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CHEMICAL AND THERMOMAGNETIC STUDIES ON IRON CATALYSTS FOR THE SYNTHESIS OF HYDROCARBONS

By

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Translation by R. Brinkley

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CHEMICAL AND THERMOMAGNETIC STUDIES ON IRON CATALYSTS FOR THE SYNTHESIS OF HYDROCARBONS[1]

By

H. Pichler[2] and H. Merkel[3]

Translation by R. Brinkley[4]

PREFACE

By L. J. E. Hofer[5]

This document contains much of the data supporting recent German views on the importance of carbides in iron Fischer-Tropsch catalysts. The report is in the form of a Ph.D. thesis by Heinrich Merkel and is based on research carried out at the Kaiser Wilhelm Institut für Kohlenforschung under the direction of Helmut Pichler. Preliminary experiments at the Bureau of Mines have so far confirmed the thermomagnetic sections of the paper.

This study is, to date, the only extensive experimental series of investigations of the changes occurring in the catalyst structure during induction and synthesis. The conditions of formation of two new carbides of iron and some of their chemical and physical properties are discussed. The relative catalytic activities of cementite and the two new carbides are reported. A study of the formation of free carbon in the catalysts during the Fischer-Tropsch synthesis was also made.

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While still in Germany, Pichler described the contents of the thesis to Guenther von Elbe, of the United States Technical Oil Mission. At that time all the data, including an early draft of the thesis and all the laboratory notebooks, were unavailable because Merkel was using them to obtain his degree. Merkel himself could not be located. Pichler's description of the function of carbide in the Fischer-Tropsch reaction was considerably more advanced than was the information presented in the older documents found by the Technical teams at the Kaiser Wilhelm Institut für Kohlenforschung.[6]

Later, when Pichler came to the United States as a consultant, he brought with him the preliminary draft of the thesis, but no graphs or tables. Merkel had in the meantime returned to the Kaiser Wilhelm Institut. Although the draft contained evidence of two higher carbides of iron, other than cementite, Pichler was dissatisfied with it because it did not clearly demonstrate that these higher carbides existed. However, the draft was translated and Pichler planned to reproduce the graphs from memory and write an addendum to express his viewpoint.

Before these plans could be fulfilled, Pichler succeeded in obtaining from Merkel a revised manuscript, complete with tables and graphs, which had been accepted by the Technische Hochschule, Aachen,

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[6] Leva, M., Translations of German Documents on the Development of Iron Catalysts for the Fischer-Tropsch Synthesis, Part I, (Technical Oil Mission Reel 101, Document PG-21559-NID, Report on the Middle-Pressure Synthesis with Iron Catalysts, June 1940): Office of Synthetic Liquid Fuels Report 2774-Q:18 Revised, Pittsburgh, 1946, pp. 1-48.

in partial fulfillment of the requirements for the Ph.D. degree. The entire last half of the manuscript had been rewritten and expanded. Pichler thought that his views were adequately represented in the revised manuscript, except for some minor points, and he read and approved of the entire translation.

In order to integrate the formation in the thesis with existing data which were either unpublished or inaccessible to Pichler and Merkel in the writing of their paper, a Foreword entitled, "Introduction to the Carbides of Iron and Their Physical and Chemical Properties", by L. J. E. Hofer follows below. Immediately following the Foreword are inserted Appendices A-D, describing the hexagonal iron carbide of Halle and Herbst.

Titles of footnote references enclosed in brackets are translations of the title from the language in which the work cited was published.

ACKNOWLEDGMENTS

H. Pichler wishes to express his sincere thanks to F. Fischer for his inspiration and great interest in the work. Thanks are also due to Mrs. Ruth Brinkley, who translated the German manuscripts and E. M. Cohn, who critically edited and annotated the translations.

Thanks are given to Enseigne de Vaisseau J. Foucher, of the French Navy, and W. F. Faragher, through whose efforts the German manuscripts describing the hexagonal iron carbide of Halle and Herbst were obtained late in 1947.

FOREWORD

By L. J. E. Hofer[7]

INTRODUCTION TO THE CARBIDES OF IRON AND THEIR PHYSICAL AND CHEMICAL PROPERTIES

Almost simultaneously with the first announcement of the Fischer-Tropsch reaction, the formation of carbides was suggested as an intermediate in the synthesis.[8] This hypothesis was supported at first largely because carbides of iron, cobalt, and nickel were known to react with hydrogen to form hydrocarbons under the conditions of temperature and pressure used in the Fischer-Tropsch synthesis itself[9]; in addition, it was known that hydrocarbons are formed when carbides of these elements react with acids.[10] Later, Fischer demonstrated the presence of carbide in used Fischer-Tropsch catalysts by showing the evolution of hydrocarbons during decomposition of the catalyst with

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[7] Hofer, L. J. E., work cited (footnote 5).

[8] Fischer, F. and Tropsch, H., [Hydrocarbon Synthesis at Atmospheric Pressure from Gasification Products of Coal]: Brennstoff Chem., vol. 7, 1926, pp. 97-104.

[9] Hilpert, S. and Dieckmann, T., [The Catalytic Effect of Iron Carbides on the Decomposition of Carbon Monoxide]: Ber. Deut. chem. Gesell., vol. 48, 1915, pp. 1281-1286.

[10] Ledebur, A., On the Modification of Carbon in Iron: Jour. Iron and Steel Inst., vol. 44, Part II, 1893, pp. 53-76.
Mathews, J. A., Review and Bibliography of the Metallic Carbides: Smithsonian Miscellaneous Collections 1090, 1898.

acid.[11] As has been previously suggested, the so-called "cubic iron oxide" of Lefebvre and LeClerc[12] which forms in iron catalysts during synthesis is probably an iron carbide.[13] The Pichler and Merkel document should dispel any doubt on this point. LeClerc and Lefebvre showed the presence of carbide (cubic iron oxide according to them) in the more active iron catalysts; the less active catalysts were largely magnetite. Eidus[14] and his collaborators, in a general study of the kinetics of

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[11] Fischer, F. and Tropsch H., [Hydrocarbon Synthesis]: Ges. Abhandl. Kenntnis Kohle, vol. 10, 1932, pp. 313-501.

[12] Lefebvre, H. and LeClerc, G., [Thermomagnetic Study of Iron Fischer-Tropsch Catalyst]: Comptes rendus, vol. 203, 1936, pp. 1378-1380. [Synthesis with Hydrogen and Carbon Monoxide Over Iron Catalysts]: Congres chim. ind. Comptes rendus 18th Congres, Nancy, Sept.-Oct., 1938, pp. 725-730.
LeClerc, G., [Catalytic Activity of Cubic Iron Sesquioxide in Synthesis with Hydrogen and Carbon Monoxide at Atmospheric Pressure] Comptes rendus, vol. 207, 1938, pp. 1099-1101.

[13] Storch, H. H., Anderson, R. B., Hofer, L. J. E., Hawk, C. O., Anderson, H. C., and Golumbic, N., Synthetic Liquid Fuels from Hydrogenation of Carbon Monoxide, Part I: Bureau of Mines Technical Paper 709, in press.

[14] Eidus, Ya. T., et al., [Investigations of Catalysts for Hydrogenation of Carbon Monoxide by Simultaneous Application of the Static and Dynamic Method III. The Part Played by the Alkaline Activator in the Formation of the Surface of the Catalyst Iron-Copper-Thoria-Potassium-Carbonate-Kieselguhr]: Bull. Acad. Sci. U.R.S.S., Classe Sci. Chim., 1945, pp. 62-70. Universal Oil Products Company Surv. For. Petrol. Lit., Transl. 537. [Investigation of Catalysts for Hydrogenation of Carbon Monoxide by Simultaneous Application of the Dynamic and Static Methods. IV. Kinetics of Carbide Formation and of Hydrogenation of Carbon Monoxide on Cobalt, Nickel, and Iron Catalyst]: Bull. Acad. Sci. U.R.S.S., Classe Sci. Chim., 1946, pp. 447-453. Universal Oil Products Company Surv. For. Petrol. Lit., Transl. 656.

14/ (Continued)

Eidus, Ya T. and Altshuller, S. B., [Investigation of Catalysts for Hydrogenation of Carbon Monoxide by Simultaneous Use of Static and Dynamic Methods II. Activity of Catalysts Containing Various Components of the Catalyst Iron-Copper-Thorium Dioxide-Potassium Carbonate-Kieselguhr]: Bull. Acad. Sci. U.R.S.S., Classe Sci. Chim., 1944, pp. 349-357. Universal Oil Products Company Surv. For. Petrol. Lit., Transl. 507.

Eidus, Ya T., and Elagina, N. V., [Effect of the Composition of the Catalyst and the Nature of the Carrier on the Activity and Stability of the Catalyst Iron-Copper-Thoria-Potassium Carbonate in the Synthesis of Liquid Hydrocarbons from Carbon Monoxide and Hydrogen]: Bull. Acad. Sci. U.R.S.S., Classe Sci. Chim., 1943, pp. 303-311. Universal Oil Products Company Surv. For. Petrol. Lit., Transl. 468.

Eidus, Ya T., Epifanskii, P. F., Petrova, L. V., and Elagina, N. V., [The Activating Effects of Oxides of Some Metals on the Iron-Copper Catalysts Used for Synthesis of Gasoline from Water-Gas]: Bull. Acad. Sci. U.R.S.S., Classe Sci. Chim., 1943, pp. 145-151. Universal Oil Products Company Surv. For. Petrol. Lit., Transl. 441.

the Fischer-Tropsch synthesis, compared the rate of the synthesis,

$$2xCO + xH_2 \longrightarrow (CH_2)_x + xCO_2$$

with the rate of carbide formation,

$$2CO + 2Fe \longrightarrow Fe_2C + CO_2$$

and showed that the rate of formation of the carbide and hydrogenation of the carbide for certain iron catalysts was more rapid than the rate of synthesis. Eidus concluded that the synthesis on these catalysts proceeded by way of carbide as an intermediate.[15]

The evidence cited above suggests that carbide is an intermediate in the reaction. This interpretation of the data is based on the implicit assumption that carbide in bulk[16] rather than surface carbide is the intermediate.[17] But this seems quite unlikely since it is well known that most heterogeneous gas reactions proceed on active

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[15] Eidus, Ya. T., [Investigation of Catalysts for Hydrogenation of Carbon Monoxide by Simultaneous Application of the Dynamic and Static Methods. I. Activity of the Complex Catalyst Iron-Copper-Thoria-Potassium Carbonate-Kieselguhr]: Bull. Acad. Sci. U.R.S.S., Classe Sci. Chim., 1944, pp. 255-262. Universal Oil Products Company Surv. For. Petrol. Lit., Transl. 492A.

