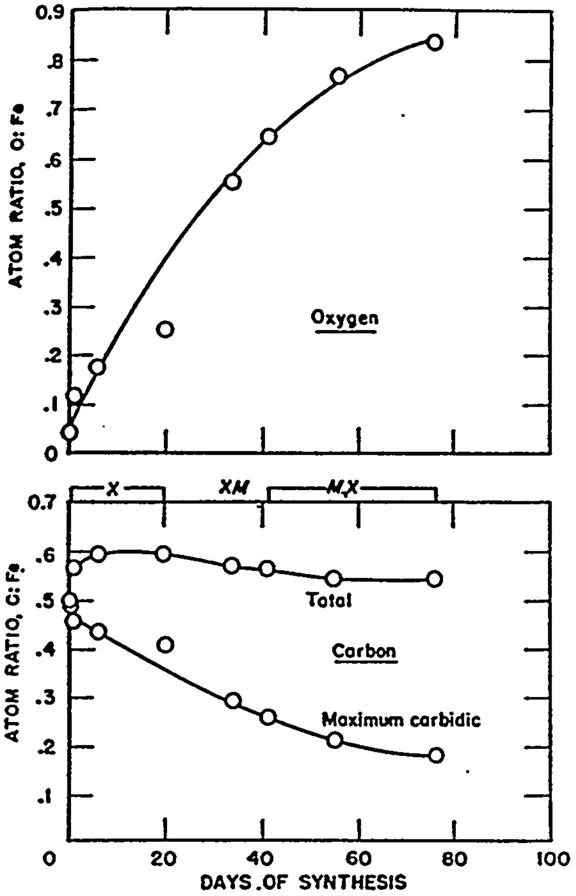

Figure V-6. Composition changes of carbided catalyst, D3001, in synthesis with $1H_2$ + 1CO gas at 11.1 atmospheres, text X408 (developed from data in from ref. V-22).

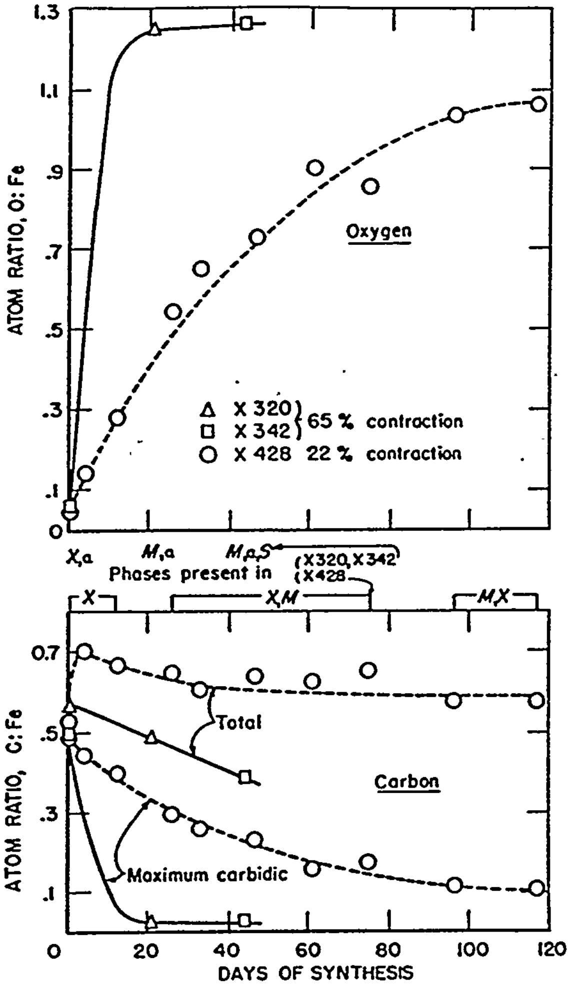

Figure V-7. Composition changes of carbided catalyst, D3001, in synthesis with $1H_2$ + 1CO gas at 21.4 atmospheres (from ref. V-22).

with a material that was primarily iron (α in Figure V-8), cementite (C in Figure V-8) or Hägg carbide (χ in Figure V-8) or a mixture of cementite and iron {method A involves induction of reduced catalyst with CO and method C utilizes induction of the reduced catalyst with methane}. It appears that, based on both initial activity and catalyst durability, Hägg carbide is the preferred component following induction.

