VI - INDIVIDUAL CATALYSTS

Theoretical

The catalytic metals used by Fischer and Tropsch in their early experiments were iron and cobalt, the former being activated with copper and the latter with zinc oxide. Their experience using nickel was disappointing and and they attributed this to the powerful hydrogenating influence of nickel, believing that it caused the direct hydrogenation of CO to methane. However, they later found nickel to yield liquid hydrocarbons when combined with other catalytic materials (164). In the light of the theory that the Fischer-Tropsch catalyst must encourage both polymerization and hydrogenation, the failure of nickel alone to catalyze the synthesis may be attributed to the lack of polymerizing ability. It was also found that ruthenium could be used as a catalyst for the Fischer-Tropsch reaction. All four of these metals are known to form unstable carbides.

While admixture with other catalytic or activating materials is necessary in the case of nickel, it is also desireable in the case of the other metals. The added material may serve one or more of the following purposes: 1) supply a catalytic effect not possessed by the catalytic material alone, 2) activate or promote the catalyst, 3) facilitate catalyst preparation, conditioning, or regeneration, 4) inhibit catalyst poisoning, 5) improve the physical nature of the catalyst, 6) provide a support for the catalytic metal. Superior results have been obtained with those multi-component catalysts in which 1) each component has been selected for its particular effect upon the reaction, and 2) the relative proportions of the components have been adjusted to give composite masses capable of directing the synthesis toward the production of hydrocarbons of the desired molecular weight and structure. The practical application of the Fischer-Tropsch process already requires "complex-action" catalysts, and it would appear that the development of modifications of the process to yield special type hydrocarbons will largely depend upon the results of catalyst research and development. The choice of the catalyst metal itself has a definite influence on the degree of saturation of the reaction products. Cobalt is intermediate in hydrogenating power, its replacement by nickel leads to the formation of a more saturated product, and replacement by iron leads to a greater yield of olefins (164, 165). Riesz and his coworkers (173) point out that the functions of the catalyst components are not fully understood. They propose that the metals act as hydrogenating agents and that the oxides serve as polymerization agents. They also consider it possible that the oxides may act to stablize the catalyst surface. Natta (172) describes three types of catalyst promoters as follows: 1) those that form solid solutions, entering into and deforming the crystal lattice, 2) those that combine on the surface of the catalyst, and 3) those that are mechanically dispersed on the exterior of the catalyst surface. In his description of the ensemble and aggragation principle, Kobozev (169, 170, 171) attributes catalytic activity to atomic ensembles which consist of some definite number of atoms. Atomic groups containing fewer or more atoms are inactive. He sees the action of the promoter as either that of decreasing the size of the migration regions or of fixing the active ensembles, not letting them grow larger to become inactive. He pictures the carrier as "a collection of separate closed regions of 'free migration' in each of which the formation of atomic ensembles proceeds independently."

Roginskii (174) attributes catalytic activity to promotion, either overt or disguised promotion. He claims that without some type of promotion, there are no active metallic catalysts for hydrogenation. He also expresses the opinion that the best promoters are catalyst poisons introduced in very small quantities. Proceeding from these conclusions, Roginskii has described methods for the formation of active catalysts (175). Due to the pyrophoric nature of the Fischer-Tropsch catalysts, the problem of handling and storing them is of great importance. Braude, Shurmovskaia and Bruns (161, 162) have described procedures for the preparation and handling of catalysts without contact with air. Natta (172) emphasizes the importance of the solid-state reactions in the preparation of catalysts. He has found that well-crystallized samples are the most active.

Balandin and Eidus (160) have correlated the activity of hydrogenating catalysts with their lattice constants. They have shown that different planes of the same crystal may differ in catalytic activity. Khvatov (168) points out that, for the interaction of carbon monoxide on nickel, the activation energy is not dependent upon the activity of the catalyst. Wright, Dimrock and Davis (184) have reported methods used in evaluating the activity of catalyst.

Surface studies of the working catalyst have been made by means of x-ray analysis and the electron microscope. Chakravarty and Sen (163) found that in precipitating nickel and thoria on kieselguhr, the crystalline portion of the kieselguhr became amorphous but that the structure of the ferric oxide remained unchanged. They also report that the lattice constant for nickel does not change either during precipitation nor during its use in the Fischer-Tropsch synthesis. Shekter, Roginskii and Isaev (180) studied the effect of heat treatment upon two samples of asbestos. They found that the anthophyllite asbestos was more heat resistant than chrysotile asbestos. They also reported that in all cases, the catalyst particles cling to the asbestos fibers in the form of isolated, sharply defined grains and that these grains are widely dispersed.

Teichner (183) correlated the change in the surface area with the loss of volatile material by the catalyst. They concluded that the increase in the specific surface is not due to a laminated structure but to holes caused by the loss of volatile material. Sips (181) has developed a rigorous mathematical method for the determination of the distribution function of the adsorption energy from the adsorption isotherm. This is worked out for both molecular and atomic adsorption.

The poisoning of the catalyst surface has been studied extensively. Herington and Rideal (167) studied the effect of poisoning on hydrogenation catalysis. They found that the behavior during poisoning can be duplicated by the poisoning of a uniform set of sites. For the Fischer-Tropsch reaction, they observed that the first part of the catalyst layer was poisoned first and then proceeded along the catalyst layer. Roginskii (176, 177, 178, 179) studied the various types of poisoning of the catalyst surface. He has described three different types of poisoning by blocking, viz., microscopic blocking, macroscopic blocking and that of withdrawing of an entire zone of the surface from the system.