[16] Hofer, L. J. E., Preparation and Properties of Metal Carbides with Critical Comment as to Their Significance in the Fischer-Tropsch Synthesis: Bureau of Mines Report of Investigations 3770, July 1944, 39 pp.

[17] The following definitions have been found useful and have been implied in this discussion:

Surface carbide - atomically dispersed adsorbed carbon.

Bulk carbide - homogeneous metal-carbon phase in which the carbon is atomically dispersed. (The only bonds are carbon-metal bonds of an intermetallic nature.)

Free carbon - carbon in which carbon-carbon bonds have been established.

surfaces rather than in bulk. It is hard to conceive how bulk carbide can be intermediate in the reaction. Recently, Kummer, De Witt, and Emmett[18], using C^{14} tracer carbon, have produced evidence to show that the amount of hydrocarbon formed from bulk carbide during Fischer-Tropsch synthesis was small compared with the amount formed by some alternative mechanism. Great weight must be attached to the conclusion of these investigators, since their method is much more direct than that of others.

Information is beginning to accumulate which shows that bulk carbide is not an intermediate in the synthesis as carried out on cobalt, nickel, and ruthenium catalysts. The presence of cobalt carbide is deleterious in cobalt-thoria-kieselguhr catalysts.[19] Indeed, such catalysts are almost completely inactive under ordinary synthesis conditions when fully converted to carbide. In nickel-type catalysts, the so-called "hexagonal nickel",[20] formed by the action of carbon monoxide on the face-centered cubic form of nickel, is inactive in the Fischer-Tropsch synthesis, according to LeClerc and Lefebvre.[21] Undoubtedly,

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[18] Kummer, J. T., De Witt, T. W., and Emmett, P. H., Some Mechanism Studies of the Fischer-Tropsch Synthesis Using C^{14}: Abstracts of Papers of 111th Meeting American Chemical Society, April 14-18, 1947, Division of Physical and Inorganic Chemistry, 29 pp.

[19] Weller, S., Hofer, L. J. E., and Anderson, R. B., Effect of Cobalt Carbide on the Fischer-Tropsch Synthesis: Abstracts of Papers of 112th Meeting American Chemical Society, Sept. 15-19, 1947, Division of Physical and Inorganic Chemistry, 1 p.

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[20] LeClerc, G. and Michel, A., [Preparation and Properties of Hexagonal Nickel]: Comptes rendus, vol. 208, 1939, pp. 1583-1585.

[21] LeClerc, G. and Lefebvre, H., [Comparison of the Catalytic Activity of Two Allotropes of Nickel]: Comptes rendus, vol. 208, 1939, pp. 1650-1651.

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this "hexagonal nickel" is really nickel carbide.[22] This was originally pointed out by Crawford and Rideal. The crystal structure of the two forms seems to be identical[23]; the conditions of formation and decomposition are similar; both are either strongly paramagnetic or weakly ferromagnetic.

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[22] Crawford, S. R. and Rideal, E. K., Mechanism of the Synthesis of Hydrocarbons from Water Gas: Jour. Chem. Soc., Part II, 1939, pp. 1604-1614.

[23] Jacobsen, B. and Westgren, A., [The Relationship of Nickel Carbide to the Carbides of the Scandium-Nickel Series]: Ztschr. physik. Chem., vol. B20, 1933, pp. 361-367.
Schmidt, J., and Osswald, E., [The Nonexistence of a Higher Nickel Carbide]: Ztschr. anorg. Chem., vol. 216, 1933, pp. 85-93.

If the bulk carbide of nickel or cobalt were a good catalyst for the synthesis, an improvement in activity would be expected in its presence. If the bulk carbide were an intermediate in the synthesis, at least a temporary increase in activity would be anticipated. However, neither effect is observed and it can be concluded that bulk carbide is neither a good catalyst nor an intermediate in the synthesis.

It may be postulated, that the carbides only fulfill the role of intermediates when in the presence of relatively large amounts of reduced metal. This possibility is difficult to deny; but there is no experimental evidence to support it. It may also be postulated that the intermediates are not these particular carbides but some other carbides of cobalt and nickel. This seems unlikely, since the observed carbides were formed under conditions of temperature and pressure similar to those used in the synthesis, although the gas composition (pure CO) was somewhat different.

There is strong evidence that bulk carbide is not involved when ruthenium is the catalyst. At the partial pressure of carbon monoxide used in the synthesis pure carbon monoxide reacts with ruthenium to form volatile carbonyls and apparently no carbide.[24]

Although bulk carbide itself does not seem to be the intermediate in the reaction, surface carbide may be the intermediate. Surface carbide is a very elusive concept which is difficult to study experimentally. However useful the concept of surface carbide may be for many purposes, its discussion is not germane to a review such as this of directly obtainable experimental data.

Various methods of studying carbides have been used. The most important are thermomagnetic, X-ray diffraction, and chemical analyses. Individually, these methods are not very satisfactory, but if all three are employed simultaneously, a fairly complete picture can be evolved, since they are mutually supplementary. Unfortunately, investigators have rarely used more than two of these methods at the

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[24] Manchot, W. and Manchot, W. J., [Preparation of Ruthenium Carbonyls and Nitrosyls]: Ztschr. anorg. Chem., vol. 226, 1936, p. 385.
Pichler, H., Private communication.

same time. This situation is particularly unfortunate in the study of iron catalysts, where several carbides are known to exist and chances for ambiguity are correspondingly greater.

In order to determine which carbides may be involved in the Fischer-Tropsch reaction on iron catalysts, an analysis of the available data on iron carbides is pertinent. The characteristics of some carbides are described below.

Cementite

The best known iron carbide is cementite; its physical and chemical characteristics are well known. It occurs in carbon steels as pearlite, the eutectoid mixture of α-iron (ferrite) and cementite (0.9 percent carbon); ledeburite, the eutectic mixture of γ-iron (austenite) and cementite (4.2 percent carbon); and as primary and secondary cementite. A study of the iron carbon diagram is very instructive.[25]

It is almost impossible to form pure cementite by quenching a stoichiometric melt of iron and carbon, because of the rapidity of graphitization. It is an open question whether large single crystals of cementite have ever been formed in this way except when stabilized with manganese or some other stabilizing agent. Cementite stabilized with manganese is often mentioned in the literature as "spiegeleisen" and "cohenite". It is possible to isolate the cementite in pearlite

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[25] Epstein, S., The Alloys of Iron and Carbon, vol. 1, Constitution: McGraw-Hill Book Company, New York, 1936, 476 pp.

and ledeburite by dissolving away the matrix of ferrite (α-iron) or austentite (γ-iron) with dilute sulfuric acid in an inert atmosphere.[26] Under these conditions, cementite is quite resistant to acid. Electrolytic solution of the matrix can also be employed.[27]

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[26] Schenck, R. and Stenkhoff, R., [Acid Decomposition of Iron Carbide]: Ztschr. anorg. allgem. Chem., vol. 161, 1927, pp. 287-303.

[27] Arnold, J. O. and Read, A. A., Chemical Relations of Carbon and Iron: Jour. Chem. Soc., vol. 65, 1895, p. 788.

Cementite may also be formed by carburizing iron with carbon monoxide or methane at temperatures in the region of the α to γ transition (910 ± 3°C. for pure iron) and cooling the product to room temperature. This process consists of two stages: First, the formation of a solid solution of carbon in γ-iron (austentite) during the actual carburization, and second, the formation of α-iron (ferrite) and cementite- α-iron eutectoid upon cooling the solid solution below the eutectoid temperature (723°C.) to room temperature; or if the carbon content is above the eutectoid composition, the formation of cementite and the cementite- α-iron eutectoid upon cooling the solid solution below the eutectoid temperature. If this cooling takes place too rapidly, retained austenite or martensite is produced. Carburizing media other than those mentioned can be used. In pack carburizing, coal, coke, and an "energizer" such as sodium or barium carbonate are used. It is believed that CO is the true carburizing agent in pack carburizing. Liquid carburizing is carried out in baths which may contain calcium cyanide, calcium cyanamide, or other carbon-rich agents plus various other salts acting as solvents, such as sodium chloride.

Cementite can also be formed by the direct action of carbon monoxide on α-iron at temperatures below 300°C.[28] This process is very slow and proceeds at appreciable rates only on very finely divided metal, but it is this process which is most likely related to cementite formation in the Fischer-Tropsch reaction. Samples of nearly pure microcrystalline cementite can be prepared in this way. Carbon monoxide and hematite form cementite at about 500°C.[29] Other methods for preparing cementite have been reported, such as the decomposition of potassium ferrocyanide.[30]

Mittasch, Kuss, and Emert[31] decomposed $Fe(CN)_2$ with hydrogen

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[28] Hägg, G., [Powder X-ray Patterns of a New Iron Carbide]: Ztg. Krist., vol. 89, 1934, pp. 92-94.

[29] Lipson, H. and Petch, N. J., The Crystal Structure of Cementite, Fe_3C: Jour. Iron Steel Inst., vol. 142, 1940, pp. 95-106.

[30] Brill, R. and Mark, H., [X-ray Study of the Decomposition of Complex Iron Cyanides]: Ztschr. physik. Chem., vol. 133, 1928, pp. 443-455.

[31] Mittasch, A., Kuss, E., and Emert, O., [Thermal Decomposition of Complex Iron Cyanides and Relationship with Synthetic Ammonia Catalysts]: Ztschr. anorg. allgem. Chem., vol. 170, 1928, pp. 193-212.

and nitrogen at various temperatures and concluded by fairly complex reasoning that two carbides might be intermediate in the reaction. One carbide reacted very readily with hydrogen at 200°C.; the other, only slowly at 400°C. The latter carbide they identified from its Curie Point as cementite. No X-ray work was done.