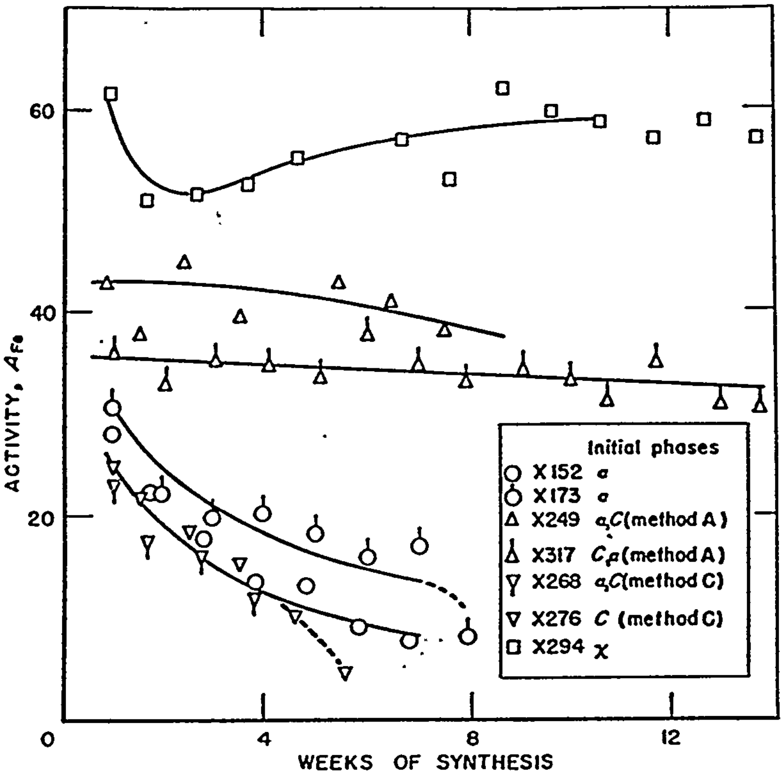

Figure V-8. Activities of reduced and carbided catalysts at 7.8 atmospheres as a function of time (from ref. V-22).

During the reduction with hydrogen of catalyst D3001 from 400 to 600°C, the external volume of the particles did not change. Reduction proceeded from the exterior to the center of the particle, and at any reduction temperature the surface area increased linearly with the extent of reduction up to about 90%. For reduction at 450°C, the average pore diameter varied from 30 to 35 nm, and increased slightly near 100% reduction.

Precipitated iron catalysts are usually high-area, small-pore gels of hematite or magnetite; however, treatment with hydrogen, synthesis gas or CO changes the pore geometry drastically. For example, in reduction with hydrogen the surface area of one catalyst decreased from 169 to 9 m^2/g. Serious sintering did not occur at 300°C in nitrogen, but in hydrogen serious sintering occurred at 250°C. The sintering occurred in hydrogen even though reduction at 250°C resulted in producing magnetite, and not

Fe. Following reduction, the porosity was larger than that of the raw catalyst but the mechanical strength of the reduced or carburized samples was low (V-23).

A precipitated catalyst (P3003.24;Fe,100:Cu,10:K_2CO_3,0.5) was also inducted and tested as the fused-iron catalyst described above. No correlation was found between the carbide content of the used catalyst and activity or selectivity. Catalysts containing the largest quantities of elemental carbon had the highest activity, and those containing the larger amounts of oxide yielded products of the higher molecular weight. The induction procedure described by Ackermann (V-24), which involves pretreatment with a mixture of H_2:CO = 2:1 that was utilized by Kölbel, produced the most active conventional iron catalysts that had been tested at the Bureau of Mines to1963; these catalysts produced high yields of hydrocarbons at temperatures less than 200°C (V-22). **Apparently pretreatment of the oxide under conditions that deposit substantial quantities of elemental carbon in the catalyst is required for preparing precipitated catalysts of high activity.** This carburization step would probably adversely affect the mechanical properties of the catalyst, but Schultz et al. (V-22) did not observe difficulties using this catalyst in a fixed bed reactor. Catalysts that were reduced in hydrogen as part of their pretreatment yielded products containing lower amounts of wax and higher amounts of gaseous hydrocarbons than the catalysts treated directly with CO or with synthesis gas. The catalysts that were pretreated only with CO or synthesis gas contained the largest amounts of oxygen after use in the synthesis, and these catalysts yielded the products of higher molecular weight, despite the presence or absence of substantial quantities of Fe_2C carbides.

Shultz et al. (V-25) compared the compositional changes of massive iron and fused iron oxide catalysts during the Fischer-Tropsch Synthesis. The fused iron oxide catalyst was the D3001 catalyst described above and the massive iron catalyst was steel lathe turnings (SAE 1018 steel lathe turnings L2201, approximate dimensions 8x3x0.4 mm, oxidized with steam at 600°C to convert 24.6% of the iron to magnetite and then impregnated with potassium carbonate solution to give 0.13 wt.% K_2O). Both catalysts were reduced in hydrogen at 450°C and then exposed to a H_2:CO = 1:1 synthesis gas mixture at 21.4 atm and an hourly space velocity of 300 for 9 days. The fused iron catalyst was tested at 260°C during the entire period but the massive iron catalyst had an activity which was too low; thus, the temperature was increased to 286°C and the activity increased so that it had sufficient activity at the end of nine days to operate at 268°C. The surface area of the massive iron catalyst, after use in synthesis and extraction of adsorbed hydrocarbons, was slightly larger than the original reduced catalyst, 0.45 and 0.54 m^2/g, respectively. Hägg carbide was the principal phase in the activated layer, and the catalyst was not extensively oxidized. The fused iron oxide catalyst was about 75% oxidized during the 9 days of synthesis, and magnetite was the principal phase. The surface area of the fused iron catalyst, after extraction of adsorbed hydrocarbons, had decreased to about 7% of its original value (14.8 and 0.75-1.0 m^2/g, respectively). The significant difference between the two types of catalysts is that the entire particles of the fused iron oxide catalyst are activated by reduction, whereas massive iron catalysts have only a thin layer, about 0.1 mm, of active material on a core of massive iron. These authors contend that the pores of the catalysts are filled with wax even at the synthesis reaction temperature (V-26). The rate of diffusion of H_2 and CO in the liquid-filled pores is considered to be slow with respect to the rate of the synthesis reaction. If this is correct, the inner portion of the particles of the fused iron oxide catalyst is exposed to high ratios of

H_2O/H_2 and CO_2/CO, and this strong oxidizing atmosphere results in the oxidation to magnetite. A basis for this consideration is that the composition of the particles at the top to the bottom of the fixed bed reactor do not differ significantly; if the oxidation depended primarily on the bulk gas composition the particles at the bottom of the reactor should be oxidized to a much greater extent than those at the top of the reactor where the conversion is low. The massive catalyst was not oxidized severely during synthesis, but the carbon content of the activated layer exceeded that of Fe_2C. The presence of finely divided elemental carbon was considered to be a possible explanation for the slight increase in surface area for this catalyst. Hägg carbide with possible traces of cementite were the only phases identified in the activated layer.