In 1943, Fischer (166) reported that with the use of ThO_2, $ThO_2 + Al_2O_3$, and $ZnO + Al_2O_3$, the yield of hydrocarbons which was obtained contained a significant quantity of iso-hydrocarbons. Tatanskii, Papok, and Semenido (182) have reported the findings of the Russian commission on the catalysts which were used in the German synthetic fuel industry.

Cobalt Catalysts

In 1926, Fischer and Tropsch (219) found that catalysts containing nickel or cobalt were more active for the synthesis of hydrocarbons from carbon monoxide and hydrogen. In the period from 1926 to 1938 more active promoted nickel and cobalt catalysts were developed. In 1932, Fischer and Koch (197) described a catalyst composed of Co-ThO_2-kieselguhr in a ratio of 100:18:100. The experiments of Fischer and his co-workers have been reported by Koch (214) and Pichler (215). Since then the "standard catalyst" for the Fischer-Tropsch synthesis has become a kieselguhr-supported mixture of cobalt and thorium oxide (and/or other activating materials). In the period 1938-1944, all of the German Fischer-Tropsch plants were using a Co-ThO_2-MgO-kieselguhr catalyst (219). Catalysts of this type give relatively high yields of primary product and exhibit fairly long active lives. According to information obtained from captured German documents, it was possible to produce (using the wartime catalyst) 168 g. of primary product from 1000 m^3 of synthesis gas (224).

Supported cobalt catalysts may be prepared by either precipitation or by roasting. In the latter case, the carrier is impregnated with a boiling solution of the nitrate salts. This is then roasted forming the oxides and the catalyst is finally reduced in an atmosphere of hydrogen. In general, a catalyst prepared by roasting has been found to be approximately as active as the same catalyst which has been prepared by precipitation from an aqueous solution (221, 222). However, Rubinshtein and his co-workers (217) found that they could obtain a yield of 160 cc/m^3 of feed gas on a precipitated Co-Cu-Mn-kieselguhr catalyst but that the same catalyst prepared by roasting was not as effective.

Precipitated cobalt catalysts, which are most prevalent, are prepared in the following manner: a solution of the nitrates of the component metals is prepared; a boiling solution of the nitrates, an aqueous slurry of kieselguhr, and a boiling solution of sodium or potassium carbonate are poured simultaneously into a container which is equipped with a mechanical stirrer. The pH is carefully controlled since the formation of the bicarbonates is detrimental to the activity of the catalyst (201). The mixture is filtered and washed with boiling water until it is free of nitrate ions. The precipitate is then dried, screened, and reduced at a temperature of 350 - 400°C. (194, 228, 229, 235, 236).

Anderson et al (188) found that pelleted catalysts are as active as the granulated catalyst of the same preparation, although they produce more light hydrocarbons.

Groombridge and Nevins (226) have described a method for the preparation of a cobalt catalyst in which finely divided cobalt oxide (or nickel oxide) is sintered at 900°C. with thorium oxide. Upon reduction with water-gas at 350°C. this forms a porous nonfriable structure of cobalt (or nickel) permeated with finely divided thoria.

As stated above, the most widely used cobalt catalyst is one containing Co-ThO_2-kieselguhr. Craxford (194) reports that the best promoters for a cobalt catalyst are ThO_2, MgO and MnO. He states that ThO_2 and MnO favor wax formation and MgO favors the formation of lower molecular weight hydrocarbons and that catalysts which contain ThO_2 are less sensitive to the normal poisons. In an investigation of the role of thoria and kieselguhr, Craxford (193) found that they were both powerful specific promoters for the formation and reduction of carbide. In order to improve the mechanical strength of this catalyst, part of the thoria was replaced by magnesia and the amount of kieselguhr was increased (190). The substitution of MgO for part of the ThO_2 decreased the production of paraffins, the formation of methane, and the deposition of carbon (191, 192).

Several Japanese investigators have studied kieselguhr supported cobalt catalysts, reporting quite high yields from compositions consisting of 5 - 10% Cu, 4 - 12% MnO, and 4 - 12% ThO_2, Al_2O_3 or UO_2 (198, 213, 223). Fischer (196) reported that the addition of 2% Cu to a Co-ThO_2-kieselguhr catalyst greatly increased the ease of reduction. The use of such a catalyst is also described by Dreyfus (238). Hamai and his co-workers (205, 207, 209) studied the effect of various promoters on a supported cobalt catalyst. They found that the presence of thoria favored a low oil yield and a high yield of methane. They reported 20 - 30% of thoria as the optimum amount. They also report that 10 - 15% CeO_2 favors a high oil yield and a low yield of methane. This was also reported by Herington and Woodward (210, 211). The Japanese investigators also studied the composition of a Co-U_3O_8-Cu-kieselguhr catalyst. For this catalyst they found that Be_2O_3 increased the activity and improved the quality of the products.

Ghosh and his co-workers (199, 200) compared the yields from a Co-ThO_2-Cu-kieselguhr catalyst and from a catalyst containing these components plus 46% Cr_2O_3. The latter gave much higher yields, 160g/m^3 of synthesis gas (1CO:1H_2) at a temperature of 205°C., 5 atm. pressure and with a space velocity of 600 ml/hr/ml. of catalyst. Cobalt catalysts which are promoted by the addition of alkali metal compounds (240) and silver or silver compounds (227, 239) have also been described in the literature.

