

Research included the characterization of interstitial compounds of iron, cobalt, and nickel; development of catalysts; characterization of catalysts and synthesis products; and reaction mechanism and kinetics.

Interstitial Compounds of Iron, Cobalt, and Nickel

With few exceptions, Fischer-Tropsch catalysts contain iron, cobalt, nickel, or ruthenium. Before discovery of the Fischer-Tropsch reaction, metallurgists had known that iron can react with carbon to form cementite and that this carbide reacts with acids to form traces of higher hydrocarbons. Fischer used these facts to support the theory that carbides are intermediates in the Fischer-Tropsch reaction.

A considerable body of knowledge became available on carbides of iron, cobalt, and nickel (1, 8, 9, 49-52) and the phases present in used catalysts. However, this information was only partly integrated because most of the investigators employed only one or at most two experimental approaches, such as X-ray, thermomagnetic, or chemical analysis (29, 38, 45-47, 67).

When the Bureau of Mines launched a study of the solid phases found in Fischer-Tropsch catalysts, its aims were to determine whether metal carbides were intermediates in the Fischer-Tropsch synthesis, to correlate and expand knowledge about carbides, to determine what phases are good Fischer-Tropsch catalysts and prepare these phases with large surface areas, and to investigate phases previously untried as catalysts.

The question of carbides as intermediates in the Fischer-Tropsch reaction was settled by the discovery that nickel carbide and cobalt carbide catalyzed the reaction only slightly, if at all, and by the tracer studies of Kummer and associates (42). The thermomagnetic, crystallographic, and chemical properties of three iron carbides were explored and correlated further. All these carbides (cementite, χ -carbide and ϵ -carbide) were active in the synthesis, although the carbides of cobalt and nickel were relatively inactive. Metallic iron, cobalt, and nickel were also active. The nitrides of iron, as well as the carbonitrides, were found to be not only good catalysts but to have a long life (1, 6) and yield a product (66) containing large amounts of alcohols.

Thus, almost all active Fischer-Tropsch catalysts are ferromagnetic, indicating that activity is related to the presence of an unfinished "d" shell, a necessary but not adequate condition for ferromagnetism.

Methods for Preparing Catalysts Containing Interstitial Compounds of Iron

The methods presented here are based mostly on experience with fused-iron catalyst D3001, containing total iron 67.4, ferrous iron 21.7, MgO 4.61, K₂O 0.57, SiO₂ 0.71, and Cr₂O₃ 0.65 percent. Magnesia, silica, and chromia serve to prevent sintering of metallic iron at the high temperatures used in reducing the original oxide.

To make Hägg or χ -iron carbide, by treatment of the reduced catalyst with pure carbon monoxide (space velocity, 100 per hour), the carbiding temperature

is increased from 150° to 350° C. at such a rate as to keep the CO₂ content of the exit gas at 20 percent. Approximately 20 hours is required to deposit carbon corresponding to Fe₂C. This method minimizes deposition of free carbon and oxidation of the catalyst. Gas of composition 1H₂ + 4CO can also be used (69).

Two methods, both at atmospheric pressure, are recommended (68) for preparing cementite, Fe₃C:

1. The first method is based on the observation that Hägg iron carbide reacts with metallic iron to form cementite (36). This reaction proceeds more rapidly than decomposition of Hägg carbide into cementite and free carbon. Reduced catalyst is carburized with carbon monoxide to convert two-thirds of the iron to Hägg carbide. Helium is then passed over the catalyst and the temperature increased to 475° C. and maintained for 2 hours.

2. Catalysts containing mostly cementite are prepared by carburizing reduced samples for 6 hours with 2H₂ + 1CO at an hourly space velocity of 2,500 and 310° C.

For nitriding iron to ε-iron nitride (6), anhydrous ammonia is used at 350° C. for 2 to 5 hours at an hourly space velocity of 750. An ε-iron carbonitride is prepared by the action of carbon monoxide on ε-iron nitride. An hourly space velocity of 80 at 400° C. suffices to convert nitride in 10 hours (33) to carbonitride of atomic ratio C:Fe = 0.30 and N:Fe = 0.18.