The Bureau of Mines investigated a moving bed process; this process utilized an oil and depended upon the oil recirculation to maintain a suspension of the fused-iron catalyst. Crowell et al. (V-27) emphasized the importance of bringing a fresh catalyst on stream properly which was also stressed by many German investigators (V-28). To a large extent, the catalyst activity and ultimate catalyst life are determined by the method of inducing the catalyst. Conditions for the optimum induction procedure for the submerged bed system were still being investigated at the Bureau of Mines at the time the report was written. The method of induction employed in the experiments reported below was as follows. The catalyst (an iron synthetic ammonia type (Fe_3O_4,93.51%:MgO,4.61%:Cr_2O_3,0.65%:Mn_3O_4,0.03%:K_2O,0.56%:SiO_2,0.64%)) was reduced by substantially dry hydrogen in a separate unit. Operating conditions for the reduction were: 450°C; atm. pressure; 48-72 hours; total space velocity per hour, 2000; hydrogen linear velocity, ft./sec., 1.8; moisture content of fresh feed hydrogen, g/cu. meter, 0.3-0.4; the gas contained about 0.6% nitrogen and 0.2%

oxygen with traces of CO and CO_2. Following the reduction of the catalyst, it was stored under CO_2.

The cooling oil was charged to the proper level in the convertor through which a nitrogen flow was being maintained. Then the catalyst, which had been stored under CO_2, was added, the convertor was sealed, and the oil circulation rate was adjusted to the required value. The nitrogen flow was then interrupted, and the normal flow rate of synthesis gas was set at a space velocity per hour of 600 for moving bed experiments and 300 for fixed bed experiments (based on the volume of the settled bed). After the system was purged of nitrogen by the incoming synthesis gas, the unit was brought up to full operating pressure (usually 300 pounds per square inch gauge), and recycling of tail gas was started. Heat was then applied at the circulating oil. A stepwise induction procedure was pursued in which the convertor temperature was steadily raised from an initial conversion temperature of about 150°C until a 30% conversion of the synthesis gas was reached (around 210°C); this conversion was held for 24 hours. In a like manner the conversion was further raised to and maintained for 24 hours at 45 and 60% levels, respectively, by increasing the operating temperature in the required steps. Continuing this schedule, there was attained on the fourth day, a normal synthesis gas conversion of 70%, which was held for the duration of the test. During one experiment with a moving bed, the induction was carried out as follows in Table V-3:

Table V-3

Induction of a Fused Iron Catalyst (from ref. V-27)

Date	H_2 + CO Conversion, %	Average Temp., °C	Temp. Differential, °C
May 18, 1949	30.8	213	4
May 19, 1949	46.3	226	5
May 20, 1949	59.6	235	6
May 21, 1949	67.9	239	7

The Bureau of Mines operated an oil-circulation process (V-23). A pilot plant with a 3" i.d. x 8' bed height operated successfully only when the entire catalyst charge was submerged in oil. Pelleted precipitated iron catalysts disintegrated and the fines caused considerable pressure drop after only a few weeks of operation; thus, a fused, synthetic ammonia type iron oxide catalyst was used.

The Bureau of Mines (V-23) operated a slurry process using a 3"i.d.x10' high slurry (about 15 liters). A precipitated Fe_2O_3-CuO-K_2CO_3 catalyst was used. The most reproducible pretreatment utilized synthesis gas at atmospheric pressure and 270°C. No appreciable synthesis took place, but carbon dioxide was formed by reduction of the oxides and carburization. During synthesis at 100 to 300 psi and hourly space velocities of 100 to 300 volumes of gas per volume of slurry in the reactor, 65-70% of gas was converted at about 270°C. It was found that catalyst concentrations of 50 to 500 grams of iron per liter of slurry are operable.

A demonstration plant was operated at Louisiana, Missouri during 1950-53 (V-23). The catalyst was prepared from mill scale with smaller amounts of magnesia and potash and was fused prior to reduction in hydrogen. The process utilized a reactor with the catalyst immersed in oil, with an expanded bed of 4-10 mesh catalyst particles. The catalyst was inducted by raising the temperature from about 221°C by 11-14° C each day over a 5-day period; during this period the conversion of the synthesis gas increased from 10 to more than 70%. Catalyst spalling resulted in up to 25 wt.% fines in the coolant oil so that the process was a combination of slurry-expanded bed operation. Up to 10 wt.% fines enhanced the activity but higher concentrations caused problems with pumps.