There has been much interest in the role which the kieselguhr carrier plays. Hamai, Hayashi and Shimamura (209) reported that kieselguhr was necessary for the formation of oil. When the kieselguhr was not present, it led to the formation of methane. Anderson et al (189) studied cobalt catalysts which were supported on different kieselguhrs. They found, as did Craxford (194) that catalysts supported on natural kieselguhrs are more active and have a greater surface area than those supported on calcined kieselguhr. They proposed that the function of the carrier is more complex than that of a diluent or bulking agent, possibly due to the formation of cobalt hydrosilicate. Craxford (194) has proposed that the kieselguhr maintains the metallic cobalt in a finely divided form as well as the porosity of the catalyst. Storch et al (220) claim the possibility that the kieselguhr, in conjunction with the thoria, inhibits the conversion of the cobalt from the cubic (active) form, which is unstable at room temperature, to the hexagonal (inactive) form. Anderson and his associates (187) claim that the kieselguhr's prime importance is due to the fact that it prevents a decrease in the bulk volume of the catalyst upon reduction. Most of these sources agree that the kieselguhr has little effect upon the surface area.

Aldrich (187) reported a study of the Co-MgO-ThO_2-kieselguhr catalyst which was used at Harnes, France. In this report, he has described the purity specifications for the catalyst components. These purity requirements are of great importance since very small amounts of impurities, such as calcium oxide or iron, will poison the catalyst. The cobalt must be 99% pure, the remaining 1% being copper or nickel. The thoria must contain no trace of lead or phosphorous, and the calcium oxide content must be less than 0.2% by weight. The kieselguhr must contain over 92% silica and it should be completely free of iron or lime. The organic matter is completely removed by roasting at 800°C. However, this temperature should not be exceeded since above that temperature the physical structure of the particles is destroyed. As for the different commercial kieselguhrs, Aldrich states that the German kieselguhr from Kieselguhr-Industrie-Hannover No. 120 is one of the best. Johns-Mansville's "Filtra-cel" is purier, but its size is not as accurately controlled. Acid treatment is considered detrimental to their physical structure (191).

Craxford (194) believes that the reduction is the most crucial step in the preparation of cobalt catalysts. Sintering must be prevented and therefore the reduction should be done in the shortest possible time at the lowest temperature. Only 50 - 60% of the cobalt oxide is reduced (187, 192, 194, 203, 220) and in technical preparations this is still lower, between 35 - 40% (231, 232). The reduction is carried out in a stream of dry ammonia - synthesis gas ($H_2:N_2 = 3:1$) within the temperature range of 350 - 400°C. and at a space velocity of about 7000 volumes of gas per volume of catalyst per hour. The high reduction temperature suggests the possibility of the formation of a chemical compound between the cobalt and the kieselguhr (194). The reduction usually takes about 40 to 120 min. (194, 203). Eidus (195) studied the rate of the reduction of a Co-ThO_2-kieselguhr catalyst in a stream of H_2. He found that the maximum velocity of the reduction is attained at the beginning of the process. Hamai and co-workers (206, 208) have studied the influence of pretreatment upon cobalt catalysts and they have presented their results in tabular form. Braune and Schaefer (230) describe a process in which the reduced catalyst is treated with ammonia at a temperature close to that of the synthesis.

The physical properties of unreduced and reduced cobalt catalysts have been subjected to extensive investigation. Studies of the x-ray diffraction pattern of a Co-ThO_2-Kieselguhr catalyst before reduction indicate that this catalyst is almost completely amorphous (220). Craxford (194) points out that the reduced cobalt catalyst does not give a characteristic diffraction pattern. He attributes this to the fact that the cobalt layer is not more than two molecules thick. Anderson et al (187) report that x-ray diffraction data indicated that the cobalt in the supported and promoted catalyst, upon reduction, had an anomalous structure. However, Storch and his associates (220) reported that the reduced catalyst showed the lines of cubic cobalt crystals. The x-ray diffraction data also shows (187) that an appreciable fraction of the surface was occupied by the promoter. Weller, Hofer and Anderson (225) found that the x-ray diffraction pattern of the cobalt catalyst did not change during the synthesis.

The surface areas for unreduced and reduced cobalt catalysts have been determined by means of adsorption isotherms. This method has been discussed in a general form by Ries et al (216). For unreduced catalysts, the surface area was found to range from 66 - 149.6 m^2/g. (186, 220) and the pore sizes varied from 500 - 770Å for granular catalysts, to 165 - 310Å for pelleted catalysts (186). The surface area of the reduced cobalt catalyst varies from 36.9 m^2/g (220) to 80.0 m^2/g (225). The change in the surface area during usage is from 80.0 m^2/g to 43.6 m^2/g. This may be increased to 70.5 m^2/g. by regeneration with hydrogen at 200°C. for two hours (225).

In general, the supported cobalt catalysts operate in the temperature range of 175 - 200°C. at pressures of 1 - 20 atm. (188). The optimum temperature is usually considered to be 180 - 200°C. Above 207°C., the activity is decreased and it is permanently impaired above 218°C. (201). The cobalt catalyst was found to exhibit its maximum life when it was used at 5 - 15 atmospheres, the highest yields being obtained at 15 atm. (201, 218). Above 30 atm., the activity of the cobalt catalyst is decreased due to the formation of the carbonyl. The influence of the rate of gas flow has been widely studied. Craxford (193) reported a large difference in the product distribution when the space velocity was varied at 185°C. He used a Co-ThO_2-MgO-kieselguhr catalyst and found that the yield of liquid products and methane increased as the space velocity decreased. Anderson and his co-workers (188) found an increase in the olefin content with an increase in the space velocity. They reported the maximum space time yield as 43.7 g/kg. of gas/hr. at a space velocity of 600. Storch (218) found that the maximum space-time yield was obtained at 41/hr/g. of cobalt.