Pore Geometry of Fischer-Tropsch Catalysts

Surface areas and pore volumes (volume of pores with openings smaller than 5 microns in diameter) have been determined on the principal types of Fischer-Tropsch catalysts. The relationship between surface area and activity may be a complicated function, and a direct proportionality between these quantities need not be expected. Nevertheless, information on the pore geometry is the starting point of any rational consideration of a catalytic process, and surface areas and pore volumes provide information regarding the functions of promoters and supports and their influence on structural changes in pretreatment and synthesis.

Data obtained with Co-ThO₂-kieselguhr and Co-ThO₂-MgO-kieselguhr indicated that kieselguhr was essentially an inert material and that the areas of the cobalt-promoter complex (everything except kieselguhr) in raw catalysts were the same in the presence or absence of kieselguhr. Kieselguhr helped to prevent sintering during reduction but was less effective than promoters. The effectiveness of various types of kieselguhr decreased in the order: Natural, calcined, flux-calcined. The principal function of kieselguhr was to produce and maintain a structure of large pore volume.

Carburization with carbon monoxide at 208° C. produced chiefly cobalt carbide; carburization at 275° C., however, deposited chiefly elemental carbon. Surface areas remained essentially constant in carburization at 208° C. Carbon monoxide treatment at 275° C. increased both the surface area of cobalt

(estimated by chemisorption of carbon monoxide) and the total area. Presumably, a portion of the carbon was formed by the growth of nuclei of elemental carbon within the crystal lattice of the cobalt, resulting in partial disintegration of the cobalt structure and a corresponding increase in the number of accessible cobalt atoms (fig. 58).

Data obtained with a precipitated cobalt catalyst before, during, and after synthesis showed that the surface area and pore volume had not changed in 12 weeks of synthesis. However, the pores of the catalyst were largely filled with wax; the synthesis mechanism apparently involves dissolution and diffusion of reactants and products through films of hydrocarbons that are liquid at synthesis temperatures.

The pore geometries of fused, precipitated, and massive iron catalysts were studied. In the reduction of fused iron catalyst D-3001 at temperatures from 400° to 600° C., the external volume of the particles did not change during reduction, and the resulting porosity of the catalyst could be accurately computed from the volume changes involved in the transformation from magnetite to metallic iron. The reduction apparently proceeded from the exterior to the center of the particle, and at any given reduction temperature the surface area increased linearly with the extent of reduction up to about 90 percent. The average pore diameter for reduction at 450° C. varied from 300 to 350 A. and increased slightly near 100-percent reduction.

Electron micrographs of replicas stripped from polished surfaces of raw fused catalyst showed no structure, while replicas from particles reduced at 450° or at 550° C. exhibited a variety of peaks and ridges whose shortest dimension ranged between 500 and 800 A. Some of the structure in figure 59 appeared to be in the form of short fingers, as shown at the edge of the folded replica. No differences were observed between samples reduced at 450° or at 550° C.

Precipitated iron catalysts are usually high-area, small-pore gels of hematite or magnetite; however, treatment with hydrogen, synthesis gas, or carbon monoxide changes the pore geometry drastically. For example, in reduction with hydrogen the surface area of one such catalyst decreased from 169 to 9 m.² per g. Serious sintering did not occur at 300° C. in nitrogen, whereas in hydrogen extensive sintering occurred at 250° C. even when the sample was reduced only to magnetite. External surfaces of precipitated catalysts decreased with sintering and reduction. The porosity of sintered and reduced samples were larger than that of the raw catalyst, but the mechanical strength of reduced or carburized samples was low.

Massive iron catalysts were prepared by partial oxidation of suitable forms of iron or steel, such as lathe turnings, steel wool, or spheres. Reduction then resulted in a layer of porous, active iron on a core of nonporous, inert iron. The surface areas and pore volumes of the active layer (per gram of active layer) were about 4 m.² per g. and 0.070 cc. per g., respectively. These values are similar to those observed for fused catalysts reduced at 550° C.