Cementite seems to be the most stable of all the carbides of carbon. The Hägg carbide (see below) decomposes into cementite,[32] although Lipson and Petch claim the reverse occurs.[33] The carbide of Halle and Herbst (see below) decomposes into the Hägg carbide. Martensite and retained austenite (carbon-rich) also decompose to cementite and α-iron. On the other hand, cementite decomposes only into free carbon or graphite and α-iron.

The crystal structure of cementite has received much attention. It has an orthorhombic unit cell with lattice parameters a_o = 4.514-4.507Å, b_o = 5.079-5.073Å, and c_o = 6.730-6.734Å.[34] The carbon atoms lie in the spaces between the iron atoms. There are four formula weights of Fe_3C in the cell, using the density 7.74 obtained by Benedicks.[35] The Curie Point

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[32] Jack, K. H., Iron-Nitrogen, Iron-Carbon, and Iron-Carbon-Nitrogen Interstitial Alloys; Their Occurrence in Tempered Martensite: Nature, vol. 158, July 13, 1946, pp. 60-61.

[33] Lipson, H. and Petch, N. J., work cited (footnote 29).

[34] Hume-Rothery, W., Raynor, G. V., and Little, A. T., The Lattice Spacings and Crystal Structure of Cementite: Jour. Iron Steel Inst., vol. 145, 1942, pp. 143P-152P.
Petch, N. J., Interpretation of the Crystal Structure of Cementite: Jour. Iron Steel Inst., vol. 149, 1944, pp. 143P-150P.

[35] Benedicks, C., [Physical and Physico-chemical Study of Carburized Steel]: Dissertation, Uppsala, 1904, p. 215.

of cementite occurs at about 205° to 220°C.[36]

Cementite reacts with certain acids to form hydrocarbons and ferrous ion. The reaction,

$$Fe_3C + 6H^+ \longrightarrow 3Fe^{++} + (CH_2)_x + 2H_2$$

is not quantitative under all conditions. High hydrogen and low ferrous ion concentrations favor complete conversion to hydrocarbons. This is not simply an example of the mass action law because high ferrous ion concentration favors carbon deposition. The reaction is not well adapted to quantitative analysis because carbon may be produced and because the hydrocarbons formed are not always gaseous.[37] Cementite may be formed in iron Fischer-Tropsch catalysts under certain conditions, but its presence is undesirable, according to Pichler and Merkel.

Martensite

Martensite may be regarded as a super-saturated solid solution of carbon in α-iron.[38] It is formed by very rapid quenching of a solid

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[36] Honda, K. and Murakami, T., [On the Thermomagnetic Properties of the Carbides Found in Steels]: Sci. Rep., Sendai ser. 1, vol. 6, 1917, pp. 23-29.

[37] Schenck, R. and Stenkhoff, R., work cited (footnote 26).

[38] Lipson, H. and Parker, A. M. B., The Structure of Martensite: Jour. Iron Steel Inst., vol. 149, 1944, pp. 123, 141.

solution of carbon in γ-iron. Martensite is very reactive, decomposing to cementite and α-iron at temperatures below 300°C. and as low as 100-200°C. The structure is body-centered tetragonal. Its axial ratio c/a, depends on carbon content, varying from 1 (0 percent carbon, pure α-iron) to 1.06 (for 6 atomic percent carbon). Austenite, martensite, and ferrite may all be considered to be body-centered tetragonal structures differing only in axial ratios; for austenite the ratio is $\sqrt{2}$:1 (1.41:1) while for ferrite it is 1. The axial ratio of martensite is intermediate.

Little is known about the action of acid or of hydrogen on martensite. It probably would behave like cementite, forming hydrogen and hydrocarbons with acids, and hydrocarbons only with hydrogen. The method of formation almost certainly precludes any possibility that martensite is involved in the Fischer-Tropsch reaction. Furthermore, the temperature of the synthesis is probably too high for the maintenance of martensite.

Austenite with Dissolved Carbon

Austenite, face-centered cubic γ-iron, can dissolve as much as 1.7 ± .3 percent carbon at 1150°C.[32] The lattice parameter varies with carbon content from 3.564 Xu for pure γ-Fe to 3.62 Xu for γ-Fe with 1.74 percent dissolved carbon. With sufficiently rapid cooling austenite can be retained at room temperature in a metastable state, especially in the presence of chromium or nickel. A solid solution of carbon in austenite decomposes into martensite and eventually

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[32] Petch, N. J., The Positions of the Carbon Atoms in Austenite: Jour. Iron Steel Inst., vol. 145, 1942, pp. 111P-128P.

cementite and ferrite at temperatures well below 300°C. At higher temperatures austenite decomposes directly to cementite and α-Fe.

Carbon dissolved in austenite probably does not enter into the Fischer-Tropsch reaction, since the conditions for stable austenite do not occur during synthesis.

Ferrite with Dissolved Carbon

The maximum solubility of carbon in ferrite (α-iron) is 0.03 ± .02 percent at the eutectoid temperature (723°C.). At room temperature, the maximum carbon content is 0.006 ± .003 percent.[40] Because carbon in solid solution in α-Fe diffuses very rapidly and the phase is stable at synthesis temperature, it is possible that this phase is involved in the synthesis.

Carbide of Brill and Mark

This carbide was proposed[41] to explain the appearance of certain extra lines in the diffraction pattern of the product obtained when hydrogen and nitrogen act on ammonium ferrocyanide at 400°C. The other constituents of this product are cubic $Fe(CN)_2$ and α-Fe. Only a few lines were found, as indicated in table 1. There is no positive evidence that these lines are due to a carbide of unknown structure.

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[40] Köster, W., [The Effect of Heat Treatment Below the A Point on the Properties of Technical Iron]: Archiv. Eisenhüttenwesen, vol. 2, 1929, pp. 503-522.

[41] Brill, R. and Mark, H., work cited (footnote 30).

Certainly the formula for this carbide cannot be determined from the evidence presented.

Carbide of Hofmann and Groll

Hofmann and Groll[42] investigated the action of carbon monoxide on iron oxides at various temperatures. In the diffraction patterns of the products obtained at 320°C. or lower, they found lines due to an unknown constituent which they believed was an iron carbide. From the changes in weight during treatment with carbon monoxide, they concluded that the formula of the carbide was Fe_2C. Some of the spacings in the diffraction patterns observed by Hofmann and Groll were identical with those of Brill and Mark.

Carbide of Tutiya

Tutiya[43] prepared carbides by the action of carbon monoxide on iron and iron oxide at various temperatures. In his early work, he was not able to identify in the diffraction patterns the spacings of

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[42] Hofmann, U. and Groll, E., [Carbon Deposition from Carbon Monoxide on Iron III. Formation of Iron Oxides and Carbides]: ~~Ztschr.~~ Ztschr. anorg./Chem., vol. 191, 1930, pp. 414-428.
allgem.

[43] Tutiya, H., [Catalytic Decomposition of CO (I). Iron as a Catalyst]: Sci. Papers Inst. Phys. Chem. Research, Tokyo, vol. 10, 1929, pp. 69-82. (In Esperanto.) [Catalytic Decomposition of CO (II). Is the So-called X-carbide Really Formed in the Iron ~~Carbide~~ Catalyst]: Bull. Inst. Phys. Chem. Research, Tokyo, vol. 8, 1929, pp. 609-613.

Table 1.–Comparative X-ray diffraction data of the carbides of Halle and Herbst, Tutiya, Hofmann and Groll, and Brill and Mark

Indices hkl	Halle and Herbst d/n	Halle and Herbst I	Tutiya d/n	Hofmann and Groll d/n	Hofmann and Groll I[a]	Brill and Mark d/n
100	2.38	m.	2.32	2.263	m.	2.28
002	2.15	m.	2.20	2.172	m.	-
101	2.07	v.st.	2.065	2.050	st.	2.12
	-	-	1.815	1.802	v.w.	1.826
	-	-	1.706	-		1.716
102	1.60	m.	-	1.543	m.	-
	-	-	-	1.465	w.	1.491
110	1.38	m.	1.377	1.372	w.	1.367
103	1.24	m.	1.251	1.244	v.w.	-
	-	-	1.212	1.212	m.	1.206
112	1.166	m.st.	1.165	1.167	m.	1.148
201	1.153	m.				

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a/ Intensity, m. = medium, st. = strong, w. = weak, v. = very

Brill and Mark, nor those of Hofmann and Groll. Later, he claimed that his diffraction patterns did contain the same spacings as reported by Hofmann and Groll. (See table 1, data of Tutiya[44].)

Carbide of Halle and Herbst

The available data describing this carbide are given in appendices A-D. Apparently, the carbide has the formula Fe_2C and decomposes at about 290°C. into the Hägg[45] carbide. It is stabilized by the presence of copper and its presence promotes the Fischer-Tropsch synthesis.

The iron atoms are arranged in the close-packed hexagonal structure; hence this carbide is apparently isomorphous with Fe_2N.[46] This carbide was not formed by the action of carbon monoxide on Fe_2N[47] probably because of the high temperature used. The lattice

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[44] Tutiya, H., [Catalytic Decomposition of Carbon Monoxide (III). The Behavior of Iron Carbides]: Bull. Inst. Phys. Chem. Research, Tokyo, vol. 10, 1931, pp. 556-562.

[45] Hägg, G., work cited (footnote 28).

[46] Hägg, G., [X-ray Investigation of Iron Nitride]: Ztschr. Physik. Chem., vol. B8, 1930, pp. 455-474.

