

Figure V-16. Ferromagnetic phases in catalyst B-6 during carburization. H_2/CO (3/1) at 1 atm.; for temperature see Figure V-15 (from ref. V-55).

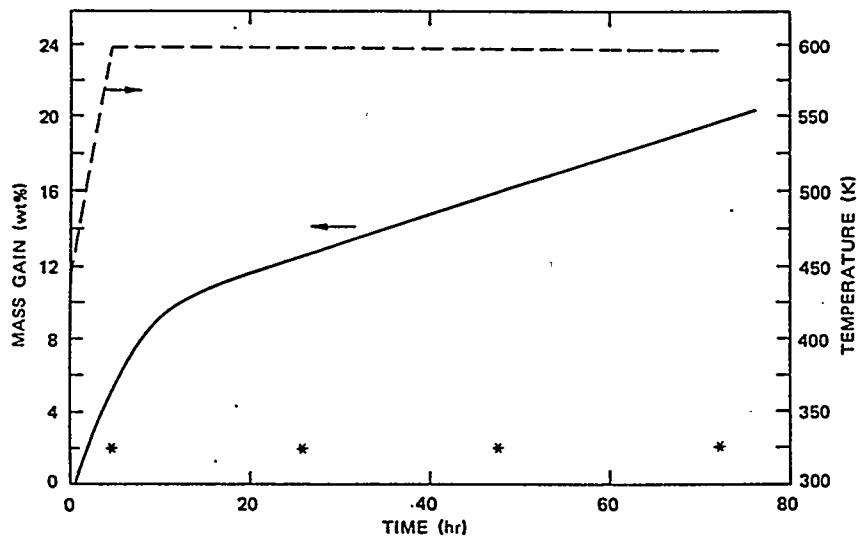


Figure V-17. Mass gain during carburization of catalyst B-6 in H_2/CO (3/1) at 1 atm. Asterisk (*) indicates time at which thermomagnetic analysis was made (from ref. V-55).

either formed in parallel with Hägg carbide or is formed as an intermediate which then transforms to Hägg carbide; however, the Fe_3C approaches a maximum as the temperature approaches the isothermal temperature region of 600K (377°C). These results are not consistent with those described above where the carburization of iron was carried out in CO. This implies that different carburization routes are followed in CO and in the synthesis gas. These authors obtained parabolic rates for the carburization suggesting that the carburization proceeded in two distinct diffusion-limited regimes.

Lohrengel et al. (V-56) compared the impact of calcination upon the subsequent activity and selectivity of the catalyst. Portions of a precipitated iron catalyst, containing manganese, zinc, copper and potassium, were calcined at 300 or 500°C. The surface area (12-14 m^2/g) and the porosity of the two materials were essentially the same following calcination. These surface areas are very low for a material prepared by a precipitation method. The material calcined at 300°C was 5-10 times more active than the material calcined at 500°C but was much less selective towards the formation of olefins and short-chain hydrocarbons.

Butt (V-57) recently reviewed the carbide phases of iron-based Fischer-Tropsch Synthesis catalysts. He stated that "The results of a considerable amount of work on iron catalysts can be summarized rather compactly. Such catalysts in all forms (precipitated, fused and supported) are rather readily converted to one or more carbides under FT reaction conditions ..." For bulk and supported iron catalysts the carbides formed are a mixture of ϵ' - Fe_{22}C and χ - Fe_5C_2 phases (V-58). Butt reports that for supported iron the carbide phase is formed over a relatively short period of time, and the accompanying change in activity is significant for a supported iron

catalyst (4.94% Fe on SiO₂ with 8.1% exposed Fe following hydrogen reduction

(Figure V-18) (V-59).