Zarochak and McDonald (V-29) focused on the effects of pretreatment of a precipitated iron F-T catalyst on the synthesis behavior. They utilized a catalyst that contained Cu and K. Catalyst activity and selectivity were followed with time on stream and catalysts, withdrawn at intervals from the reactor, were characterized. Two pretreatment samples were utilized: "induced" catalysts were exposed to a flow of 1/1 H_2/CO at 533 K and 200 psig throughout the entire history of the run and "CO-pretreated" catalyst was exposed to a flow of CO at 553 K and 200 psig for 24 hours before exposure to synthesis condition. Catalyst characterization using Mössbauer spectroscopy revealed that the calcined starting catalyst was α-Fe_2O_3. During 24 hours pretreatment in CO, the catalyst was essentially completely reduced/carbided to χ-carbide, with only traces of Fe_3O_4 visible in the Mössbauer spectrum. After only 24 hours on synthesis gas, the carbide phase was diminished, with a corresponding increase in the Fe_3O_4 phase. During the next 48 hours, more oxidation to Fe_3O_4, with a corresponding decrease in the carbide phase, occurred but no further changes were noticed during the next 238 hours of synthesis. The induced catalyst, after 24 hours of exposure to the synthesis gas, was mainly the hexagonal ϵ'-carbide, with small amounts of χ-carbide and Fe_3O_4. After 479 more hours exposure to synthesis gas, the Fe_3O_4 phase had completely disappeared and the catalyst was completely carbided.

Zarochak and McDonald (V-29) reported activity and selectivity data for catalysts that had been inducted and CO-pretreated during time on stream. For the induced catalyst, hydrogen and CO conversions were initially substantial but declined threefold during 400 hours on stream. They (V-29) reported that the induced catalyst had slightly lower initial activity than the CO-pretreated catalyst and deactivated much more rapidly. In contrast, the initial activity for the CO-pretreated catalyst was strikingly high, with both CO and hydrogen conversions approaching the maximum achievable. Furthermore, the activity declined slowly with time on stream. At early periods of the run with the CO-pretreated catalyst, the selectivity favored light hydrocarbons but this shifted over time to heavier, more olefinic products. The initially high selectivity for light hydrocarbons was attributed to the high conversions, which produced an H_2/CO ratio greater than 6/1 in the CSTR. The large amounts of water produced at these high conversions were responsible for the oxidation of the catalyst. However, oxidation of the CO-pretreated catalyst did not produce any dramatic effects on the catalyst activity.

Baltrus et al. (V-30) examined samples of the above catalyst following a CO-pretreatment or the "inducement" in syngas using XPS, Auger spectroscopy and ISS. They followed the changes in surface speciation of iron and carbon, and the distribution of K and Cu on exposure to the various pretreatment conditions. The transformation of the surface from Fe_2O_3 to Fe_3O_4 to iron carbide was enhanced by pretreating the catalyst with H_2/CO compared to CO only, and was retarded by the addition of water vapor to the pretreatment gas. Peaks due to K, Cu and Fe were not observed in the ISS spectrum after the catalyst was exposed to either CO or H_2/CO mixture for only 1 hr. *in situ* in the preparation chamber of the instrument. The authors attributed this to the immediate build-up of a carbonaceous layer on the catalyst surface. When the catalyst was reduced in hydrogen at 533 and 673 K for 1 hr. the surface concentration of K relative to Fe increased, and the increase was more pronounced at the higher temperature. Whereas the K increased concentration was within the first few angstroms of the surface, the concentration of copper increased just below the first few angstroms. The Auger data show that graphitic carbon represents a large fraction of the surface carbon on the surface of the catalysts pretreated in the preparation chamber of the instrument. Comparing the relative proportions of the graphitic to the carbidic carbon showed that the CO-pretreated catalyst had a slightly greater proportion of carbidic surface carbon. The authors observed an increase in the hydrocarbon species on the surface of the catalyst, especially those exposed to H_2/CO, at longer pretreatment times were correlated with the increase in the fraction of K on the catalyst surface. Potassium has been shown to promote hydrocarbon growth (V-31). Furthermore, the data was consistent with the observation that the migration of K to the surface of iron catalysts occurs in a H_2/CO atmosphere (V-32), and can be attributed to the reducing nature of the pretreatment gas (V-33). Baltrus et al. (V-30) reported that, due to its low concentration, the behavior and effects of the copper promoter, other than being fully reduced, could not be defined during the pretreatment process.

V.4. OPERATION AT SASOL

For the fluid-bed operation, an ammonia-synthesis-type catalyst was used at SASOL (V-34). The catalyst is manufactured by melting natural magnetite in an electric furnace with the required additives (V-35). **It is reported that the composition of the catalyst is highly critical in regard to conversion activity, stability and product selectivity.** Various structural promoters (alumina, MgO, etc.) may be used together with alkali (usually potassium carbonate). This catalyst may be improved by other acidic additives. It is reported that the optimum composition for each catalyst can be partially predicted from the surface and chemisorptive properties of the system in the reduced state. The conditioning treatment consists of crushing and sizing, almost completely reducing with hydrogen, and then subjecting to a pretreatment. The reduced-iron catalyst is converted during the synthesis into a mixture of metallic iron, iron carbides, and magnetite (Figure V-9, ref. V-36).