[47] Jack, K. H., work cited (footnote 32).

parameters, a_0 = 2.76 Å and c_0 = 4.36 Å, are large as compared with the lattice parameters, a_0 = 2.48Å and c_0 = 3.94Å, of a hexagonal close-packed arrangement of iron atoms without interstitial carbon. This expansion of the unit cell indicates the instability of the hexagonal close-packed iron carbide. Comparison of the interplanar spacings of the close-packed hexagonal carbide with those of the carbides of Tutiya, Hofmann and Groll, and Brill and Mark (table 1) indicates that the carbides of Tutiya and Hofmann and Groll, in particular, were probably impure specimens of the hexagonal carbide. Reasonably close analogs of all the lines of the hexagonal carbide could be found in the X-ray diffraction patterns of these carbides (with the possible exception of the 102-line). The Hofmann and Groll and the Tutiya carbides produced a few extra lines. The statement by Herbst that the hexagonal carbide is not identical with that of Hofmann and Groll is surprising. (See Appendix D.)

This hexagonal iron carbide completes the series of iron carbonitrides, described by Jack,[48] which covers the range from 100 percent iron-nitrogen to 100 percent iron-carbon without modification in the essential hexagonal close-packed 12 b 6 structure.[49]

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[48] Jack, K. H., work cited (footnote 32).
[49] Hagg, G., [Regularities in the Crystal Structures of the Hydrides, Borides, Carbides, and Nitrides of the Transition Elements]: Ztschr. physik. Chem., vol. B 12, 1931, pp. 33-~~48~~. 56

Carbide II of Pichler and Merkel

By reducing an iron catalyst (1 percent Cu and 1.5 percent K_2CO_3) with hydrogen at 250°C. for 240 hours and then treating with carbon monoxide at 220°C., a product was formed with two Curie Points (C.P.), one at 380°C. and one at 265°C., characteristic of two distinct carbides. Catalysts carbided at still lower temperatures contained more of the phase with the 380°C. Curie Point. Catalysts exhibiting the 380°C. Curie Point were active in the synthesis. At 300°C. the Curie Point 380°C. carbide was transformed to cementite (Curie Point 205 to 220°C.). According to the data of Pichler and Merkel, the formation of this Curie Point 380°C. carbide is favored by reduction of the catalyst by hydrogen prior to treatment with carbon monoxide, and by promotion with copper.

Recent X-ray diffraction and thermomagnetic work at the Bureau of Mines has shown that the 380°C. Curie Point carbide of Pichler and Merkel is identical with the hexagonal close-packed iron carbide of Halle and Herbst. The results of this study are being published.

Carbide of Bahr and Jessen

Bahr and Jessen[50] showed that carbon monoxide reacts with iron metal to form a substance whose formula is Fe_2C, if the reaction is carried out below 225°C. The carbon in this substance is particularly reactive and readily forms methane with hydrogen at

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[50] Bahr, H. A. and Jessen, V., [Decomposition of Carbon Monoxide by Iron and Iron Oxide]: Ber. Deut. chem. Gesell., vol. 66, 1933, pp. 1238-1247.

temperatures below 300°C. If carbon monoxide reacts with iron at temperatures above 250°C., products having no definite composition by weight and containing more carbon than corresponds to Fe_2C are formed. The carbon in the product formed above 250°C. consists of an easily hydrogenated fraction and a difficultly hydrogenated fraction. The former fraction, always less than the amount corresponding to Fe_2C, is identified as carbidic carbon, while the latter is free carbon. No X-ray or thermomagnetic analyses were made by these authors.

Carbide of Hägg

Hägg,[51] closely following the procedure of Bahr and Jessen, prepared carburized products at various temperatures. The X-ray diffraction patterns showed that the products formed at 300°C. comprised large amounts of cementite. At lower temperatures, the diffraction pattern contained lines of another phase, which predominated in the products formed at 225°C. or below. Hägg considered this new phase to be a carbide of iron of the composition Fe_2C. This seems reasonable, in view of the results of Bahr and Jessen. This carbide decomposes to cementite and iron at about 500°C.

Carbide of Jack

The action of carbon monoxide on iron nitride at 500°C. or below leads to the formation of a phase[52] whose reflecting interplanar

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[51] Hägg, G., work cited (footnote 28).

spacings are the same as those of the carbide of Hägg. Jack considered the crystallites to be orthorhombic and the lattice parameters to be $a_o = 9.04$ kx, $b_o = 15.66$ kx, $c_o = 7.92$ kx.

Cubic Iron Sesquioxide of LeClerc and Lefebvre

Lefebvre and LeClerc[53] claimed that precipitated iron catalysts reduced to magnetite by the action of hydrogen are gradually converted during synthesis to "cubic iron oxide", that is γ-Fe_2O_3 stablized with K_2O. Their reasons for this conclusion were based solely on thermomagnetic curves which showed that during the first 48 hours of operation the catalyst which originally exhibited only one Curie Point at 580°C. gradually developed another Curie Point at 250°C. The latter point was thought to be characteristic of a saturated solid solution of K_2O in γ-Fe_2O_3 according to Michel and Chaudron.[54] In a later paper in which considerably more data were presented, Michel stated that the lowest possible Curie Point of a

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[52] Jack, K. H., work cited (footnote 32).

[53] Lefebvre, H. and LeClerc, G., work cited (footnote 12).

[54] Michel, A. and Chaudron, G., [Study of Stabilized Cubic Iron Sesquioxide]: Comptes rendus, vol. 201, 1935, pp. 1191-1193.

saturated solid solution of K_2O in γ-Fe_2O_3 is 630°C.[55] In view of this contradiction in the literature, other explanations for the 250°C. Curie Point observed by Lefebvre and LeClerc may be advanced.[56] Pichler and Merkel consider the Curie Point 250°C. phase to be a distinct new carbide. The presence of this carbide favors the synthesis.

Carbide I of Pichler and Merkel

A precipitated iron catalyst containing 0.25 percent K_2CO_3, whose characteristics were apparently similar to the alkalized catalyst of Lefebvre and LeClerc, was treated with carbon monoxide. Thermomagnetic analysis of the product revealed a Curie Point at 265°C. Pichler and Merkel believe that the phase giving rise to this Curie Point is a new carbide of iron.

By treating a precipitated iron catalyst (1 percent Cu and 1.5 percent K_2CO_3) with carbon monoxide (1/10 atmosphere pressure and 325°C.), Fe_3O_4 (magnetite) was obtained first, then the Curie Point 265°C. carbide. In twelve hours all the iron was in the form of carbide. This catalyst had high activity.

When a copper-free catalyst containing 1.5 percent K_2CO_3 was treated by the method of Bahr and Jessen[57] (reduction with hydrogen

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[55] Michel, A., [Magnetic Properties of Some Solid Solutions]: Ann. de Chim., 11th series, vol. 8, 1937, pp. 317-423.

[56] Storch, H. H., Anderson, R. B., Hofer, L. J. E., Hawk, C. O., Anderson, H. C., and Golumbic, N., work cited (footnote 13).

at 250°C. for 240 hours followed by carburization with carbon monoxide at 220°C. for 219 hours), a product containing magnetite and the Curie Point 265°C. carbide in 1:1 proportion was obtained.

Under the conditions of the normal-pressure synthesis with iron (Fe + 0.25 percent Cu), the Curie Point 265°C. carbide was gradually developed.

Pichler and Merkel's analyses were made exclusively by the thermomagnetic method; no X-ray studies were attempted. It is not possible to compare their results directly with those obtained by the use of the X-ray technique alone. However, as they pointed out, this 265° Curie Point is beyond question due to the same phase which Lefebvre and LeClerc[58] considered cubic iron oxide (γ-Fe_2O_3).

Recent X-ray diffraction and thermomagnetic work at the Bureau of Mines indicates that the Curie Point 250° or 265°C. carbide is identical with the carbide of Hägg. These data are being prepared for publication.

Carbide of Durand

Calcium carbide reacts with an aqueous solution of ferrous chloride to yield the corresponding acetylide and a solution of

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[57] Bahr, H. A. and Jessen, V., work cited (footnote 50).

[58] Lefebvre, H. and LeClerc, G., work cited (footnote 12).

calcium chloride.[59] A side reaction is the effect of water on calcium carbide to form calcium hydroxide and gaseous acetylene. Iron acetylide is stable at room temperature in air and in water but forms acetylene when treated with hydrochloric acid. No X-ray diffraction studies have been made.

SUMMARY

The outstanding characteristics of the iron carbides are summarized in table 2. The data are very meager in some cases and not at all sufficient to establish identity. Some of these carbides are unquestionably identical with others in the table.

There can be no doubt as to the identity and nature of cementite, martensite, and the solid solutions of carbon in austenite and ferrite, because these are well-known phases.

The carbides of Hofmann and Groll, Tutiya, and Halle and Herbst are similar in their X-ray diffraction patterns. This identification may be open to question because Halle and Herbst denied the identification of their carbide with that of Hofmann and Groll. Tutiya also questioned the results of Hofmann and Groll, although he later supported them. The X-ray diffraction data in table 1 show that the carbide of Brill and Mark do not fit in well with those of the Hofmann and Groll, Tutiya, and Halle and Herbst carbide. The Pichler and Merkel carbide II, with Curie Point 380°C. has been identified with

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[59] Durand, J. F., [Double Decomposition of Metallic Acetylides and Salts in Aqueous Solutions]: Comptes rendus, vol. 177, 1923, pp. 693-695.

the Halle and Herbst carbide and presumably with the Hofmann and Groll-Tutiya carbide by means of new Bureau of Mines data.

The carbide of Bahr and Jessen was never characterized by either X-ray diffraction or a Curie Point. The formula Fe_2C is not characteristic. The data of Hägg indicated that this carbide was a mixture of the Hägg carbide and cementite, but this identification was based on similarity of preparation and must be treated as hypothetical.

The carbides of Hägg and Jack are undoubtedly identical: both have the same X-ray diffraction pattern. The carbides were obtained in nearly pure form and identification was based on the matching of numerous sharp lines. Hägg specifically reported that his carbide differed from the Brill-Hofmann-Tutiya carbide.

The "cubic iron sesquioxide" (γ-Fe_2O_3) of Lefebvre and LeClerc has almost the identical Curie Point, 250°C., as the Pichler and Merkel Carbide I. This identification is substantiated by the observation that both materials are active in the synthesis and that both can develop under the conditions of the synthesis. The carbide of Lefebvre and LeClerc, and Carbide I of Pichler and Merkel have been identified recently with the Hägg and Jack carbides at the Bureau of Mines. From fragmentary data just found (FIAT Reel 116X frames 1673-1683) it appears that the Hägg carbide (Curie Point found ~250°C.) was also formed in (Moers, Ruhr Valley) catalysts during synthesis, although the distinctly different carbide was not recognized as such but was termed "unstable cementite".