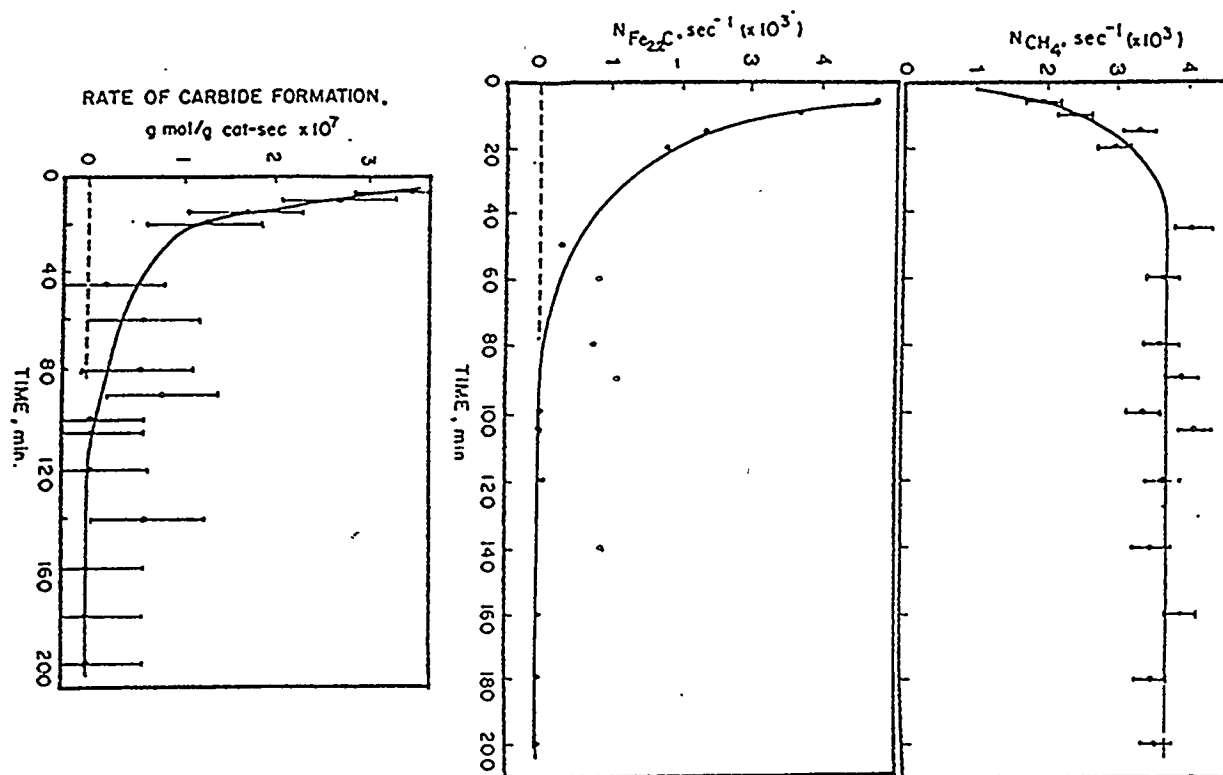


Figure V-18. Change in activity and rate of carbide formation in a supported iron catalyst. $T = 225^{\circ}C$, $CO/H_2 = 1/3$ (from ref. V-57).

Butt (V-57) points out that Mössbauer spectroscopy is a preferred technique for the determination of the iron carbide phases that are present since the iron position and stoichiometry varies little from one phase to another. Butt reports that it has taken some time to obtain agreement that the carbide phase formed on supported Fe is primarily ϵ' -Fe_{2.2}C. At the same time, Butt offers the caution that this conclusion is attained only following a long line of qualifiers. Most of the data to support the presence of the ϵ' -Fe_{2.2}C were obtained at low total conversions of CO, at atmospheric pressure, moderate temperatures (150-300°C) and a molar feed stoichiometry of 1/3 CO/H₂. Butt reported that K (Fe/K= ca. 55) and Fe/Cu catalysts

carborized completely upon exposure to reactants ($\text{CO}/\text{H}_2 = 1/3$) at 250°C for 3 hours. More surprising, K and Cu had no detectable effect on the kinetics of carburization or the structure of the carbide that was formed.

Kuivila et al. (V-60), following Dwyer and Hardenbergh (V-48, V-61) utilized XPS and Auger spectroscopy to define the forms of iron present on the surface of a catalyst. The behavior of both prereduced and unreduced iron catalysts indicated that carbide phases were formed within the surface region of Fe foils under Fischer-Tropsch conditions. For the reduced sample, the carbide fraction increases for 15 hours and then remains constant; the turnover number for CO conversion shows an increase that parallels that of the formation of iron carbide. The increase of graphitic carbon at longer reaction times, however, has little influence on the overall synthesis activity. For the unreduced sample, it was observed that the oxide possesses CO conversion activity that increased slightly with time. The XPS data indicated a partial reduction to divalent iron but no discernible XPS contributions for metallic iron or carbide was possible. Carbon XPS indicated graphitic carbon was present but not carbon of a carbide form. Butt therefore concluded that quite active catalysts can be produced that contain carbide phases as, at most, minor components. FT activity has been reported for Fe_3O_4 (V-62) but this has been disputed by others (V-63). Butt summarized the situation as "the initial activation of reduced iron seems directly correlated with the formation of a carbide phase, but it can be argued with reason that this is more a promotion than a geometric (that is, site formation) effect. The majority of the evidence both from characterization and reaction studies points to the role of carbide phases as involved spectators who have an indirect influence on the outcome of the game."