One of the most important reasons for the deactivation of the catalyst is sulfur poisoning. However, there are several other processes which may lead to the deactivation of the catalyst. These are: a) the deposition of hydrocarbons on the catalyst surface, b) a change, possibly the oxidation of cobalt, which takes place slowly and which may be reversed by the original high temperature reduction, and c) a more gradual and more fundamental change, probably a physical alteration of the active surface of the catalyst which can be overcome only by the remanufacture of the catalyst (204). Hall and Smith (204) found that a Co-ThO-MgO-kieselguhr (100:5:8:180-200) catalyst can be maintained in a high state of activity for 18 months by intermittent treatment with hydrogen at the temperature of the synthesis. They found that when a reaction temperature of 195°C. became necessary, the activity could be restored by a repetition of the original reduction process. The hydrocarbons which have been depositied on the surface can be removed by either solvent extraction (194) or by treatment with H_2 at a temperature of 200 - 300°C. (212, 237, 241, 242). However, when a physical alteration of the active surface has occurred, the catalyst must be replaced.

Several methods have been patented for the recovery of cobalt from a spent catalyst (233, 234). Aldrich (187) has given a detailed description of the regeneration of a spent cobalt catalyst as it was carried out at the Carrieres-Kuhlmann plant at Harnes, France. The spent catalyst is first dissolved in nitric acid. Sufficient acid is added to convert all of the metals to the nitrates. The kieselguhr is then removed by filtration. This is not recovered. Enough sodium carbonate is added to the solution of nitrates to give a pH of 4.2. The following reaction takes place:

$$Co(NO_3)_2 + Ca(NO_3)_2 + Th(NO_3)_4 + Mg(NO_3)_2 + XNa_2CO_3 \longrightarrow$$

$$Co(NO_3)_2 + Ca(NO_3)_2 + Th(CO_3)_2 + MgCO_3 +$$

$$XNaNO_3 + Na_2SO_4 + \text{traces of } Fe(OH)_3.$$

The precipitate is filtered off and sodium fluoride is added to the remaining solution. The reaction is:

$$Co(NO_3)_2 + Ca(NO_3)_2 + 2NaF + XH_2O \longrightarrow$$

$$Co(NO_3)_2 + CaF_2 + 2NaNO_3 + XH_2O.$$

The CaF_2 is removed by filtration and the $Co(NO_3)_2$ is ready for the preparation of new catalyst. The mixture of $MgCO_3$, $Th(CO_3)_2$, $Fe(OH)_3$ and Na_2SO_4 is nitrated with nitric acid. Sodium hydroxide is added resulting in the formation of the insoluble hydroxides of magnesium and iron. The thorium forms the soluble compound $ThOSO_4$. The solids are removed by filtration and the solution is heated above 80°C. The precipitate $Th(OH)_4$ is filtered and is then ready for use again. The magnesium is not recovered.

Hale (202) has described analytical methods for the determination of cobalt and thoria in an unreduced Fischer-Tropsch catalyst.

Nickel Catalysts

Although nickel alone is not a satisfactory catalyst for the Fischer-Tropsch synthesis, it has been found that mixtures of nickel plus activating agents, produce satisfactory yields of liquid hydrocarbons. Such catalysts are usually prepared by the co-precipitation of the chemically active ingredients upon an inert carrier. The general method involves the addition of alkali carbonates to the solution of the nitrates of the catalyst components in the presence of sufficient kieselguhr to act as a support. During the precipitation, the kieselguhr is kept in suspension by mechanical agitation. The mixture is then filtered, washed, dried and reduced (243, 263).

Fischer (262, 264) early patented complex nickel catalyst prepared by the co-precipitation technique, specifying thorium, aluminum, and cerium compounds as suitable catalysts. In the case of a $Ni\text{-}Mn\text{-}Al_2O_3$ catalyst, carrying out the precipitation in the presence of ammonia is said to increase the yield in the subsequent synthesis step and to lower the temperature of the optimum reduction (249). Nickel catalysts can also be prepared by roasting of the nitrates. Tsutsumi (259) studied the activity of a $Ni\text{-}Al_2O_3$ catalyst for the Fischer-Tropsch reaction. He found the activity was not very great (20%). In another study (260), Tsutsumi found that a Ni-Mn-Al_2O_3-kieselguhr catalyst prepared by precipitation was more effective than one of the same composition prepared by roasting. Trambouze (254) studied the change in the catalyst during the preparation process. He found that after precipitation, the nickel was in the form of oxides, hydroxides or carbonates which were converted upon boiling to aluminates. He assumed that the formula for this compound was Al_2O_3, $8NiO \cdot nH_2O$.

Tsutsumi (260) also studied the effect of the reduction temperature upon the precipitated catalyst. He found that as the reduction temperature increased, the activity was reduced. This was more pronounced in the case of those catalysts prepared by precipitation. However, Trambouze (255) found that preheating augmented the activity of the nickel catalyst. He also reported that this increased the ratio of oxide to aluminate. Chakrovarty et al (247) studied the effect of traces of potassium carbonate in a Ni-ThO_2-kieselguhr catalyst. They found that even traces of the carbonate caused the catalyst to lose its activity in the early stages of the reaction. The presence of K_2CO_3 brought about the formation of C, CO_2 and H_2O rather than volatile hydrocarbons. Eidus et al (248) reported that the degree of washing after precipitation had a great influence upon the activity of the catalyst.