Table 2.—Characteristics of iron carbides

Formula	Name	Diffraction pattern	Crystal class	Space group	Lattice parameters	Curie point °C.	Specific magnetization C.G.S. units/gram	Decomposition temp., °C.	Preparation
Fe_3C	Cementite	well known	Orthorhombic	V_h^{16}	a_o=4.51 b_o=5.08 c_o=6.73 kx	205–220	139 (Pichler and Merkel first draft of paper)	700–800	a. Rapid cooling of solution of carbon in Fe to room temperature. b. Carburization of γFe with carbon-rich gas followed by cooling to room temperature. c. Decomposition of higher carbide.
-	Martensite	well known	Tetragonal	-	varies with carbon content (supersaturated solid solution in α iron).	-	-	~100	Extremely rapid quenching of solutions of carbon in iron.
-	Carbide of Brill and Mark	previously unobserved	-	-	-	-	-	-	Action of $H_2 + N_2$ on $(NH_4)_4\ Fe\ (CN)_6$ at 400°C. The carbide appears as an impurity in a mixture of $Fe(CN)_2 + Fe$.

Table 2.—Characteristics of iron carbides (cont'd.)

Formula	Name	Diffraction pattern	Crystal class	Space group	Lattice parameters	Curie point °C.	Specific magnetization C.G.S. units/gram	Decomposition temp., °C.	Preparation
Fe_2C	Carbide of Hofmann and Groll	similar to that of Brill and Mark	-	-	-	-	-	-	Action of CO on iron oxides at temperatures of 320°C. and lower.
Fe_xC	Carbide of Tutiya	similar to Hofmann and Groll, and Brill and Marks carbide	-	-	-	-	-	-	Action of CO on iron oxide.
	Carbide of Hallo and Herbst	-	Hexagonal (close-packed)	-	$a_o \cong 2.76$ Å $c_o \cong 4.36$ Å $c_o/a_o = 1.58$	-	-	Decomposes to Hägg carbide	Develops in Fe Fischer-Tropsch catalysts during synthesis at comparatively low temperatures.
Fe_2C	Carbide of Pichler and Merkel II.	-	-	-	-	380	~140	About 300	Develops in reduced Cu-promoted Fe Fischer-Tropsch catalysts which are carburized at 205°C. obtained only in presence of Pichler and Merkel carbide I.

Table 2.–Characteristics of iron carbides (cont'd.)

Formula	Name	Diffraction pattern	Crystal class	Space group	Lattice parameters	Curie point °C.	Specific magnetization C.G.S. units/gram	Decomposition temp., °C.	Preparation
Fe_2C	Carbide of Bahr and Jessen	-	-	-	-	-	-	-	Action of CO on reduced iron oxide at 225°C., product nearly free of free carbon.
-	Carbide of Hägg	different from all above patterns	-	-	-	-	-	-	Similar to Bahr and Jessen's carbide. Carburization of reduced Fe oxide at 225°C.
Fe_2C	Carbide of Jack	similar to Hägg carbide	Orthorhombic	-	a_o= 9.04 kx b_o= 15.66 kx c_o= 7.92 kx	-	-	-	Action of CO on iron nitride.
"Cubic iron oxide" of Lefebvre and LeClerc		-	-	-	-	250	-	-	Develops in Fe Fischer-Tropsch catalysts during synthesis.
Fe_2C	Carbide of Pichler and Merkel I.	-	-	-	-	265	~140	about 400	Develops in Fe Fischer-Tropsch catalysts during carburization at 325°C.

Table 2.–Characteristics of iron carbides (cont'd.)

Formula	Name	Diffraction pattern	Crystal class	Space group	Lattice parameters	Curie point °C.	Specific magnetization C.G.S. units/gram	Decomposition temp., °C.	Preparation
FeC_2	Carbide of Durand	-	-	-	-	-	-	-	Action of CaC_2 on aqueous solution of $FeCl_2$.

APPENDICES[60]

APPENDIX A

Two reports of the I.G. Farbenindustrie[61] recently discovered among the documents of the War Department, read as follows:

"As long as 12 years ago, Fischer added copper to his iron catalyst in order to facilitate reduction. X-ray studies initiated by Dr. Halle, and continued and completed 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 our standard catalyst, a new hexagonal carbide, Fe_2C, not mentioned in the literature, 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 catalyst 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 percent of copper, for instance, raises the conversion temperature by about 50°."

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[60] Editor's note. The translations of Appendices B-D were made from German copies which contained some obvious typing errors. Appendix C was incomplete. Appendix D has been rearranged and repetitions eliminated; however, no facts and opinions have been omitted. The figures mentioned in Appendix D were not available.

[61] Group leader conference Ludwigshafen, TOM Reel 26, Bag 2463.
Report Dr. Wenzel, TOM Reel 134. Item II/10.

"Experiments at Oppau (Amm. Lab. Ber. 1676 Dr. Herbst) show that hexagonal iron carbide Fe_2C forms in KW 17 (NH_3-fused catalyst) during synthesis and that at temperatures above 290° it is converted into the inactive Hägg Fe_2C."

APPENDIX B

Ammoniaklaboratorium Oppau

July 22, 1939

JOURNAL EXTRACT ON A NEW IRON CARBIDE

(Work done 1938 under Dr. Brill's direction)

During Debye-Scherrer X-ray analysis of Fischer-Tropsch catalysts used by Dr. Meisenheimer, a new hexagonal iron carbide was found which was identified as Fe_2C, by its structure and chemical analysis. Table 3 shows the intensities, Bragg angles (for Fe-K$_\alpha$ radiation) and indices (hkl) of the respective planes. The hexagonal unit cell has the dimensions

$$a = 2.76\ \text{Å};\ c = 4.36\ \text{Å};\ c/a = 1.58.$$

The carbide has the same lattice structure as the analogous Fe_2N and similar lattice dimensions.[62] Thus, carbon can enter the iron lattice during the Fischer-Tropsch synthesis in the same manner as nitrogen does during nitride formation.

The occurrence of the new hexagonal carbide, Fe_2C, depended on the composition of the catalysts. It was never observed alone, but always in conjunction with the promoters. It occurred in all active catalysts containing Fe-Cu-K and either Al_2O_3 or MgO. After use these

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[62] Hägg, G., work cited (footnote 46).

Table 3.–X-ray diffraction data on the new hexagonal Fe_2C

Intensity[a]	Bragg angle[b] (degrees)	Indices of planes hkl	d/n[c]
m	24.0	100	2.377
m	26.7	002	2.151
v. st.	27.8	101	2.073
m	37.1	102	1.603
m	44.3 (45.1)	110	1.384 (1.365)
m	51.2	103	1.240
m. st.	56.0	112	1.166
m	57.0	201	1.153

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[a] m = medium, v = very, st = strong.

[b] Average of measurements on ten different samples. Two samples measured 45.1° instead of 44.3° for the 110 plane. The reason is unknown. The crystal lattice may be only pseudo-hexagonal.

[c] Calculated by editor.

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catalysts were completely carbided. (Iron catalysts containing nickel cannot be considered here because nickel is catalytically active.) Fe_2C was not found in the less active, and thus unimportant, catalysts Fe-MgO-K and Fe-Ag-K.

It may be assumed that a direct connection between catalyst activity and the presence of Fe_2C exists. Fe_2C may be an intermediate in the synthesis, which is stable only in certain catalyst structures. When the catalysts have the structure which stabilizes the carbide, it is formed very quickly (experimentally proved) and carbiding is complete throughout the volume of the particles. Attempts to show the coexistence of free iron and this carbide were unsuccessful. The rate of this reaction is much faster than the rates of formation of other carbides of iron, cobalt, and nickel, where metal and carbide could be observed simultaneously (cf. laboratory report 1450, September 15, 1936).

Signed, HALLE AND BRILL

APPENDIX C

I. G. Ludwigshafen
Ammoniaklaboratorium Oppau
January 30, 1941

(See also Dr. F. Halle, Laboratory Journal Extract No. 199)

Observations on the New Hexagonal Iron Carbide

Copper-Promoted Catalysts

With few exceptions, X-ray diagrams of our precipitated Fe-Cu-Al_2O_3-K and Fe-Cu-MgO-K-Kieselguhr catalysts (whose principal products are paraffinic hydrocarbons) always show lines attributed to a so-called new hexagonal iron carbide (Fe_2C). On the other hand, fused and calcined copper-free catalysts whose chief products are olefins and alcohols, respectively, produce X-ray diagrams of the Hägg carbide (Fe_2C). There is thus a possibility that the catalytic activity of precipitated catalysts (operated at low synthesis temperature) is related to the crystal structure which is developed during synthesis. Further study is planned in this direction. However, it appears desirable first to summarize the results obtained from experiments at atmospheric pressure (synthesis experiments by Dr. Meisenheimer, X-ray analysis by Dr. F. Halle).

The first evidence of the formation of a new iron carbide is found in a report (memorandum 70) of July 5, 1938, by Dr. Halle. The catalyst contained a ratio of Fe:Cu = 4:1, and 3 percent MgO, based on the total metal content (Fi 323). Prolonged reduction of the catalyst (216 hours) with a mixture of hydrogen and carbon monoxide at 250°C. did not produce the new carbide in any appreciable amount. The catalyst was considered to be the Hägg carbide. After this catalyst had been operated in the synthesis (synthesis gas comprising a mixture of 60 percent carbon monoxide and 40 percent hydrogen), the X-ray lines of a new carbide were observed. At first it was thought that the change might be the result of an expansion of 5 percent of the α-iron lattice (memorandum 71, July 6, 1938). Detailed analysis of the lines showed a hexagonal lattice (lattice constants, $a = 2.8$, $c = 4.6$, $c/a = 1.63$) whose similarity with that of iron nitride, Fe_2N, ($a = 2.7$, $c = 4.4$, $c/a = 1.62$) indicated the existence of the new iron carbide, Fe_2C (memorandum 73, July 18, 1938).