Soled et al. (V-64) report that catalysts that contain mainly oxidic phases or carbides with large concentrations of excess "matrix carbon" favor secondary reactions to form alkanes in contrast to the primary products, α -olefins. The relative concentrations of oxide and carbide phases depends on the ease of reduction of the catalyst, which can be changed by cation substitutions. For example, cobalt substitution into Fe_3O_4 lowered the reduction temperature by 20°C . When excess carbon was introduced into carbide catalysts prepared by laser synthesis, paraffin selectivity increased. These authors reported that reaction environment can also control catalyst composition and selectivity; thus the oxide/carbide phase determined by Mössbauer spectroscopy for the spent catalysts are sensitive to the extent of backmixing. In an integral fixed bed reactor, carbide phases are present in the front of the bed but show increasing amounts of oxide near the exit. Catalysts utilized in a stirred tank reactor remain all carbides.

Bukur *et al.* (V-65) has conducted activation studies on a Cu and K promoted precipitated iron catalyst (100Fe/3Cu/0.2K, parts per weight) used in the Fischer-Tropsch Synthesis in a fixed bed reactor at 250°C , 1.48 MPa, 2 nL/h-g catalyst and $\text{H}_2/\text{CO}=1.0$. Pretreatment type, (CO, H_2 , or syngas), temperature (250, 280 or 310°C), pressure (0.1 or 1.48 MPa) and duration (8 or 24 hours) were varied.

All runs utilizing CO pretreatment gave high activity ranging from 87-97% CO conversion during the first 2 hours at process conditions; however, the best stability was obtained when the catalyst was pretreated at 280°C for 24 hr or 250°C for 8 hr at 0.1 MPa. Activation in CO at 250°C for 24 hr showed the least stability for all of the CO activated runs; the activity decreased to 56% CO conversion within 91 hr of synthesis. It was found that activation at high temperature when the 8 hr pretreatment

was used gave the best olefin and α -olefin selectivity and decreased the amount of methane and C₂-C₄ hydrocarbons. In contrast the high temperature activation for 24 hr gave the same selectivities as the low temperature activation; however, the stability was highest when the activation was conducted at high temperature. In general, it was found that pretreatment with CO at 0.1 MPa was superior to pretreatment at 1.48 MPa in terms of selectivity and stability.

Hydrogen pretreatment conducted at 0.1 MPa showed a strong correlation to activation temperature and duration. It was found that activation at 250°C was superior to activation at 280°C and that activation for 8 hr was superior to activation for 24 hr. It was determined that these effects were due to sintering of the catalysts. At high temperatures the water produced from reduction of the catalyst is released more quickly than at low temperatures and since water accelerates sintering of metallic iron the catalysts were less active. Likewise, long duration H₂ activation was believed to produce fewer active sites from sintering. In all cases the CO conversion steadily increased during the FT runs. CO conversion after approximately 90 hr at process conditions ranged from 86% for the catalyst activated at 250°C for 24 hr to 30% for the catalyst activated at 280°C for 24 hr.

A comparison was made between activation in CO, H₂ and syngas (H₂/CO=0.68) at 0.1 MPa, 280°C for 24 hr. The CO and syngas activations gave similar initial activity with CO conversions about 80%; however, the syngas activated catalyst was much less stable (Figure V-19). Activation with H₂ gave a stable catalyst; however, the activity was very low. A comparison of the CO activated catalyst and the catalyst activated in H₂ at 250°C showed that after 90 hr of synthesis the activities were nearly identical (Figure V-19). Hydrocarbon selectivities were found to be very