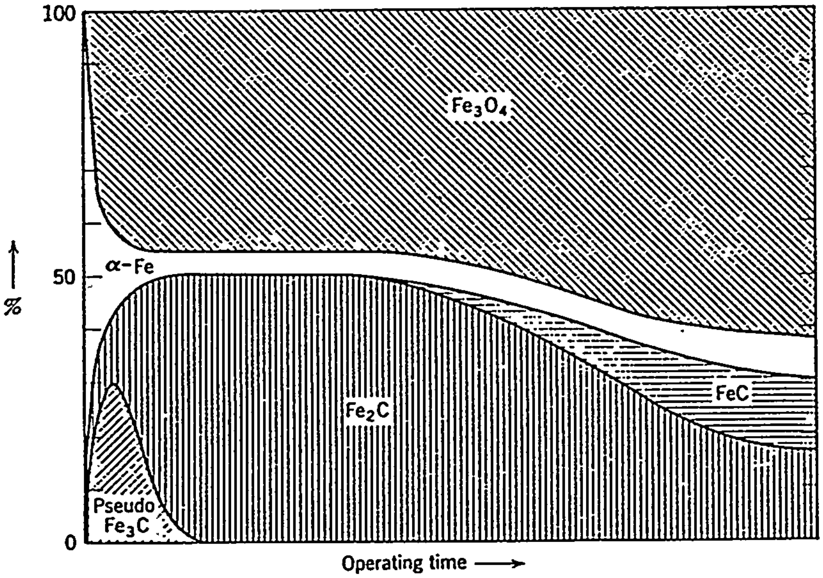

Figure V-9. Change of catalyst with time (from ref. V-36).

The fixed-bed synthesis catalyst is prepared by precipitation from a nitrate solution by the addition of sodium carbonate. Copper and potassium promoters are added to the catalyst. The catalyst is partly reduced before using it for synthesis (V-34).

Dry (V-37) reported very informative data on catalyst changes during use in commercial operation at low temperatures in fixed bed reactors and high temperature fluidized bed reactors. Full length commercial tube units were run at low temperatures for different times and then carefully unloaded to provide about 20 samples for analysis. Each sample was analyzed and activity and wax selectivity was determined using laboratory reactors under fixed test conditions. The activity, selectivity and surface area/pore volume are shown in Figures V-10, V-11 and V-12, respectively. The activity declines more rapidly at the end of the reactor than in the center. Analysis of the catalyst indicated that the decline at the entry was probably due to sulfur poisoning.

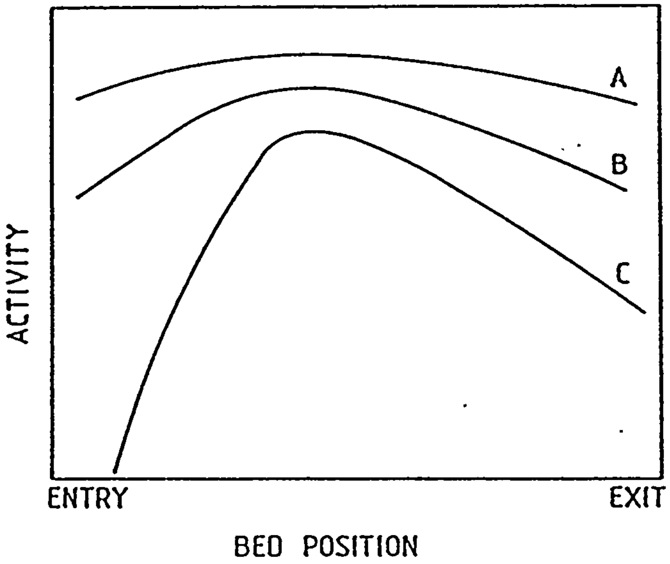

Figure V-10. Fischer-Tropsch activity profiles of catalysts along the length of the bed. The time-on-stream increases from A to B to C (from ref. V-37).

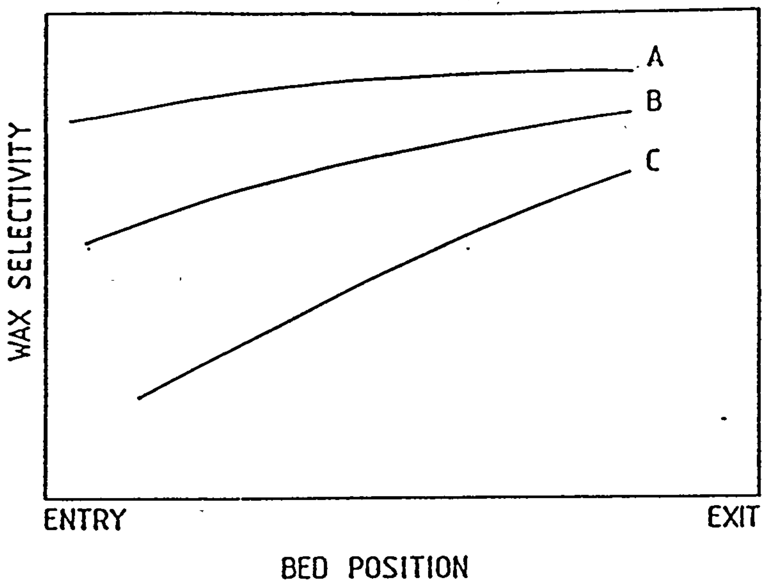

Figure V-11. Wax selectivity of catalysts sampled from different bed positions. The age of catalysts increase from A to B to C (from ref. V-37).