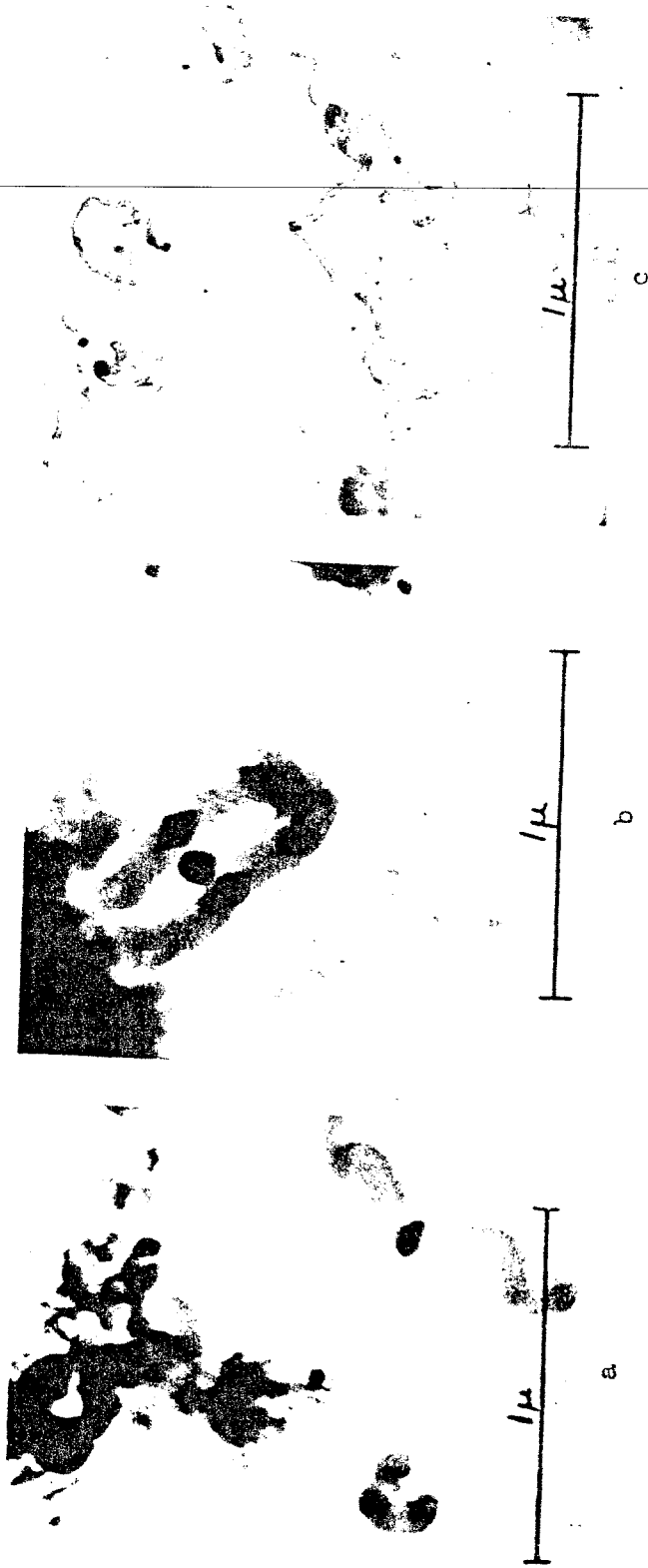


FIGURE 58. - Carbon Deposited From Carbon Monoxide on (a) Iron^{*}; (b) Cobalt^{**}; (c) Nickel^{***}.

^{*}Note filaments extending in two directions from central nucleus.

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^{***}Note tubular form of filaments.