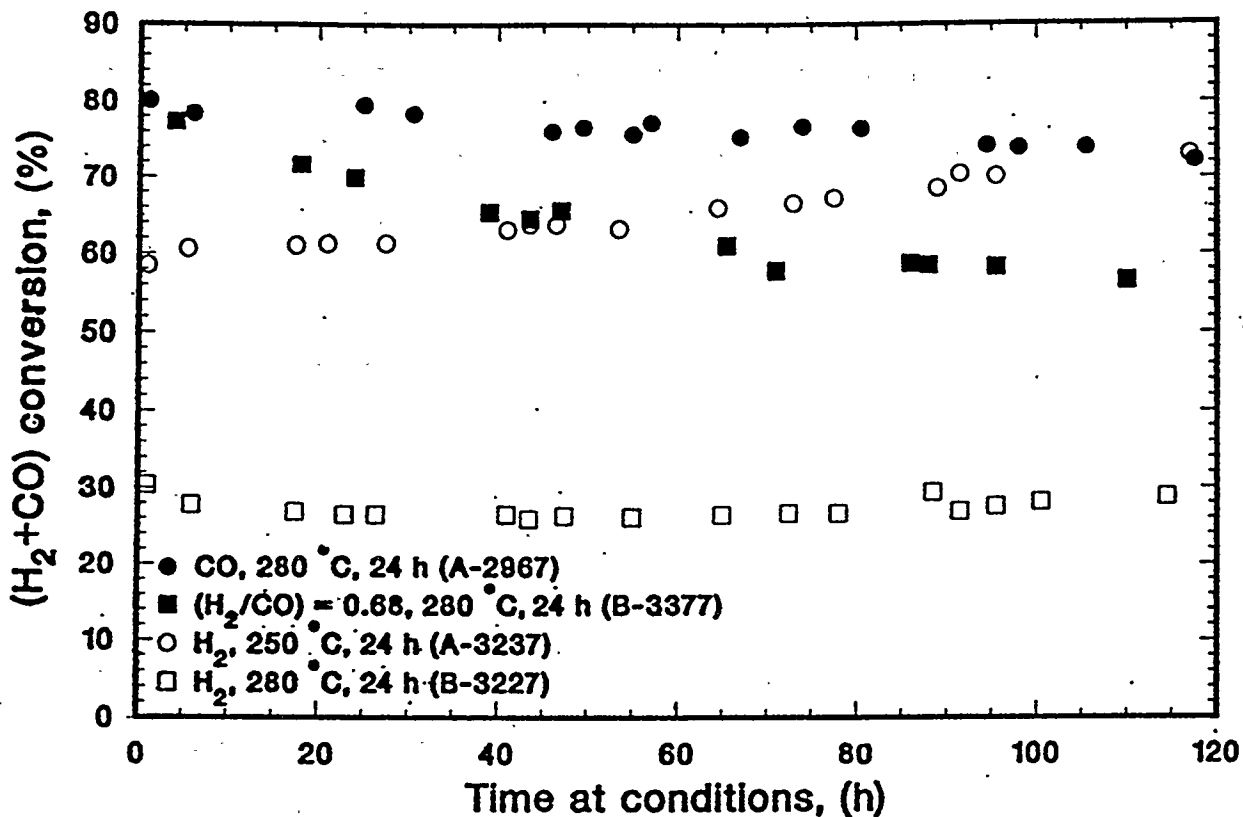


Figure V-19. Comparison of the activity and stability for selected activation procedures (from ref. V-65).

similar for the CO and syngas activated catalysts; however, it was found that H₂ activation led to a production of lighter products. It was concluded that activation in CO at 280°C for 24 hr at 0.1 MPa gives the most suitable catalyst for the plug-flow reactors.

Niemantsverdriet et al. (V-58) reported evidence for an "oxide" spectrum in the 4.2K Mössbauer spectrum for a carburized iron catalyst (CO + H₂ at 250°C) that had been exposed to air. This oxide was identified as either γ -FeOOH or an amorphous iron gel that resulted from exposure of the carburized catalyst to air and not to some oxidation reaction occurring during the synthesis. The more detailed temperature study led these authors to conclude that about 45% χ -Fe₅C₂ was present in addition to ϵ' -Fe_{2.2}C.

Free carbon formation is a concern during both the induction period and the use for the synthesis. The following indicate clearly that there are at least three types of free carbon that can be formed with iron. The one described by Maclver and Emmett (V-66) is typical of one of the forms of carbon that can be formed. CO is decomposed over iron at 450-600°C to form carbon as minute, thread-like growths having thickness of the order of several hundred angstroms. The threads often appear to be twisted into rope-like formations and always seem to contain iron. The iron in these threads is usually an iron carbide, and iron makes up about 1 wt.% of the filament. In the sample prepared by these workers the iron was present as Hägg carbide, with a trace of Fe_3O_4 , and the crystallite size of the Hägg carbide was in the range of 15-25 nm. The BET surface area of the material was 145 m^2/g . Only about 7% of this surface adsorbed CO. The mechanism for carbon filament growth has been defined (V-67).