Riesz and his co-workers (252) reported that for a Ni-Al_2O_3 catalyst, the optimum metal to oxide ratio is about 50% by weight. A decrease in the metal concentration increases the yield of volatile hydrocarbons. A yield of 100 - 160 cc. of liquid hydrocarbons per cubic meter of the synthesis gas has been reported for a catalyst of the composition Ni + 20% MnO_2 + 4-8% (ThO_2, Al_2O_3, WO_2 or UO_2) + 1.25 times its weight of kieselguhr.

Ghosh, Basak and Badami (250) found that with a $CO:H_2$ ratio of 1:1, the yield of gaseous hydrocarbons was increased over that obtained when the $CO:H_2$ ratio was 1:2. Meller (251) reported that a Ni-Al_2O_3 catalyst gave good yields with a gas having a $CO:H_2$ ratio of 3:5. Under these conditions, the catalyst has a long life if organic sulfur compounds are not present.

Zelinskii and Shuikin demonstrated the formation of methylene group on a nickel catalyst. Chakravarty (245) reported that free carbon may be adsorbed on the nickel surface forming a poisoning film. Some nickel carbide (NiC_3) may also be formed, but this compound is catalytically active in the hydrogenating process. Balandin and his co-workers (244) have made a detailed study of the action of hydrogen on nickel catalysts and of the nickel hydrides which are formed.

Patents have been issued for several other types of nickel catalysts. Tsutsumi (265) reported the use of a precipitated Ni-Cr_2O_3 catalyst with or without a carrier. Elian (266) reported yields of 155 g. of hydrocarbons from a catalyst of nickel carbide intimately mixed with copper oxide. Black (267) has patented a process which uses a fluid nickel chromite or reduced nickel chromite catalyst. This type of catalyst may be regenerated by controlled oxidation followed by reduction with hydrogen.

One of the undesireable features of nickel catalysts is that at increased pressures, the catalyst deteriorates rapidly due to the formation of volatile nickel carbonyl. The substitution of 50% of the nickel by cobalt gives a catalyst which retains the advantages of a cobalt catalyst (246). Tsutsumi (256, 257, 258) reported that his most active catalyst was one containing equal parts of cobalt and nickel plus 20% MnO_2, 20% UO_2, and 125% kieselguhr (the percentages are based on the combined amounts of nickel and cobalt).

Iron Catalysts

Recently, iron catalysts have been of great interest in the Fischer-Tropsch reaction. This is due in part to their availability and relative cheapness. However, Schroeder (301) has said that the catalyst cost has a relatively slight effect on the final cost of the product. The interest in the iron catalysts is due mainly to the fact that they produce a more unsaturated product, consequently, one with a higher octane rating, and also to the fact that the water-gas shift reaction is eliminated since an H_2:CO ratio of 1 is sufficient for an iron catalyst (268).

Iron catalysts are prepared in two ways: (1) by precipitation, or (2) by roasting. The former is by far the most widely used. Murata and Makino (292) found that catalysts which were precipitated from nitrate solutions were superior to those from chloride solutions. They also reported that catalysts prepared from sulfate solutions were not active at all. Murata, Nakagawa, Toshiro and Umemura (295) made a study of the effect of preparation of an Fe-Cu-K_2CO_3-kieselguhr (100:25:2:125) catalyst. Their results led to the following general principles: a) the alkali activator should be added as quickly as possible with sufficient agitation, b) the time of adding the kieselguhr has no marked effect, c) the temperature of the precipitation has little influence, d) the washing of the precipitate requires special care but less than for the cobalt or nickel catalysts, e) the concentration of the reagents has no great influence, although it is desireable that the alkali solution be concentrated and the solution of metallic salts be dilute, f) the quality of the kieselguhr has a marked effect and kieselguhr which has been previously treated with acid produces an inferior catalyst, g) the iron and sodium carbonate need not be especially pure, h) an excess of 5 - 15% of the precipitating reagent should be used, and i) the alkali promoter must be uniformly spread over the catalyst surface.

A catalyst has been described (333) which is prepared by the co-precipitation of iron and calcium hydroxides, activated by the addition of nickel, cobalt or copper. This catalyst is said to improve the yield of solid and liquid hydrocarbons. Voorhies (342) has patented a procedure for producing an iron catalyst of high disintegrating resistance which consists of shock-chilling a reduced iron oxide from the molten state. Other methods for preparing active iron contacts have been described (315, 318, 319, 332, 339).

Alkali promoted Fe-Cu catalysts were used by Fischer and Tropsch (275) in many of their early experiments. However, they found that these catalysts were inferior to the cobalt or nickel catalysts both in the yield of products and length of life (274).

Eidus (272, 273) has found that of the alkaline activating agents, K_2CO_3 is the most favorable. The effect of adding K_2CO_3 to an iron catalyst is that of increasing the mean molecular weight of the reaction product (284). The optimum amount varies in relation to the other components. For a catalyst containing H_3BO_3, 7-20 parts of K_2CO_3 by weight is the optimum. However, in the absence of H_3BO_3, 4-5 parts by weight produced the best yields (282).

Copper may be added to the iron catalyst to facilitate the reduction step in the preparation and to favor the adsorption of the alkali salt (274, 303). Copper has an excellent accelerating action on the activity of iron catalysts (297) and, like K_2CO_3, it has a tendency to increase the mean molecular weight of the reaction product, but to a lesser degree (284). The optimum amount of copper is approximately 10% although it varies for catalysts with different compositions. The amount of copper which is present has no effect on the optimum reaction temperature or on the composition of the feed gas (297). By using less copper, one pair of investigators (270) claimed to have obtained improved results although others (278) found little difference in the activities of catalysts with iron-copper ratios of 1:2, 1:1, 3:1. The latter observed that catalysts containing 0.5% alkali possessed longer lives than those containing greater proportions.