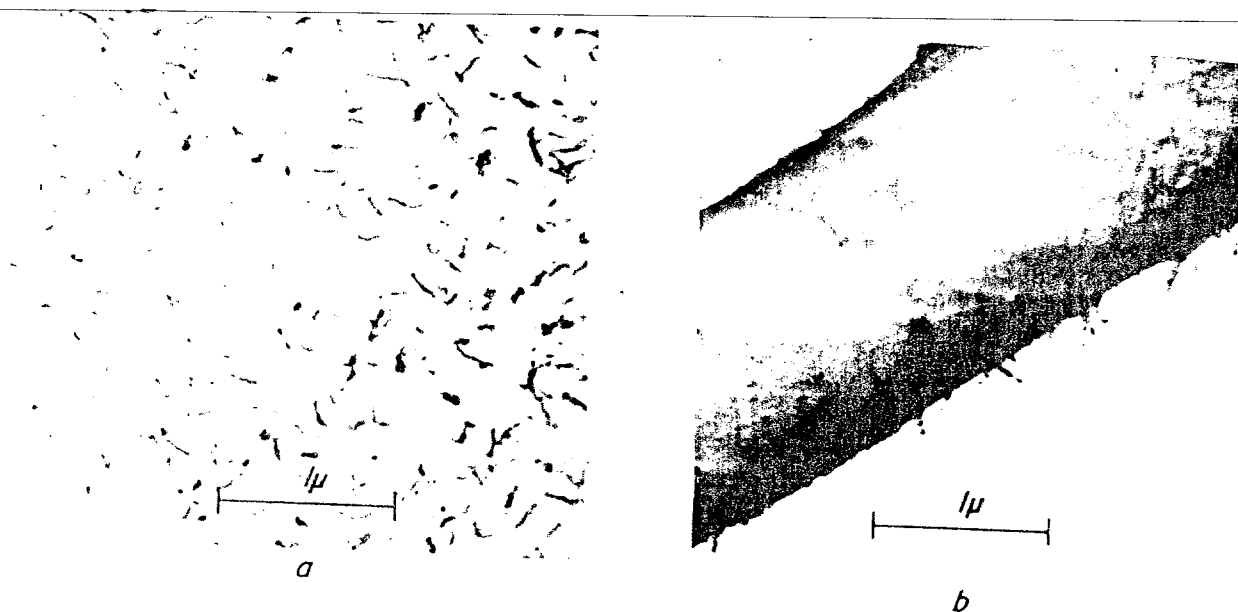


FIGURE 59. - Electron Micrographs of Silica Replicas of Reduced Fused Iron Catalysts. Folded specimen in (b) shows profile of replica surface.

Kinetics of Fischer-Tropsch Synthesis

The task of obtaining meaningful kinetic data for the Fischer-Tropsch synthesis is difficult because detailed and accurate analyses of products are not easily obtained and catalyst behavior often changes during testing.

With cobalt supported on kieselguhr, the rate of synthesis was approximately independent of pressure between 1 and 7.8 atmospheres in experiments in which the pressure was increased for successive runs with the same batch of catalyst. Decreasing the pressure between runs during a test strongly diminished the activity, and cycles of operation at 1 and 7.8 atmospheres progressively decreased the activity further. At atmospheric pressure the rate of synthesis increases with the hydrogen content of the feed gas to a maximum value between $2\text{H}_2 + 1\text{CO}$ and $3\text{H}_2 + 1\text{CO}$. The overall apparent activation energies for synthesis on cobalt were about 25 kilocalories (kcal.) per mole at atmospheric pressure, and 20 at 7.8 atmospheres. The relative usage of hydrogen and carbon monoxide on cobalt catalysts was about $2\text{H}_2:1\text{CO}$ for a wide range of feed-gas compositions and conversions.

Apparent overall activation energies for iron catalysts varied from 19 to 21 kcal. per mole. The rate of synthesis on fused iron catalysts increased linearly with increasing pressure at least up to 21 atmospheres. The empirical equation below (see Iron Catalysts) can adequately express the pressure

dependency by replacing the constant B with B'P, where P is the operating pressure. In contrast to cobalt catalysts, the relative usage of hydrogen and carbon monoxide on iron varied from 2H₂:1CO to 0.5H₂:1CO. The primary reaction appears to have a relatively high usage ratio, H₂:CO, in excess of 1.5. As the conversion is increased, the usage ratio is decreased by a subsequent reaction; the water-gas shift ($\text{H}_2\text{O} + \text{CO} \rightarrow \text{H}_2 + \text{CO}_2$). The rate of this secondary reaction appears to vary about the same as the rate of synthesis, as pressure and temperature are changed.

Mechanism of Fischer-Tropsch Synthesis

Mechanism studies by the Bureau of Mines considered first the validity of the carbide intermediate hypothesis and later the mechanism of chain growth. Finally, a detailed mechanism involving oxygenated intermediates was proposed.

With cobalt catalysts, bulk carbide is relatively inactive in the synthesis. These results indicate that, at most, surface carbide is an intermediate. Studies of Kummer, DeWitt, and Emmett demonstrated that less than 10 percent of the synthesis on iron and cobalt proceeds by the carbide intermediate mechanism (42).

Herington had postulated that hydrocracking, a major step in Craxford's carbide mechanism, did not occur, and had derived equations for evaluating the probability that a chain would grow rather than terminate at a given carbon number (34). Bureau of Mines workers extended his mathematical treatment and plotted yields of wax (C₁₉₊), diesel oil (C₁₂-C₁₈), and gasoline (C₅-C₁₁) as functions of the constant for growth of carbon chains (fig. 60). The data supported Herington's hypothesis and predicted, for example, that not more than 29 percent of diesel oil should be formed in a single pass of gas; this yield was, indeed, easily approached, but never exceeded (26).