A second type of free carbon, and one that is probably the more important for iron Fischer-Tropsch catalysts, is illustrated by the work of Nolan, et al. (V-68). These workers contend that the filament-type of carbon described in the preceding paragraph will only grow in the presence of an adequate amount of hydrogen; since Maclver and Emmett, as well as others, have formed the filaments with iron in contact with only pure CO the requirement of hydrogen is questionable. Carbon was deposited on supported Ni or Co catalysts using a mixture of CO/CO₂ at 400°C. Carbon was deposited as lamellar graphite layers extending parallel to the surface of the Ni particle as shown in Figure V-20. Similar results were obtained for Co as shown in Figure V-21. However, under the same conditions but with 1% hydrogen present, filamentous carbon was formed (Figure V-22. Without hydrogen present,

carbon was found to deposit on supported Ni and Co catalysts in the form of specific numbers of lamellar graphite layers. It was observed that various specific carbon layer thickness was preferred for different catalysts. Iron should behave similarly.

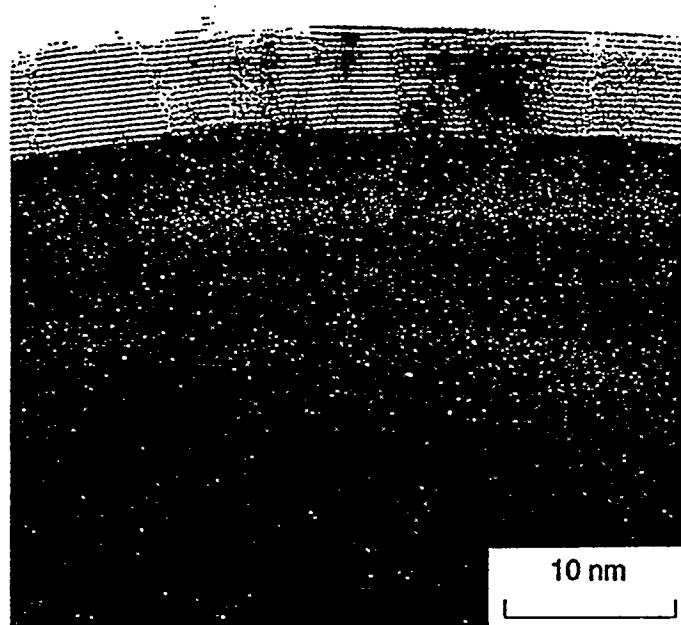


Figure V-20. A portion of a Ni particle from the Ni/Kieselguhr catalyst after carbon deposition from CO disproportionation at 673 K (from ref. V-68).

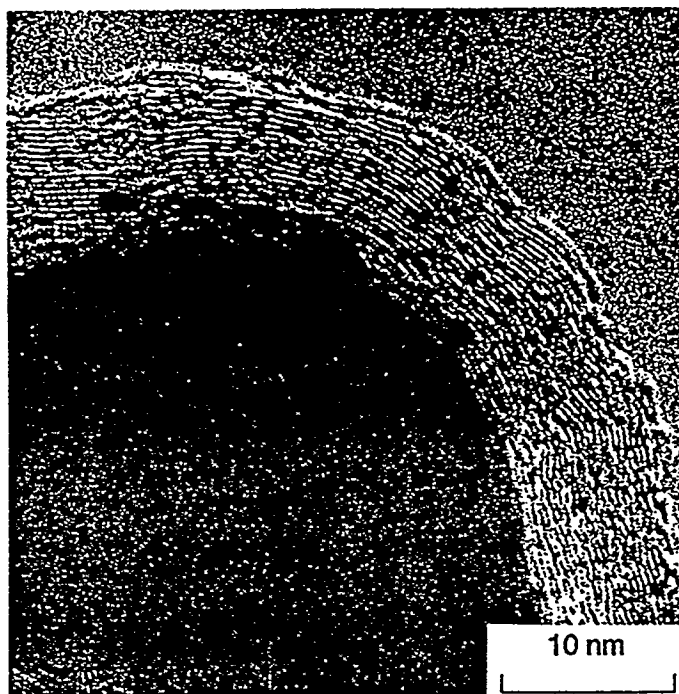


Figure V-21. A portion of a CO particle from the laboratory-prepared CO/alumina catalyst, after carbon deposition at 673 K. Approximately 20 graphite layers are observed (from ref. V-68).