Such additions as H_3BO_3 and manganese tend to decrease the mean molecular weight of the reaction product (272, 283). The various boron compounds are effective even when introduced by mechanical mixing (297). This is not true of the alkaline additions.

Murata and his co-workers (296) studied the effect produced by various additions. They found that organic acids were injurious to the catalyst as were most zinc compounds (with the exception of $Zn(OH)_2$ and $Zn_3(BO_3)_2$) and most chromium compounds (with the exception of chromia). Alumina, when added before precipitation, decreased the yields but when added after precipitation, the benzine yield was increased. Most other aluminum compounds decrease the yields and $Al_2(SO_4)_3$ and $AlCl_3$ reduce the yield to zero (289, 337). Makino, Koide and Murata (288) studied the addition of Ag_2O and found that the benzine yield either remained the same or diminished. They also found that in replacing copper in the catalyst by silver, some paraffin wax was formed. Such additions as barium, calcium, cadmium, bismuth, lead, tin or tungsten were found to result in inferior benzine yields.

The effect of other additions such as tellurium (336), sulfur (335), silica and silicate solutions (324, 343) and pyroantimonates (338) has also been cited in the literature.

Kodama et al (285) studied the influence of various carriers. The carriers which were studied were diatomaceous earth, active carbon, white clay, and Japanese acid clay. Murata (291) reported that hardly any oil was produced when active carbon was used as the carrier. The authors, however, found an increase in the volatile fractions. They also found that the Gasol yield is very small when white clay is used, but that it is high in the C_3 and C_4 hydrocarbons. The degree of unsaturation of the product is very high (70 - 85%). The Japanese acid clay increased the yield of gaseous hydrocarbons and gave the maximum Gasol fraction.

The promoting effect of the alkali addition is believed to consist of stabilizing the cubic ferric oxide (Fe_2O_3) thereby preventing its transition to the magnetic iron oxide which is less active (286). A number of x-ray diffraction and magnetic susceptibility studies have been made of such catalysts (268, 269, 287). More recent investigations have indicated that the inactive catalyst contains β-FeOOH and that the active catalyst contains either αFeOOH or αFe_2O_3, or both, but no βFeOOH (277, 305, 341). It was found that the highly active catalysts had higher magnetic susceptibilities and were ferromagnetic, a suggested explanation being the possible presence of ferromagnetic alkali ferrites in the active catalyst.

Kodama and Tahara (279) studied the change in the iron catalyst as its activity decreased from usage: they found that the x-ray lines corresponding to the spinel structure disappeared and that lines corresponding to a face-centered lattice appeared. They offered no interpretation of these results.

Catalysts prepared by impregnating asbestos with the nitrates of the catalytic metals and small amounts of rare-earth oxides have been found to give the following yields per thousand cubic feet of the feed gas: Fe-Cu-Ni (4:1:0.01)-1.8; Fe-Cu-Ni (4:1:0.02)-2:8; Fe-Cu-Ni-CeO_2-ThO_2 (4:1:0.05:0.001:0.006)-5.0 (276). With precipitated catalysts, the first composed of Fe-Cu-K_2CO_3-kieselguhr (4:1:0.08:5) and the second having 0.08 parts of manganese added (293, 306), yields of 5.2 and 5.5 lbs./thousand cubic feet of water-gas (1 CO:1H_2), respectively, were obtained. The addition of 5% nickel or cobalt to these catalysts increased the yields when a synthesis gas (2H_2:1CO) was used, but they proved undesireable when an equimolar mixture of carbon monoxide was used.

Partial sintering of precipitated iron-aluminum catalysts by reduction at about 1550°F. has been patented by the I. G. Farbenindustrie A. G. (310, 311, 313). It has also patented catalysts of the iron group which have been prepared by heating the metal carbonyl at a temperature above 930°F. but below the melting point of the metal. By this method, partial sintering occurs (312, 321, 329). Other patents which have been issued on sintered iron catalysts are (317, 327, 329, 330).

In addition to use in the normal vapor-phase type of operation, sintered-iron catalysts may be used in liquid-medium processes (316). They may also be pelleted by mixing iron-powder with an alkaline metal salt solution, compressing, and reducing with hydrogen at about 1550°F. Although single-pass yields are low, a satisfactory ultimate yield may be obtained by recycling the partially spent synthesis gas. An I. G. Farbenindustrie report (268) which was written in 1939, describes a rapid hot-gas recycle process over a pelleted sintered-iron catalyst. The gas was passed through the reactor at hourly space velocities of 5,000 - 35,000 and the heat evolved was absorbed in an external heat exchanger. The reaction was carried out at 605 - 660°F. and 295 psi. The conversion was about 1% per pass and about 1% of fresh synthesis gas (0.9H_2:1CO) was added per cycle, an equivalent amount of recycle gas being removed, freed of CO_2 and sent to a second smaller recycle system. Conversion in the first stage was about 78% and in the second, about 13.5%. The product was highly unsaturated consisting mainly of gasoline having a Research octane number of 85. A polymer of 97 octane number was produced from the C_3 and C_4 unsaturates. The yield of primary product was about 10 lbs. product/1000 cu. ft. of gas. Approximately 0.87 lbs./1000 cu. ft. was oxygenated compounds.

The hydrocarbons synthesized over sintered-iron catalysts consist largely of branched chain paraffins while those produced over non-sintered iron catalysts contain very little iso-compounds. It is considered likely that sintering produces a critical spacing of the metal atoms in the iron carbide lattice which is condusive to the production of iso-paraffins (304).