From the type and amounts of straight-chain and branched hydrocarbons produced in the Fischer-Tropsch synthesis, schemes of chain growth were postulated based on the primary assumptions that (1) carbon atoms are added stepwise, one at a time; (2) addition occurs only at end or adjacent-to-end carbons of the growing chain; and (3) addition does not occur on a carbon atom already attached to three carbon atoms. In the first scheme addition is permitted at both ends of the growing chain (76); in the second, addition is at only one end (26). Distributions of products from cobalt and iron were shown to fit both schemes, the second being better for products from iron.

A detailed reaction mechanism consistent with this scheme and involving oxygenated intermediates was postulated (72). The following assumptions were made: (1) Hydrogen is adsorbed as atoms on surface metal atoms; (2) chemisorption of carbon monoxide occurs on metal atoms with formation of bonds similar to those in metal carbonyls; and (3) the adsorbed carbon monoxide is partly hydrogenated. The double bonds between carbon and metal atoms were assumed to be more resistant to hydrogenation when the carbon atom is also attached to a hydroxyl group. Equations were proposed for terminating the growing chain to give aldehydes, alcohols, olefins, and paraffins and for producing acids and esters. These postulates were confirmed by the research of

Kummer and associates on incorporation of alcohols in the Fischer-Tropsch synthesis (43, 44).