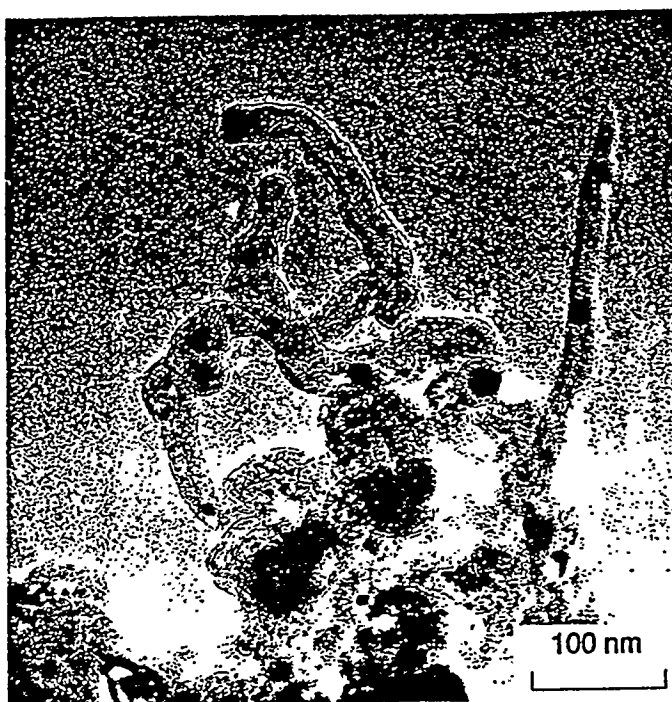


Figure V-22. Filament growth on a Ni/Kieselguhr catalyst after exposure at 673 K to reaction gas with approximately 1% H₂ present (from ref. V-68).

Presumably a third type of free carbon can be formed. Since the various layers of carbon must gradually build-up, the initial carbon that is deposited must form some type of free carbon that is in a less ordered form, and this has been considered to be some amorphous form of carbon that is more reactive than the lamellar graphite layers described above.

Niemantsverdriet and van der Kraan (V-45) considered that the various inductions can be classified into three models: (1) the carbide model, (2) the competition model and (3) the slow activation model. In the carbide model, iron is not active for the Fischer-Tropsch Synthesis and the real catalyst has a bulk carbide structure. Strong support for this view is taken from the observation of Raupp and Delgass (V-69) whose Mössbauer measurements showed that the Fischer-Tropsch Synthesis activity increased almost linearly with the extent of carbidation. These

authors suggested that this relationship results because the number of surface active sites is controlled by the bulk phase that is present.

In the competition model iron atoms at the surface are the active sites. CO and H₂ adsorb and dissociate at these sites. Surface carbidic carbon, C*, can then react according to the following equations:



Reaction Eq. V-5 implies bulk diffusion of carbon into metallic iron, and this process is stated to occur very rapidly. Thus, in the early stage carbon is primarily consumed by the carbidation reactions. As more and more carbide phase is formed, carbon remains more and more on the surface where it is available for hydrocarbon formation Eq. V-6 or for catalyst deactivation Eq. V-7. The reactions compete as long as CO dissociation is slower than carbidation.

In the slow activation model, both CO adsorption and dissociation are faster than all subsequent reactions so that sufficient carbon is present on the surface to fulfill the demands of both bulk carbidation and hydrocarbon synthesis. The authors state that hydrocarbon formation and bulk carbidation are independent but presumably mean that they are coupled so that one can not occur under the assumed conditions unless the other occurs. In this model some surface couples consisting of iron, carbon and hydrogen atoms must be present in a certain configuration; the initial low activity is due to the slow rate of formation of the proper configuration of these three elements.

The authors contend that all three models can account for the presence of at least three forms of carbon in the active iron catalyst, namely bulk carbidic, inactive and surface carbidic carbon. These authors contend that the slow activation model and the carbide model fail to explain the experimental data that they considered. They consider iron itself to be an active Fischer-Tropsch Synthesis catalyst and that competition between carbidation, hydrogenation of surface carbon and deactivation govern the rate. Thus, these authors favor the competition model. In the case of iron the carbidation rate is faster than the synthesis rate and this results in a carbon deficiency in the early stage of the synthesis. The difference between iron and the other Fischer-Tropsch Synthesis catalysts is therefore considered to be due to different rates of carbon diffusion into the metals.