The amount and type of product which is produced over an iron catalyst is influenced by many factors. The genesis and additions have already been discussed. However, the treatment of the catalyst before its use also shows a marked influence upon its activity. Murata and his co-workers (294) found that a mixture of CO and H_2 is preferred to pure H_2 for the reduction of the iron catalyst. They found, in fact, that reduction in pure H_2 for a period of 4 - 8 hours at 450°, brings about a total loss of activity in the catalyst. A patent (323) has been issued which describes a pretreatment of the iron catalyst with gases containing CO. Another patent (322) describes the reduction of an iron catalyst in hydrogen, but at a lower temperature, and the process is continued until only 5 - 10% of the theoretically reducible iron is reduced to the metallic state.

The effect of heating has also been studied (294, 302). It has been reported that iron catalysts increase their activity somewhat upon being heated at temperatures ranging from 100 - 400°. When the temperature is above 400°F., the activity decreases and above 600°F., the activity is completely lost. Eidus (271) in studying the activity of a complex iron catalyst found that its activity increased continuously for the first 5 - 6 hours of the contact process. He also calculated the apparent heat of activation to be 28.7 Kcal./mole. in the temperature range 245 - 265°C. (273).

A study of the effect of the feed-gas composition shows that an optimum $CO:H_2$ ratio is approximately 1.3 (300). The influence of diluents such as N_2, CO_2, CH_4, and O_2 is to decrease the yield in all cases (298, 299). Oxygen shows the greatest influence and methane the least. Morozov (290) has made a detailed investigation of the adsorption of hydrogen on a pure iron catalyst. He found that there were three different types of sorption: a) van der Waal's adsorption, b) activated adsorption, $E = 20,000$ cal., and c) activated difusion, $E = 8000$ cal.

The durability of the iron catalyst has been found to be better than that of the cobalt catalyst (281) and it is increased by the application of medium pressure since that allows a lower reaction temperature to be used (300). The regeneration of the iron catalyst has not been studied extensively since, in general, it is less expensive to prepare a fresh catalyst than to attempt to regenerate the spent catalyst. However, several methods have been described including hydrogenation at 600 - 900°F. (340) and oxidation with air at 750 - 875°F. (334, 344).

Ruthenium Catalysts

Studies of the Group VIII metals (rhodium, palladium, osmium, iridium, platinum and ruthenium) have shown that the latter is the best suited for the Fischer-Tropsch synthesis. The ruthenium catalyst used at elevated pressures was found to surpass all other catalysts for the synthesis of the higher hydrocarbons (349). With this catalyst, very little methane was formed and 65% of the total yield is wax (m.p. 118 - 120°C.) (350). The ruthenium catalyst was found to have an unusually long life, showning no change in its activity after six months use at 100 - 1000 atmospheres pressure (354). Yields obtained with such a catalyst are approximately 6.2 lbs. of paraffin wax and 3.1 lbs. of liquids per 1000 cu. ft. of synthesis gas at 380°F. and 1500 psi (347).

The effect of pressure upon the yield and type of product from the ruthenium catalyst is very pronounced. Below a pressure of ten atmospheres, no significant conversion is observed, the product consisting of liquid hydrocarbons (346, 349). As the pressure increases, the total yield of hydrocarbons is also increased and the maximum conversion (95%) is attained at 300 atmospheres pressure (349, 354). At all pressures, solid paraffins amount to about 60% of the total yield of liquid and solid hydrocarbons, and gaseous hydrocarbons constitute 25% of the total yield. The maximum space-time yield is attained at a space velocity of 9 liters/hr./g. of Ru, (352, 354). Fischer and Pichler (348, 351) also studied the effect of pressure upon the synthesis over a ruthenium catalyst, but they investigated only the range up to 1500 psi. Pichler and Buffleb (352) investigated the synthesis in the range from 100 - 1000 atm., 75% of the solid and liquid product consisted of paraffin waxes.

The use of a ruthenium catalyst for the commercial production of high-melting wax is not considered feasible by Dr. Mortin, director of Ruhrchemie A.-G. because of the relative scarcity of ruthenium (345). He has stated that hard wax can be produced more economically by using the conventional cobalt catalyst at low space velocities and low temperature.

Fluid Catalysts

One of the most recent developements in the search for Fischer-Tropsch catalysts with superior heat transfer characteristics is the "fluidized" catalyst, which consists of very finely divided particles suspended in the synthesis gas stream. A uniform mixture of the solid and gas is formed and the density of this "fluid" depends on the proportion of solid to gas (357). The solid particles form a continuous dense phase with a fairly well-defined surface and allow for an intimate contact of the catalyst with the reaction mixture.

By using a fluid type catalyst for the Fischer-Tropsch process, it is claimed that the heat of reaction may be removed as it is formed. The heat may be dissipated through the walls of the reaction vessel by circulating a cooling medium outside the walls of the reaction zone (361) or by suspending the catalyst in oil which also serves as a cooling medium. In one patent (362) it is claimed that the temperature can be maintained substantially constant anywhere within the range 225 - 425°F. by directly admixing relatively cool materials with the mixture in the synthesis zone. Unreacted gases and low molecular weight hydrocarbon gases are separated from the catalyst and recycled. Cool catalyst may be used to control the temperature of the reaction zone. Another, very recent patent (363) specifies the circulation of a solid heat carrier through the reactor along with the fluidized catalyst. The heat carrier must have a higher separating rate than the catalyst, in order to permit separation, cooling, and recirculation of the solid heat carrier. The physical properties of a fluidized Fischer-Tropsch catalyst have been studied. The correlations based on work with silica sand beds were briefly reviewed and the application of the correlations to process design was investigated (356).