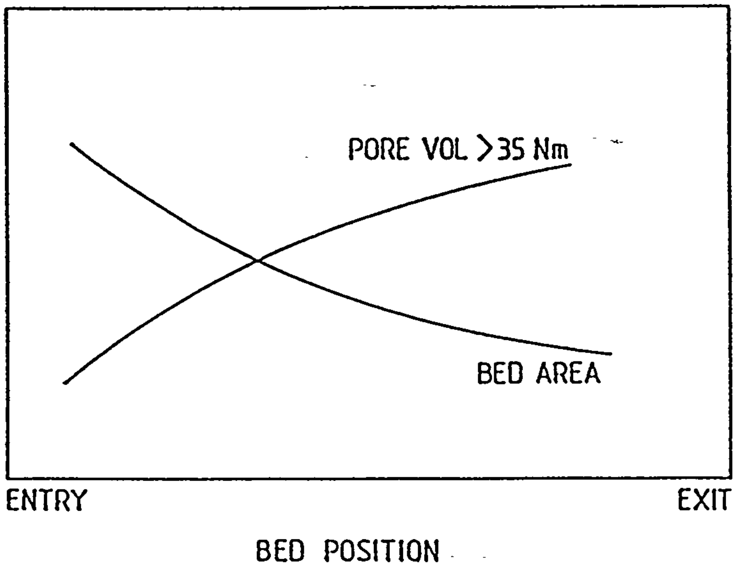

Figure V-12. The changes in surface areas and pore volume of an aged catalyst taken from different bed positions (from ref. V-37).

The crystallinity of the active iron carbide phase changed in the same direction as the magnetite phase but the carbide peaks were in general more diffuse. The activities and selectivities of the young catalyst did not depend upon the bed position, indicating that the induction procedure did not damage the catalyst. In this case, induction involved pre-reducing the catalyst in hydrogen and taking this material to full synthesis conditions using a procedure that was not specified. XRD peaks were not detected for the young catalyst samples, indicating only very small crystallites were present.

Following exhaustive solvent extraction, BET surface areas were measured. The surface area progressively decreases from the entry to the exit, and the pore volume that was present in pores greater than 35 nm increased in the opposite direction. XRD crystallite size increased from entry to exit, as did the extent of oxidation. The loss in activity with time at the exit of the reactor is presumed to be due to loss of surface area.

For low temperature fixed bed iron catalysts the parameters influencing selectivity are the H_2/CO ratio in the reactor, the temperature and the basicity of the catalyst. Since the first two were fixed, the change in selectivity was presumably due to change in catalyst basicity with time. This decrease may be partly due to migration of potassium under the operating conditions and due to loss of the finer catalyst particles; however, it is likely that carbon deposition led to the reduction in basicity .

Under the high temperature conditions, the Boudouard CO decomposition reaction occurs readily so that after several weeks there was, on an atomic basis, twice as much carbon as iron present in the catalyst. However, in spite of the massive deposition of carbon, the decrease in conversion was relatively small. If the fines are not lost, the deposition of carbon increases the bed volume so that there may actually be an increase in conversion. The implication is that Boudouard carbon does not impact the performance decline with time in a major fashion.

Analysis of the small and large catalyst particles led to the model for the catalyst shown in Figure V-13. Thus, the large particles have a core of Fe_3O_4 that is surrounded by a layer of iron carbide. Small particles, on the other hand, are essentially iron carbide. This is explained as being due to the depletion of CO and H_2 in the interior of the large catalyst pellet due to the synthesis reaction; thus, the water and carbon dioxide products are present in high concentration in the core of the pellet and provide an oxidizing atmosphere.

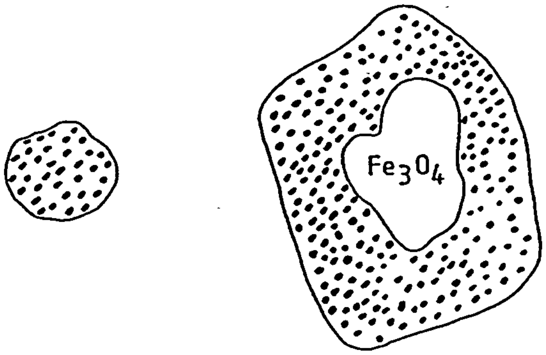

Figure V-13. Illustration of polished cross sections of small and large aged catalyst particles taken from a high temperature Fischer-Tropsch reactor. The black dots represent iron carbide particles embedded in a matrix of carbon. The core of the large particle consists only of magnetite (from ref. V-37).

V.5. Other Large Plants

A fixed, fluidized-bed process was utilized for the commercial Hydrocol plant at Brownsville, Texas. Iron ore or millscale obtained from steel-mill rolling operations was used as the raw material for catalyst preparation for this operation. The catalyst, containing about 1 wt% K_2CO_3 added by impregnation, was reduced under fluidizing conditions with dry hydrogen at 350-400°C.

A catalyst pretreated in hydrogen at 300°C or above may initially have iron present in the metallic state; however, the iron converts rapidly to carbidic phases and/or oxides when exposed to syngas under reaction conditions (V-38 - V-42). An oxidic catalyst that is pretreated in CO or directly exposed to syngas may be converted from Fe_2O_3 to low valent oxides or carbides (V-43, V-44). In these cases, the composition of the iron phases changes with pretreatment and reaction time (V-10, V-45, V-46). It has been reported that pretreatment in CO results in a better catalyst than one pretreated in hydrogen (V-10, V-46). Many studies have aimed at defining the active iron phase by correlating the structure of the catalyst to the Fischer-Tropsch Synthesis activity (V-38, V-39, V-42, V-45, V-47 - V-50). However, there is no clear consensus as to which phase provides the superior activity (V-10, V-46). Unfortunately, much of the more recent work has been conducted with supported catalysts that have been utilized only at low CO conversion levels. These low conversion levels mean that the catalyst is exposed to reducing conditions that are not representative of high conversion conditions. It is therefore not surprising that most of the recent results have shown that iron is present predominantly as a carbide phase following exposure to synthesis conditions.