This new hexagonal iron carbide was repeatedly observed in $Fe-Cu-Al_2O_3$ precipitated catalysts after they had been treated for several hours at 240°C. with a mixture of carbon monoxide and hydrogen. Moreover, the existence of the carbide appeared to be independent of any preliminary reduction of the catalyst with hydrogen (memorandum 71). Treatment of the catalyst with carbon monoxide alone at 220°C. also resulted in the formation of the new carbide (memorandum 78, August 9, 1938).

Attempts to obtain partially carbided samples were not successful. X-ray analysis showed that a carbided Fe-Cu-Al catalyst (30 percent Al based on Fe) remained unchanged after treatment with hydrogen for 4 hours, whereas a completely reduced Fe-Cu-Al catalyst (100 percent Al based on Fe) was fully carbided after treatment for one hour with a mixture of hydrogen and carbon monoxide (memorandum 74, August 4, 1938).

Most of the early experiments were carried out with catalysts containing Al_2O_3. In later experiments magnesium oxide was substituted for aluminum oxide, and it was shown by X-rays that the formation of the new carbide did not depend on the presence of aluminum oxide. Also, the catalytic activity and the content of the new hexagonal iron carbide increased with the reaction temperature (room temperature, 225°, 300°C.) (memorandum 84, September 28, 1938, memorandum 103, February 17, 1939).

Synthesis experiments and X-ray analyses seemed to show that an increase in the amount of hexagonal carbide accompanied an increase in catalytic activity. This observation indicated that the new carbide was the determining factor in the activity of the catalyst. However, repeated experiments with completely carbided Fe-Cu-MgO catalysts showed them to be inactive (Experiment 387-Fi 338; Experiment 222-Fi 442; Experiment 427-Fi 466), whereas the same catalysts were active when operated in the usual way without preliminary treatment with carbon monoxide. X-ray analysis only showed that the active samples were not as well crystallized as the inactive catalysts.

Thus, active precipitated Fe-Cu catalysts contain a hexagonal iron carbide whose composition is probably Fe_2C, but which shows no independent catalytic activity. When catalysts with the same content of iron carbide are operated under similar operating conditions, those with a less well-defined crystal structure show greater activity (memorandum 105, February 21, 1939).

Copper-Free Catalysts

All experiments thus far were carried out with catalysts containing copper which was used to facilitate reduction. It remained to determine whether copper-free catalysts had the same activity and produced the same X-ray pattern.

Catalysts containing magnesium or aluminum oxide were reduced at different temperatures (350°, 450°, 550°C.). X-ray analysis of the reduced samples showed:

(1) An increase in the amount of α-iron;

(2) An appreciable increase in the size of the iron particles;

(3) An increase in the amount of crystalline structure with increased reduction temperature (memorandum 94, October 3, 1938).

The activity in synthesis of the only two catalysts tested (containing 6 percent and 23 percent MgO, respectively) was almost negligible. The X-ray diagrams showed no evidence of the presence of the new hexagonal carbide. The only carbides present were Fe_3C and Fe_2C-Hägg (memorandum 104, February 20, 1939). However, it is possible that the absence of the new hexagonal carbide resulted from the high reduction temperatures (450°-500°C.). To date, this point has not been definitely established. Nevertheless, it should be noted that after reduction at 250°C., an alkalized iron catalyst (without additional activators) besides Fe_3O_4 . . . . [63] (Memorandum 114, May 20, 1939).

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[63] Editor's note. Rest of sentence missing.

Signed, A. SCHEUERMANN

APPENDIX D

Ammoniaklaboratorium Oppau

January 13, 1942

X-ray Study on the Thermal Stability of the New Hexagonal Iron Carbide in Catalysts Used for Hydrocarbon Synthesis, According to F. Fischer

(Work done under Dr. Brill's direction, October and November 1941)

INTRODUCTION

In 1938 a new hexagonal iron carbide (n.h.Fe_2C) was discovered by Dr. Hallo in the course of X-ray studies on Fischer-Tropsch catalysts. It was described by him in laboratory journal extract No. 199. The structure of this carbide, similar to that of the nitride, Fe_2N, and its chemical analysis indicated the formula, Fe_2C. A direct relation was believed to exist between the presence of this carbide and the effectiveness of the catalyst in the hydrocarbon synthesis. Subsequently this carbide was found not to be a catalyst itself; but it is probably very important for synthesis activity, as was pointed out by Dr. A. Scheuermann in a report, dated January 30, 1941 (Appendix C), in which he summarized the then-available information concerning this carbide. At first the carbide was found only in precipitated alkali- and copper-promoted iron catalyst which contained either Al_2O_3 or MgO. It was thought that the absence of the n.h. Fe_2C in iron synthetic ammonia catalysts might result from their high temperatures of reduction. The carbide was found on one occasion in singly-promoted alkalized iron catalyst (Fi 561/62, Ver. 594) which had been treated at 250°C. (that is, at a low temperature) with a mixture of hydrogen and carbon monoxide. Recently the n.h. Fe_2C was found in various copper-free catalysts which had been operated at relatively low temperatures.

In view of the evident importance of this carbide in the hydrocarbon synthesis, it was decided to study the thermal stability of the n.h. Fe_2C., to determine whether the stability depends on its copper content; and to investigate the nature of the decomposition products.

Material and Procedure

Table 4 shows the composition of the used Fischer-Tropsch catalysts which were studied and whose X-ray diagrams showed characteristic n.h. Fe_2C patterns.

All catalysts were obtained from Dr. A. Scheuermann's group. Only two contained cementite, Fe_3C, and these had been reduced at 450° and 500°C., respectively. All others contained only the Hägg carbide (Fe_2C) and the n. h. Fe_2C. It should be noted that the latter is not identical with the Hofmann and Groll carbide, Fe_2C. Catalysts W K 17

Table 4.-Composition of catalysts

Catalyst	Experiment	Constituents						
		Fe	Cu	MgO	Al_2O_3	K	SiO_2	Ca
WK 17[a]	D 438	86.62	-	-	3.42	0.44	-	2.58
1253	D 433	26.98	2.75	9.47	-	2.10	18.19	-
1180	D 457	28.04	7.43	10.08	-	1.67	13.9	-
1261	D 441	66.82	-	-	3.25	2.02	-	-
1219	D 357/1	25.46	6.64	-	24.50	3.48	-	-

[a] Prepared at Leuna

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and 1261 were iron synthetic ammonia catalysts; the others were precipitated catalysts. A copper-free catalyst containing MgO and the n.h. Fe_2C was not available. We believe we have observed the n.h. Fe_2C in two such catalysts. These observations were uncertain, however, since they were made on X-ray diagrams containing a large number of lines in which the n.h. Fe_2C could not be definitely identified. Its occurrence in this type of catalyst is questionable.

Soxhlet extraction with benzine was used to remove protective paraffin and oil coatings from the catalysts. The still moist samples were then placed in porcelain boats. These were put into an electric tube furnace which was immediately evacuated to a pressure of about 1 mm. of mercury. It was then heated to the desired temperature which was maintained for 3 hours unless indicated otherwise. After cooling to room temperature, carbon dioxide was introduced. The catalyst was removed after the pressure was reduced to atmospheric. The carbon dioxide served to protect the frequently pyrophoric catalysts from oxidation.

The samples were X-rayed by the Debye-Scherrer method with an open X-ray tube containing an iron target. It was operated at 25 K. V. and 5 milliamps, without filters, and exposures were about 1-1/2 to 2 hours.

Results

The X-ray diagram of catalyst WK 17 (as received) is shown in figure 2. Comparison with figure 1, the diagram for n.h. Fe_2C, shows this carbide to have been the principal component of the catalyst. A small amount of Fe_2C-Hägg was also present, as indicated by the corresponding lines. Samples of this catalyst were heated at 250°, 275°, 290°, 300°, 330°, and 400°C. each. The first change in the X-ray diagram was observed at 290°C. (figure 3). The Fe_2C-Hägg lines increased appreciably and were much more intense (compare with Fe_2C-Hägg diagram, figure 5). Heating at 330°C. resulted in complete transformation to Fe_2C-Hägg (figure 4). A sample was heated at 275°C. for 12 hours. The amount of decomposition was approximately equal to that which occurred during heating at 290°C. for 3 hours. Heating at 320°C. for 10 minutes did not result in any decomposition.

Catalyst 1188[64] as received contained all the n.h. Fe_2C lines

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[64] Editor's note. Catalysts 1188 and 1180 seem to be identical.

(figure 6) and the stronger copper and magnesium oxide lines. The first slight decomposition occurred at 350°C., as shown by a slight decrease of the relative intensities of the n.h. Fe_2C lines (figure 7). The decomposition was more marked at 400°C. (figure 8). Only Fe_2C-Hägg lines appeared at 430°C. (figure 9). However, transformation was not complete at this temperature because the intensity of the Fe_2C-Hägg lines increased still more at 450°C. (figure 10).

The X-ray diagram (figure 11) of catalyst 1253 as received was essentially the same as that of catalyst 1188 except for a lower copper content. The n.h. Fe_2C lines disappeared completely at 350°C. (figure 12) and were replaced by the Fe_2C-Hägg lines. The diagram corresponded approximately to the one obtained from catalyst 1188 at 430°C. Transformation was complete at 400°C. (figure 13) and no further change was observed at 450°C.

After catalyst 1261 (iron synthetic ammonia catalyst) was heated at 330°C., the n.h. Fe_2C lines disappeared completely, leaving only the Fe_2C-Hägg lines.

In catalyst 1219 aluminum oxide had been substituted for magnesium oxide. As in the case of catalyst 1188 (which had the same Fe:Cu ratio), the first changes were observed at 350°C. and transformation was complete around 450°C.

The data from the preceding experiments are summarized in table 5.

Table 5.–Isothermal transformation in used Fischer-Tropsch catalysts of the n.h. Fe_2C into Fe_2C-Hägg

Catalyst number	Copper content, percent	Transformation in 3 hours noticeable at °C.	Transformation in 3 hours complete at °C.
WK 17	0	290	330
1261	0	-	330
1253	2.75	-	350-400
1188	7.43	350-400	430-450
1219	6.64	350	450

Conclusions

(1) The n.h. Fe_2C was unstable at higher temperatures, as anticipated.