A major use of iron catalysts is in the synthesis of styrene by oxidative dehydrogenation at higher temperatures (600°C) than used during the Fischer-Tropsch Synthesis. However, for a catalyst that is used for a long time some of these changes should occur even at the lower temperature. Based upon a variety of complementary characterization techniques (thermogravimetry under different atmospheres, ex-situ and in-situ XRD, SPS, UPS, ISS and EXAFS) and kinetic studies, Ertl and co-workers (V-70, V-71) established the various solid-state transformations occurring in the catalyst in its precursor, formation, activated-state, deactivation, regeneration, mechanical disintegration and inactive states (Figure V-23, ref. V-72). The active state is believed to be an equilibrium between potassium ferrite, KFeO_2 , and the phase $\text{K}_2\text{Fe}_{22}\text{O}_{34}$. Hydrogen formed during the conversion reduces the active catalyst to KOH and Fe_3O_4 . When these latter two compounds form, segregation of

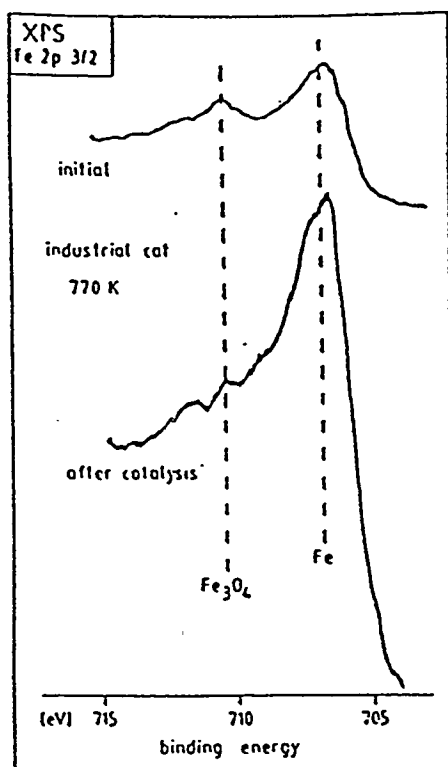


Figure V-23. XPS data of a sample of doubly promoted iron catalyst immediately after reduction and after use in ammonia synthesis at atmospheric pressure (from ref. V-72).

the phases occurs, leading to a potassium-rich core and a potassium-depleted shell in each catalyst pellet. These are not only inactive and nonselective phases but their mechanical strength is also much lower, leading to physical deterioration of the integrity of the pellet. Coke formation is not a problem because of the alkali catalyzed gasification reaction. The role of other oxides in the catalyst formulation is to retard the rate of the unwanted deactivating solid-state transformations. Geus and co-workers (V-73 - V-78) added an iron oxide phase onto a preshaped magnesia support to overcome the detrimental effects of potassium migration. In the absence of potassium, the iron is present as highly dispersed magnesium ferrite, $MgFe_2O_4$ which has a low activity and selectivity and also deactivated rapidly due to the formation of a carbonaceous layer on the catalyst surface. This $MgFe_2O_4$ reduces during the

reaction to form a solid solution of FeO in MgO with a surface layer of Fe_3O_4 . When potassium is present the magnesium ferrite reacts to form potassium ferrite, KFeO_2 , above 650° . The potassium promoted magnesia supported catalyst has an activity and selectivity comparable to the unsupported catalyst. The KFeO_2 is not reduced under dehydrogenation conditions. KFeO_2 does not completely suppress coking so that additional highly dispersed potassium is required.

V.7. ROLE OF COPPER IN IRON CATALYSTS

It was reported that Fischer, as early as 1937, had added copper to his iron catalyst to facilitate reduction (V-9). X-ray studies initiated by Dr. Halle, and continued by Dr. Herbst, showed that in addition to promoting reduction, copper plays another important part in the synthesis. In the course of the synthesis, with Fischer's standard catalyst, a new hexagonal carbide, Fe_2C , not mentioned in the literature to that time, is formed which must be considered as essential for satisfactory activity of the catalyst. Over a period of time, and especially at high temperature, this new hexagonal carbide was found by Dr. Herbst to be converted into the familiar Fe_2C carbide of Hägg. The addition of copper has a marked inhibitory effect on this change, and copper may therefore be considered to act as stabilizer for an intermediate state of the catalyst first arising during synthesis. The addition of 2% copper, for instance, raises the conversion temperature by about 50° . Experiments at Oppau by Dr. Herbst show that hexagonal iron carbide Fe_2C forms in KW 17 (fused ammonia synthesis catalyst) during synthesis and that at temperatures above 290° it is converted into the inactive Hägg Fe_2C .