A slurry-phase Fischer-Tropsch Synthesis pilot plant sized to produce 70-100 gallons of product/day was designed and operated in England by D.S.I.R. during the late 1950s-early 1960s (V-51, V-52). Fourteen runs were made, each consisting of activation of the catalyst followed by synthesis. The catalyst used for all runs was a precipitated iron oxide incorporating small amounts of potassium (1.25% K_2O) and copper oxide (1% Cu) as promoters. No investigations were made on the pilot plant level to compare different methods of activation of the catalyst. A standard method was employed which gave a consistently high catalytic activity under conditions that were reported to produce both high and low molecular weight compounds. The catalyst was suspended in wax of a high molecular weight. The catalyst suspension was pretreated in the reactor with synthesis gas (H_2/CO varied between 0.6 and 1.2 for the runs) at atmospheric pressure by raising the temperature to 285°C, maintaining this temperature for approximately 1 hr., then cooling to 200°C before pressurizing to obtain synthesis conditions. A minimum hourly space velocity was utilized to ensure that water and CO_2 were effectively removed from the reactor in order to prevent reoxidation of the catalyst. A typical run showed the chemical changes outlined in Figure V-14 during the pretreatment. It appears that the only significant reaction

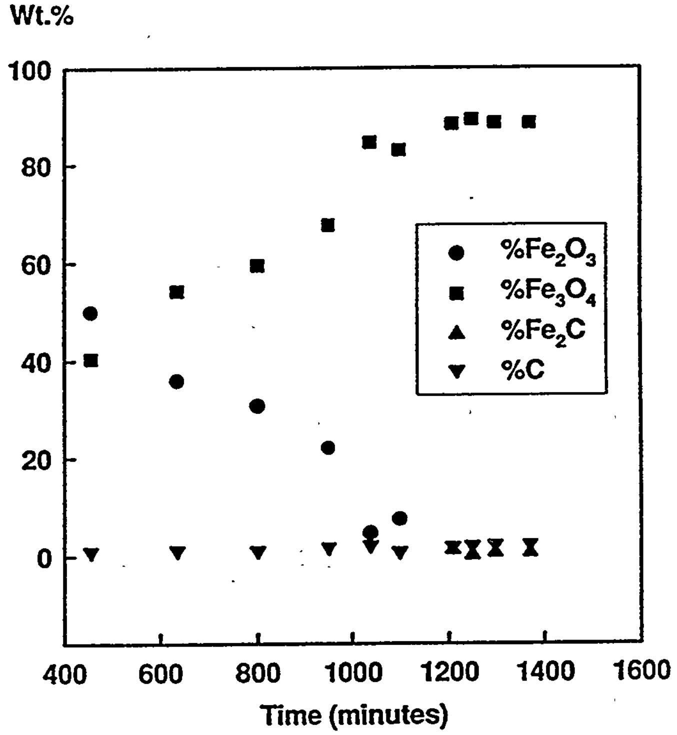

Figure V-14. Calculated compositional changes (wax free) phase activtaion at 1 atm. pressure in H_2/CO (see text) (from ref. V-51).

effected during the pretreatment was the reduction of the Fe_2O_3 to Fe_3O_4. The activity and catalyst composition changed appreciably during the synthesis run that was given in the reference (Figure V-15). Initially the activity was high for synthesis at 260°C but