(2) Fe_2C-Hägg was the decomposition product.

(3) The temperature for a certain rate of decomposition was a function of the copper content of the catalyst. The temperature at which transformation was complete in 3 hours was increased by about 50°C. when the copper content was 2 to 3 percent, and by about 100°C. when the copper content was 7 percent. The effect, if any, of the method of preparation was not established.

(4) There is no equilibrium such as the following:

$$\text{n.h. } Fe_2C \rightleftharpoons Fe_2C\text{-Hägg}$$

as shown by the extent of decomposition of catalyst WK 17 during heating at 275°C. for 12 hours, which was approximately equal to that produced by heating at 290°C. for 3 hours. Moreover, the Hägg carbide could not be changed into the n.h. carbide by prolonged heating at lower temperatures.

The n.h. Fe_2C must therefore be considered as an intermediate product of carbiding, whose stability decreases with rising temperature.

The presence of the n.h. Fe_2C being a necessary, although insufficient condition for the activity of iron catalysts, copper-free catalysts can be used only at low synthesis temperatures, certainly not higher than 250° to 275°C. Above this temperature limit the n.h. Fe_2C is no longer stable. Copper-containing catalysts can, if necessary or desirable, be operated at higher temperatures in proportion to their copper content. The presence of 7 percent copper makes it possible to increase the operating temperature by about 100°C. without affecting the stability of the n.h. Fe_2C. Because of the lack of material, it could not be established whether the temperature could be increased still further with a higher copper content.

Signed, HERBST

CHEMICAL AND THERMOMAGNETIC STUDIES ON IRON CATALYSTS FOR THE SYNTHESIS OF HYDROCARBONS

INTRODUCTION

In their early work on the reaction of carbon monoxide with hydrogen in the presence of iron catalysts, F. Fischer and H. Tropsch used alkalized iron filings. At 100 atmospheres pressure and temperatures between 350° and 450°C., they obtained a mixture of different types of oxygenated compounds, named synthol. For synthesis at atmospheric pressure, Fischer and Tropsch used iron catalysts (prepared, for instance, by decomposition of iron nitrate) which were activated further by the addition of substances such as copper, manganese, or alkali. At atmospheric pressure, a yield of 30 to 40 grams of liquid aliphatic hydrocarbons per cubic meter of water gas was obtained with these catalysts. In the period from 1934 to 1936, Fischer and coworkers succeeded in doubling the yield, by using precipitated iron catalysts having a maximum life of 4 to 6 weeks. When Fischer and Pichler used iron catalysts at medium pressure (1937 to 1940), they obtained yields of 130 to 150 grams of liquid and solid hydrocarbons per normal cubic meter of carbon monoxide-hydrogen mixture. The life of these catalysts ranged from many months to several years. The precipitated iron catalysts were pretreated with carbon monoxide-rich gas at atmospheric or lower pressure, and then operated in the synthesis at pressures between 10 and 30 atmospheres. An especially active catalyst, for instance, was formed by pretreating with carbon monoxide at 0.1 atmosphere and 325°C., and subsequently operating the synthesis with water gas at 15 atmospheres and at temperatures of 210° to 230°C.

Fischer and Pichler's pretreatment of iron catalysts for synthesis at medium pressure is fundamentally different from that of catalysts containing nickel or cobalt. The latter may be pretreated by reduction with hydrogen. The activity of iron catalysts reduced with hydrogen at different temperatures to Fe_3O_4 or to metallic iron was no greater than that of untreated iron catalysts when used in the hydrocarbon synthesis at atmospheric or at higher pressures.

Pressures of 10 to 30 atmospheres were particularly suitable for the synthesis. If an iron catalyst were used at this pressure without pretreatment, however, satisfactory reactivity of carbon monoxide-hydrogen mixtures would be obtained only at high temperatures, that is, 280° to 300°C.; and at these temperatures the fraction of undesirable gaseous hydrocarbons would be large. When, however, iron catalysts were treated with carbon monoxide-rich gas (for example, pure carbon monoxide or water gas) at pressures lower than those used for the synthesis (atmospheric pressure or preferably lower), the high activity of the catalysts resulted in satisfactory synthesis of chiefly liquid and solid aliphatic hydrocarbons at temperatures between 220° and 230°C. Thus, carburization made it possible to lower the synthesis temperature by 60° to 80°C. The increased activity persisted even after the catalyst had been used over a period of months.

The hydrocarbon synthesis occurs according to the following generalized equations:

$$2xCO + xH_2 = xCH_2 + xCO_2$$

$$xCO + 2xH_2 = xCH_2 + xH_2O$$

Carbon dioxide and water are formed in addition to hydrocarbons (paraffins and olefins in varying proportions, depending on the conditions of the reaction). Lowering the synthesis temperature, increasing the synthesis pressure, and increasing the hydrogen content of the synthesis gas favor the formation of water. An increase in temperature, a decrease in pressure, and an increase in the carbon monoxide content of the synthesis gas favor the formation of carbon dioxide. The consumption of carbon monoxide is generally somewhat higher than that of hydrogen. The two components in the synthesis gas should be present in the same ratio in which they react for optimum efficiency.

LITERATURE REVIEW

HETEROGENEOUS CATALYSIS

In their earliest publication on the gasoline synthesis, Fischer and Tropsch[65/] discussed the mechanism of the reaction between carbon monoxide and hydrogen to form hydrocarbons. It was assumed that carbon monoxide and metal react first to form carbides (the formation of higher carbides is thus to be expected) and that hydrogen then reacts with carbidic carbon to form (CH_2) radicals. These methylene groups polymerize to form more or less saturated hydrocarbon chains.

[65/] Fischer, F. and Tropsch, H., work cited (footnote 8).

The synthesis proceeds by way of heterogeneous catalysis. It is known that when a gaseous reaction is catalyzed by a solid, condensation of the gaseous substances on the catalyst surface (that is, physical adsorption) is a necessary but not always sufficient condition for catalytic activity. Of great importance is the selective chemical effect, exercised by the specific molecular forces of the catalyst surface on the reacting molecules, and resulting in a decrease of the activation energy. According to Taylor 66/, a specific effect on the reacting molecules is exerted only by certain well-defined areas of the macroscopic surface. Eckell 67/ observed that the specific catalytic structure is intimately related to lattice deformation.

66/ Taylor, S. [Active Centers and Catalysts]: Ztschr. Elektrochem., vol. 35, 1929, pp. 542-548.

67/ Eckell, J. [Relationship between Catalyst Structure and Chemical Reaction]: Ztschr. Elektrochem., vol. 39, 1933, pp. 433-439.

For highly dispersed substances the configuration of the inner surfaces is extremely significant, since their active centers are accessible to gases only by diffusion (Schwab and Zorn 68/).

68/ Schwab, G. and Zorn, H. [Kinetics of Hydrogenation of Ethylene on Skeletal Catalysts]: Ztschr. physik. Chem., vol. B32, 1936, pp. 169-201.

Graue and Riehl[69] have shown that penetration of gases into catalysts does not occur through the large pores alone. Where there is random distribution, or where the arrangement of the lattice lacks regularity, the irregular spacing of the atoms allows penetration even through openings of atomic dimensions. According to Graue and Koch[70], the atomic pores of highly dispersed materials remain accessible by the addition of certain substances.

The catalyst surface is important not only because of its geometrical configuration, but even more because of its electric fields. The influence of these specific fields (active centers) on the reagents is shown by the catalyst's affinity for them; this affinity constitutes the essential condition of catalytic activity. Thus, adsorption of hydrogen and carbon monoxide by a catalyst is a reversible chemical adsorption and much stronger than a physical adsorption. Moreover, the favorable relationship of catalyst to reagent does not depend solely on the material nature of the reacting substances, but is a function of the atomic radii (or atomic distances) of the reagent and of the atomic spacings (or lattice structure) of the catalyst.

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[69] Graue, G. and Riehl, N. [Pore Diameter and Internal Volume of Amorphous and Crystalline Substances]: Ztschr. anorg. allgem. Chem., vol. 233, 1937, pp. 365-375.

[70] Graue, G. and Koch, H., [Diffusion of Gases in Solids, Studies on Iron Oxide and Iron-Aluminum Oxide]: Ber. Deut. chem. Gesell., vol. 73, 1940, pp. 984-995.

The effect of promoters in activated catalysts has been the subject of extensive research by numerous investigators. X-ray studies of ammonia catalysts were used by Wyckoff and Crittenden[71], as well as by Brill[72], to show that certain additions produce their activating effect by favoring the formation of numerous active points and by stabilizing these specifically active metal particles.

According to a theory formulated by Ipatieff[73], increased activity is not explained satisfactorily as a purely physical effect of the promoters resulting in arrested recrystallization and the preservation of the surface. Experiments with promoted catalysts led this author to the conclusion that a new source of energy contributes to catalysis. He assumes that contact of the metallic promoter with the basic catalyst produces electric energy. Ipatieff believes that the metallic oxide promoters participate in the reaction according to their chemical nature, thus assisting the catalyst in utilizing the reaction energy. This would mean, for instance, that thoria in a cobalt-thoria-kieselguhr catalyst acts not only by its stabilizing influence on the

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[71] Wyckoff, R. W. G. and Crittenden, E. D., An X-ray Examination of Some Ammonia Catalysts: Jour. Am. Chem. Soc., vol. 47, 1925, pp. 2866-2876.

[72] Oppau Experimental Laboratory, unpublished work, 1925.

[73] Ipatieff, V. N., Mixed Catalysts: Petroleum Refiner, vol. 19, 1940, pp. 250-255.

specific structure of the catalyst, but actually takes part in the reaction as a dehydrating agent. An activating agent may thus operate by physical, chemical, or physico-chemical means.