Patents have been issued using the fluid catalyst in single-stage (360) and multiple-stage (364) processes. In the latter process, the first stage, which uses a Fe-K_2O-Super Filtrol catalyst, serves a two-fold purpose. It increases the yield of the liquid product and also produces a sulfur-free gas for the sulfur sensitive Co-ThO_2-MgO-Super Filtrol catalyst which is used in the second step.

As the hydrogenation process proceeds, the activity of the catalyst decreases. To maintain a more or less constant catalyst activity, methods have been devised for the introduction of fresh or regenerated catalyst into the reaction zone (358, 359). In the multistage process, the fresh catalyst is fed into the last zone and passes successively by overflow devices through other hydrogenating zones to the first, in which it has a relatively low activity and is withdrawn. The fluid catalyst may be regenerated by washing with normally gaseous hydrocarbons (e.g., C_4) (366) or by passing the fluid catalyst through a reaction zone which is operated at a higher temperature and a lower pressure (365). In this zone, the oily and waxy materials are volatilized and removed from the catalyst.

Beck (355) has described a laboratory scale unit for the evaluation of a fluid catalyst.

Alloy Skeleton Catalysts

The heat transfer problem involved in carrying out the highly exothermic Fischer-Tropsch synthesis over poorly conducting supported catalysts has prompted considerable investigation of catalyst, which by virtue of their finely divided state or their physical structure, permit a more rapid distribution of the heat which is evolved. Highly porous, catalytically active skeleton catalysts having a greater coefficient of heat transfer than precipitated catalysts have been developed by Raney (375, 386, 387, 388). These catalysts are prepared by alloying the desired metals with another component which can be removed, later, by leaching. For the Fischer-Tropsch synthesis, cobalt and nickel (singly or mixed) are fused with aluminum or silicon which is subsequently removed by solution in aqueous caustic. Fischer and Meyer (367) describe the preparation of a Co-Ni alloy catlyst. Lel'chuk and his co-workers (370, 371) have made a detailed study of skeleton catalysts. Lel'chuk found that a more active catalysts is prepared by rapid cooling and that a high-frequency furnace must be used to prepare catalysts which contain high-melting components.

Experiments with a Co-Ni alloy catalyst showed that 1) the optimum ratio of Co:Ni was 1:1, 2) catalysts prepared by alloying with silicon are more active than those prepared with aluminum, and 3) the presence of even small amounts of copper or manganese is not desireable (367). The catalyst prepared from Ni-Co-Si in a ratio of 1:1:2 is very dense, with an apparent specific gravity of 4.5 and it yields about 20% less liquid hydrocarbons than a precipitated catalyst containing the same weight of the metals. It has also been shown (378, 379) that catalysts prepared from alloys of nickel with aluminum, nickel with silicon, nickel with manganese and silicon, or nickel with iron and aluminum are decidedly inferior to those prepared from a nickel, cobalt and silicon alloy. A microscopic investigation of the catalyst obtained from a nickel, cobalt, and magnesium alloy shows that its crystal structure is much coarser than that of a catalyst prepared from the corresponding silicon alloy. Rapaport and Polozhentseva (376) investigated the activity of skeleton catalysts prepared from alloys of nickel and aluminum, cobalt and aluminum, and cobalt and silicon.

Detailed studies of skeleton catalysts have been made by Japanese investigators (373, 374, 377, 380, 381, 382, 383). They found that the optimum particle size for a Ni-Co (1:1) catalyst prepared from a Ni-Co-Si alloy (1:1:2) was 1 to 4 mm. for a space velocity of 100. Besides studying the effects of particle size, they investigated the effects of the bulk density of the catalyst, pretreatment with hydrogen and the material used for the construction of the reaction vessel. These investigators found that the yield of liquid hydrocarbons was about 130 cc.

(93 g.) per cubic meter of synthesis gas. Tsuneoka and Murata (372, 373) found that the degree of unsaturation of the reaction product increased with an increase of either the gas-flow or of the reaction temperature. The efficiency of the catalysis at constant gas input for a given amount of catalyst diminished when the free space exceeded or fell below a certain optimum value, which varied with the diameter of the reaction tube. Thus, for 10 g. of Ni-Co (1:1) catalyst and 4 l. per hour of synthesis gas, the optimum length for 13 mm. tubing was about 30 cm. If the length was shorter than the optimum, the average molecular weight of the liquid hydrocarbon product decreased and more gaseous hydrocarbons were produced.

The skeleton alloy catalysts deteriorated more rapidly and yielded (at best) about 20% less liquid products than precipitated catalysts having the same catalytic components (368, 369, 385). Drew (389) has patented a method for the regeneration of the nickel alloy catalyst in which the catalyst is heated to 600 - 700°F. The decomposition products are then removed by blowing with an inert gas, preferably super-heated steam.

The preparation of catalyst pellets having an "integral, porous, metallic skeleton" has been described in an American patent. In this method, the finely divided oxide of the catalytic metal (e.g., nickel or iron oxide) is mixed with a finely divided metal (e.g., copper or iron), the mixture is compressed into pellets and these in turn are heated in a reducing atmosphere at such temperature and for such time as is required to reduce most of the metal oxide to the catalytic metal and to cause alloying of the two metals, the temperature and time of heating being insufficient to cause all of the catalytic metal of the oxide to alloy with the other metal and the temperature being insufficient to cause sintering of the other metal in the absence of the catalytic metal.

In spite of the lower yields of liquid hydrocarbons and of the relatively rapid deterioration, catalysts of the alloy skeleton type have stimulated great interest in their possibility for the Fischer-Tropsch process because of their high coefficient of heat transfer.