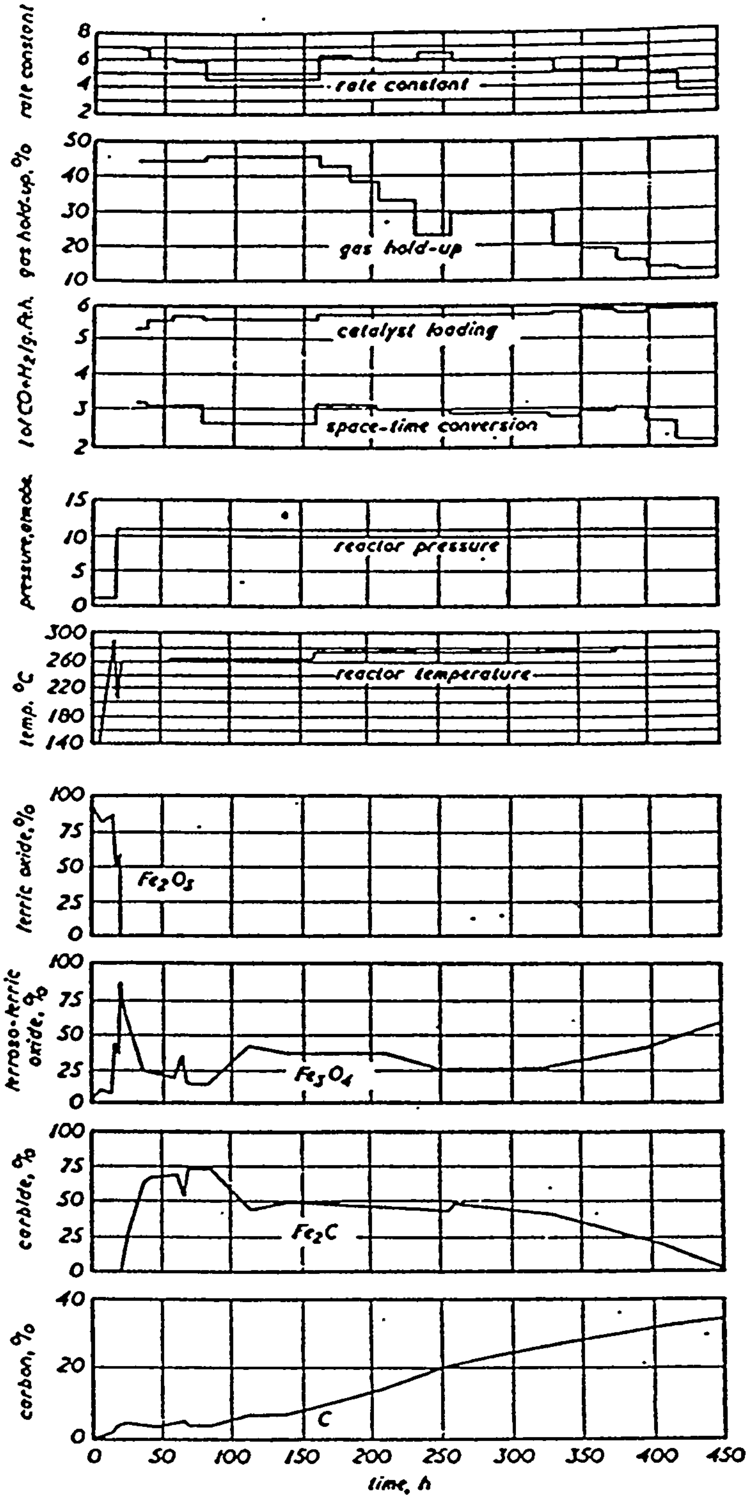

Figure V-15. Changes in performance, operating conditions, and analysis of solids in reactor during run 14 (final run) at the England slurry phase pilot plant (from ref. V-51).

it declined rapidly. The resulting fall in activity, as measured by the rate constant, coincided with loss of catalyst during the initial stages of the operation. There was essentially no loss in the space-time conversion, based upon the catalyst remaining in the reactor. There was a marked decrease in performance upon raising the reaction temperature to 280°C, and the authors associated this with the formation of free carbon. Samples of the slurry were taken and the wax removed by extraction from the catalyst that was collected. The catalyst composition changed due to oxidation with a corresponding decrease in the carbide phase; the fall in activity, indicated by the rate constant, paralleled the decrease in the carbide phase. The authors attributed the oxidation to an increase in the partial pressure of the water vapour.

V.6. Recent Literature Reports

Huang et al. (V-53) carried out induction and synthesis in an autoclave reactor that permitted the withdrawal of catalyst samples during the study period. Induction followed one of the following three options: (1) treatment with CO followed by exposure to synthesis gas, (2) treatment with H_2 followed by exposure to synthesis gas and (3) exposure to synthesis gas without a prior treatment. The catalyst utilized in these studies was an ultrafine (300 m^2/g surface area; 3.0 nm spherical particles) iron oxide. The XRD data indicated that Fe_3O_4 was the only crystalline phase present for the catalyst at the point of maximum activity, and that this does not depend upon the gas used for the activation. This result implied that Fe_3O_4 was the active phase, or that the active phase cannot be detected by XRD. However, the fact that, after 2 hours in syngas, the Fe_2O_3 had already been transformed completely into Fe_3O_4 and that this material showed only minimum activity while a Fe_3O_4 phase that was observed for the catalyst activated in hydrogen for 24 hours showed a much higher activity, indicated that bulk Fe_3O_4 is not likely to be representative of the active surface phase for CO hydrogenation. Furthermore, at maximum activity, the particle size of Fe_3O_4 for the catalyst activated in CO was 74% of that of the catalyst activated in hydrogen but the CO conversion of the CO pretreated catalyst was three times that of the catalyst activated in hydrogen. Therefore, the presence of an active surface phase that is supported on the Fe_3O_4 is likely to be the active catalyst. Independent of the catalyst activation, similar methane and CO_2 selectivities are obtained; this suggests that the active catalytic phase is the same for the three pretreatments. Mössbauer spectroscopy measurements of the catalysts showed that pretreatment in CO for 24 hours at 260°C and 8 atm almost completely converted the ultrafine oxide to iron carbide (V-54). A similar pretreatment with hydrogen resulted in the reduction of about 33% of the iron to the metallic state with the remaining 67% being present as Fe_3O_4. Exposure of the CO pretreated catalyst to a H_2:CO = 1:1 synthesis gas resulted in the gradual reoxidation of the carbides to Fe_3O_4. During the first 2 hours of exposure of the hydrogen pretreated sample to synthesis gas, the metallic iron was converted to iron carbides. Further exposure of the hydrogen pretreatment sample to synthesis gas did not result in a composition change of the catalyst. It is concluded therefore that iron carbides with different oxidation characteristics were formed during the pretreatment with CO and the contact of the reduced catalyst with synthesis gas.

Sancier et al. (V-55) conducted carburization studies of two promoted fused iron oxide catalysts. Examples of the change of phases during carburization in a synthesis gas are shown in Figure V-16 with the temperature program and weight gains shown in Figure V-17. These authors indicate that in a syngas mixture Fe_3C is