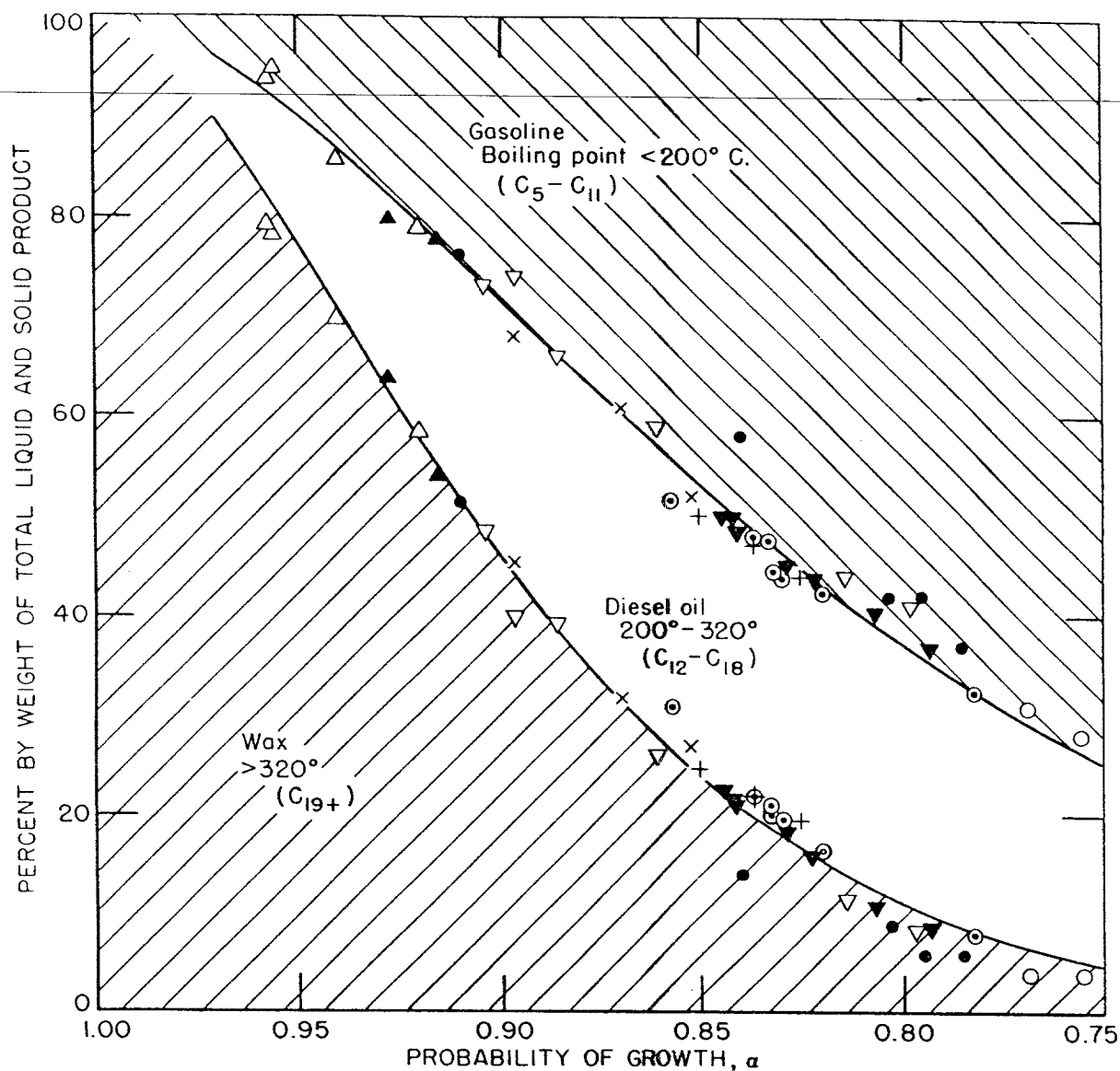


FIGURE 60. - Correlation of Theoretical (curves) and Actual (points) Product Distributions Obtained With Cobalt Fischer-Tropsch Catalysts.

Chemistry of Carbonyls

A somewhat different approach to understanding of the Fischer-Tropsch reaction was based on a study of the reactions, catalyzed by metal carbonyls, of carbon monoxide and hydrogen with organic compounds. This approach was followed because homogeneously catalyzed reactions had been elucidated in the past, and the results had been applied successfully to heterogeneous catalysis.

Early work at the Bureau had demonstrated that the reaction of olefins with carbon monoxide and hydrogen, the oxo or hydroformylation reaction,

involved homogeneous catalysis by a cobalt carbonyl; this activation of both carbon monoxide and hydrogen by a molecularly dispersed catalyst is, in some respects, a homogeneous counterpart of the Fischer-Tropsch reaction (78).

A twofold investigation was begun on the mechanism of the oxo and similar reactions. One part involved study of the reactions of synthesis gas with olefins and with alcohols at elevated temperatures and pressures ranging from 100 to 400 atmospheres. Concurrently, the synthesis, structure, and reactions of metal carbonyls and their derivatives were investigated.

The oxo reaction probably involves formation of a carbonyl-olefin complex, cleavage of the Co-Co bond by hydrogen to give a hydrogenated complex, decomposition of this complex to give the corresponding aldehyde and $\text{Co}_2(\text{CO})_6$, and regeneration of dicobalt octacarbonyl by reaction with carbon monoxide.

The postulate that a carbonyl-olefin complex is the only immediate source of hydrogen and carbon monoxide and that the transfer of hydrogen and carbon monoxide to the olefin takes place within this complex represents a new concept for homogeneously catalyzed addition of hydrogen and carbon monoxide to a substrate. To extend this mechanism to the heterogeneously catalyzed addition of hydrogen and carbon monoxide, one need only substitute a surface complex for dicobalt octacarbonyl. Thus, chain lengthening in the Fischer-Tropsch synthesis may proceed by a mechanism similar to that described above.

Preliminary results from a study of the chemistry of iron carbonyls indicate that this work may shed light on the hitherto unexplained function of alkali as a promoter in the Fischer-Tropsch synthesis. Furthermore, an Fe-C-OH bond has been found, a type of linkage postulated in surface intermediates of the Fischer-Tropsch reaction.

Preparation, Pretreatment, and Testing of Fischer-Tropsch Catalysts

This section summarizes studies on catalyst composition, preparation, pretreatment, and testing. Since the method of testing is common to all these studies, it is described first.

Apparatus

The apparatus was standardized about 1945 and has been used with only minor modifications since then. The objective has been evaluation of catalysts rather than improvement of reactor design, and this standard apparatus has provided a large, consistent group of data on catalysts. The reactor shown in figure 61 had been thoroughly tested from 1940 to 1943.

The reactor was constructed of iron pipe, and the catalyst tube had an internal diameter of 0.625 inch. Catalyst was supported on wire gauze soldered to the top of the retention tube. The temperature of the catalyst tube was maintained by controlling the pressure on the boiling liquid (tetralin for 150° to 220° C., Dowtherm A for 200° to 400° C.) in the steel jacket. The laboratory maintained 16 units suitable for operation at pressures up to 21 atmospheres (310 p.s.i.). The flowsheet for one of these units is shown in