Kölbel and Ralek (V-10) report that the addition of about 20% Cu (presumably based upon iron) one can obtain an active catalyst by precipitation from an iron(II)

solution because the presence of Cu causes the oxidation of Fe(II) during drying in the presence of oxygen of the atmosphere. In addition, these authors report that small amounts of 0.005 wt.%, based on Fe) of Cu, as well as Au, Ag or Ni, act as reduction promoters which become effective during activation.

V.8. ROLE OF ALKALI IN IRON CATALYSTS

Kölbel and Leuteritz (V-79) reported that the presence of potassium carbonate diminishes the crystallization of Fe_2O_3 up to a temperature of 400°C when the catalyst precursor is thermally treated. Kölbel and Schneidt (V-80) showed that the thermal pretreatment influenced the primary structure of a catalyst precursor containing potassium carbonate. The addition of 0.2% potassium carbonate resulted in an increase of 60% in surface area as well as increasing the heat of adsorption of reversibly adsorbed CO. Alkali is known to enhance carbon laydown (V-81).

9. SUMMARY

The induction procedures utilized in the German work through 1945 varied widely. However, as shown below (Table V-4), the induction procedure utilized by the German workers for the precipitated iron catalysts was most frequently one that involved CO at 1 atmosphere or lower total pressure, and generally at a temperature higher than utilized for the synthesis. Even when a synthesis gas was utilized for the pretreatment, it was nearly always a CO rich stream (e.g., $\text{CO}:\text{H}_2 = 4:1$). If the precipitated catalyst was reduced with hydrogen, it was usually at a low temperature ($250\text{-}350^\circ\text{C}$). When the catalyst was prepared by high temperature fusion, the pretreatment was usually, if not always, a hydrogen reduction at higher temperatures (400°C or higher). In general, the pretreatment procedures used in the extensive studies at the Bureau of Mines in the U.S. did not differ significantly from those of the

German workers. When a hydrogen rich synthesis gas ($\text{CO}:\text{H}_2 = 1:1$ or greater) was utilized, temperature programs were followed so that the extent of CO conversion was kept low so that the CO_2 in the exit gas did not exceed 20%. The conclusion from the results of these studies is that the preferred pretreatment for a precipitated catalyst that has not been calcined at temperatures above 300-400°C utilizes CO or a CO rich synthesis gas.

A variety of procedures have been employed for catalysts that have been pretreated with the view of conducting catalyst characterization. In general, it appears that most of the studies with this objective has been carried out under conditions that favor the formation of iron carbides, and this is true even for the conversion of synthesis gas since most studies utilized low conversion conditions.

Table V-4

Summary of the Catalyst Preparation and Pretreatment Procedures

<u>Company</u>	<u>Catalyst Preparation</u>	<u>Pretreatment</u>
Ruhrchemie	Conventional precipitation with Fe,100:Cu,5:CaO,10:kieselguhr,150	Hydrogen reduction, 1 hr., at 300°C; or recycle gas.
Kaiser Wilhelm Inst., Mülheim phase.	Precipitated from nitrate solution Fe,100:Cu,1-3:K ₂ CO ₃ ,0.1-1.0	CO at 325°C, 0.1 atm.; Fe ₃ C formed, claimed as active
I.G. Farbenindustrie A.G.	Paste of iron powder (from decomp. of Fe(CO) ₅ , 1% borax, sinter 800-900°C.	Hydrogen reduction at 800-850°C
I.G. Farbenindustrie AG (foam process)	Paste of iron powder (from decomp. of Fe(CO) ₅ with K ₂ CO ₃ or borate.	Hydrogen reduction at 350-400°C.
I.G. Farbenindustrie AG (tubular react.)	Paste of iron oxide powder with 5-25% 5-25% MgO or MgCO ₃ and 1-2% K ₂ CO ₃ or borate, sinter at 850°C in nitrogen.	Hydrogen reduction at 350-450°C.
I.G. Farbenindustrie AG (Synol process)	Melting iron in oxygen incorporating 2% alumina and 1% K ₂ O	Hydrogen reduction at 450°C.
Lurgie Gesellschaft für Wärmetechnik	Precipitated from nitrate solution with sodium carbonate at boiling point, wash and add K ₂ CO ₃ . Fe,100:Cu,25:alumina,9:K ₂ O, 2:kieselguhr,30.	Hydrogen reduction at 250-350°C, 1 hr.
Rheinpreussen	Precipitated catalyst with Fe,100: Cu,10:kieselguhr,50:K ₂ CO ₃ ,2.	CO at low partial pressure.

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