In certain cases a relationship is also known to exist between magnetic properties and catalytic activity. Thus, the conversion of ortho- and para-hydrogen is catalyzed by paramagnetic ions, the rate of conversion increasing with increasing magnetic moment of the ions.[74] The so-called magneto-catalytic effect is based on similar phenomena. From a large body of experimental evidence, Hedvall[75] reported a change in catalytic activity above the Curie Point temperature. The magneto-catalytic effects of nickel-iron catalysts on the decomposition and hydrogenation of carbon monoxide are of particular interest in this connection. The change in activity which occurs at the Curie Point is due to electronic changes.[76]

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[74] Farkas, A. and Farkas, L., Ortho, Para, and Heavy Hydrogen: MacMillan Co., New York, 1935, 215 pp.

[75] Hedvall, J. A. and Gustavson, E., [Catalytic Activity and Ferromagnetism]: Svensk Kem. Tids., vol. 46, 1934, pp. 64-65. C.A., vol. 28, 1934, p. 4971^6.

[76] Reinäcker, G., [Heterogeneous Catalysis and Atomic Structure]: Die Chemie, vol. 57, 1944, pp. 85-90; C.A., vol. 40, 1946, p. 4593 (review).

THE Fe-C-O SYSTEM (EXCLUDING HIGHER IRON CARBIDES)

It has already been stated that treatment of iron catalysts with carbon monoxide before synthesis is desirable. The study of the reactions which accompany this pretreatment is very closely related to the problem of carburization of iron and iron oxides.

Much has been written on the decomposition of carbon monoxide on iron. The literature will be considered here only to the extent to which it relates to iron carbides and explains the processes which occur during pretreatment.

It had long been assumed that the decomposition of carbon monoxide on iron results in carbide formation[77], but no particular importance was attached to this reaction. According to Boudouard[78], the rate of the reaction,

$$2CO = CO_2 + C + 39 \text{ kcal.}$$

is increased by the presence of iron oxides. Schenck and Zimmermann[79] assume that the rate is increased only by the free metal, particularly

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[77] Stammer, K., [Phenomena Connected with Reduction, Especially of Iron by Carbon Monoxide]: Ann. Chem., vol. 82, 1851, pp. 136-141.

[78] Boudouard, O., [Decomposition of Carbon Monoxide on Metallic Oxides]: Bull. Soc. Chim., Paris, vol. 21, 1899, pp. 463-465 and 712-713.

[79] Schenck, R. and Zimmermann, F., [Decomposition of Carbon Monoxide and Equilibrium in Blast Furnaces]: Ber. Deut. chem. Gesell., vol. 36, 1903, pp. 1231-1251.

when finely divided. According to them, the iron acts solely as a catalyst as long as sufficient carbon monoxide is present, whereas it takes part in the reaction when the equilibrium ratio of carbon monoxide to carbon dioxide is exceeded.

The problem of oxidation, reduction, and carburization equilibria of the system Fe-C-O, at temperatures ranging from 500° to 1100°C., has been studied by Schenck.[80] In the solid phase, Fe_3O_4, FeO, Fe, Fe_3C, and C may coexist. Solid solutions of iron oxides in each other are known as wüstite, and those of a metallic character, formed by the solution of ferrous oxide in free iron, are known as oxoferrite. In contrast to the oxidation and reduction equilibria, the carburization equilibria were pressure dependent, the carbiding reaction being accompanied by a change in the number of gas molecules. Cementite participates in the establishment of equilibrium even at temperatures below 400°C. On the other hand, reduction of iron oxides by free carbon does not begin until 680°C.

In connection with the action of promoters, it should be noted that oxides may cause a shift in the equilibrium between gas and solid phase. Figure 1 shows the results of Schenck's equilibria studies. It will be seen from this equilibrium diagram that the lower

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[80] Schenck, R. and Dingmann, T., [Reduction, Oxidation, and Carburization Equilibria for Iron, III]: Ztschr. anorg. allgem. Chem., vol. 166, 1927, pp. 113-154.
Schenck, R., [Reduction, Oxidation, and Carburization Equilibria for Iron, IV-V]: Ztschr. anorg. allgem. Chem., vol. 167, 1927, pp. 254-328.

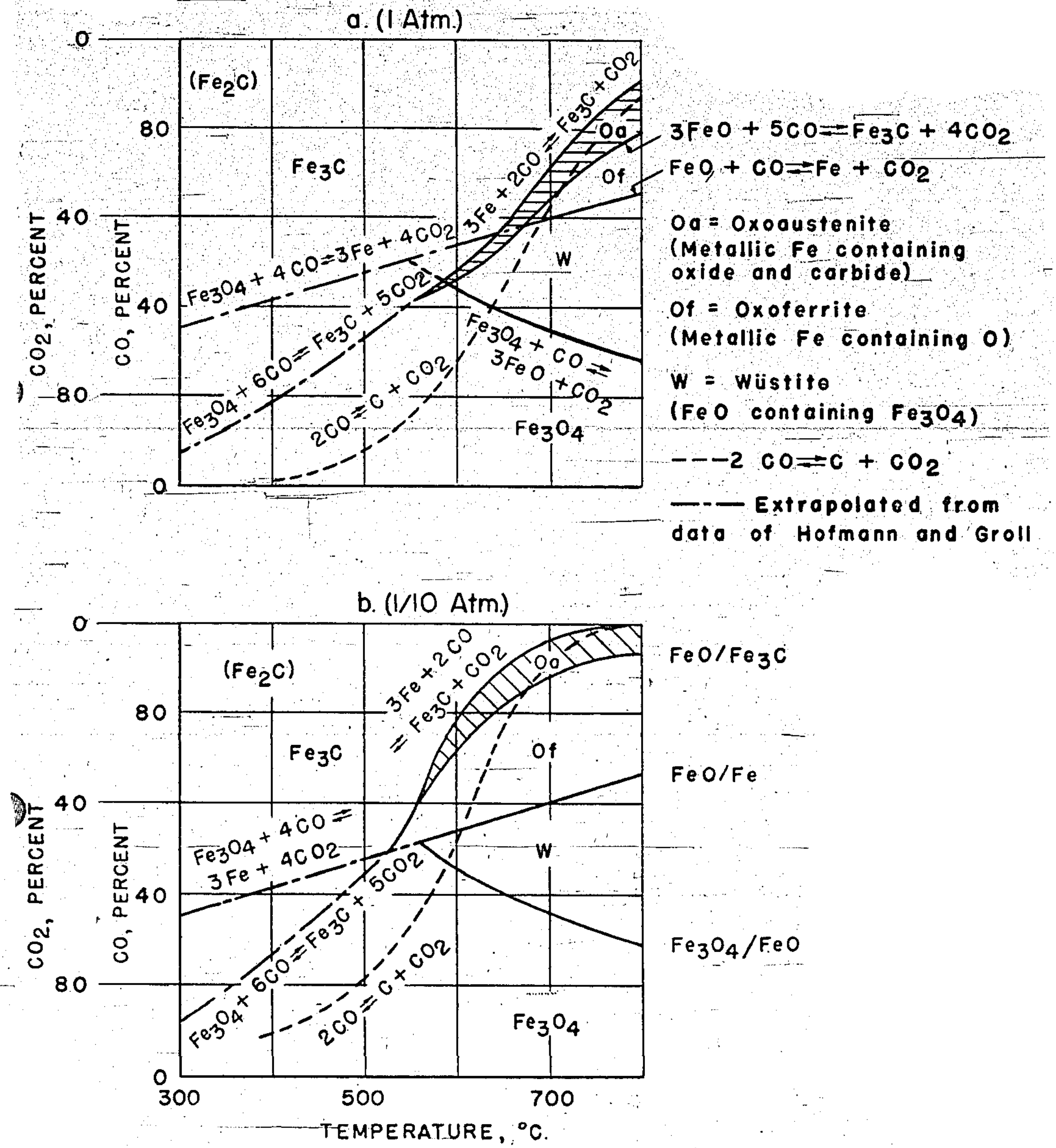

Figure 1. — Equilibria in the system Fe—C—O.

limit of stability of FeO lies at 560°C.[81] Chaudron[82] had previously shown that this oxide decomposes below 560°C. according to the equation:

$$4FeO = Fe_3C_4 + Fe.$$

Using more recent data, Jänecke[83] also interpreted the system Fe-C-O quantitatively without taking the higher carbides into account.

According to Tutiya[84], who decomposed carbon monoxide in the presence of iron wire and powder, the catalytic effect of compact iron is very slight. During prolonged experiments there is a considerable increase in catalytic activity, accompanied by formation of iron carbide and disappearance of Fe-lines in the X-ray diagram. Consequently, the active catalyst is not iron itself but the carbide whose formation

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[81] Editor's note. Figure 1 was incomplete and has been replaced by a complete diagram from Bureau of Mines Report No. 2774-G:18 of September 1946, following p. 16, work cited (footnote 6).

[82] Chaudron, G., [Reversible Reactions of Hydrogen and of Carbon Monoxide with Metallic Oxides]: Ann. Chim., vol. 16, 1921, pp. 221-281. [Reversible Reactions of Carbon Monoxide with Iron Oxides]: Compt. rend., vol. 172, 1921, pp. 152-155.

[83] Jänecke, E., [Equilibria in the System Fe-C-O]: Ztschr. anorg. allgem. Chem., vol. 204, 1932, pp. 257-290.

[84] Tutiya, H., work cited (footnote 43).

occurs upon decomposition of carbon monoxide:

$$3Fe + 2CO = Fe_3C + CO_2$$

$$2CO = CO_2 + C$$

Similarly, Fischer[85] considered carbide formation essential in the catalytic decomposition of carbon monoxide by iron. According to him, carbide formation is associated with a disruptive action of carbon on iron which results in a slow dispersion of iron in carbon. The favorable effect of iron carbide is neutralized by the deposition of a film of carbon on the crystals.

On the other hand, Baukloh[86] emphasized the catalytic action of metallic iron. A series of studies led him to the conclusion that carbon is deposited directly by carbon monoxide. For theoretical reasons decomposition of carbon monoxide is considered to be a special case of adsorptive catalysis by metallic iron.

More recently, Körber, Wiesner, and Fischer[87] have given a

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[85] Fischer, F. and Dilthey, P., [Preparation of Pure Carbon at a Low Temperature]: Ges. Abhndl. Kenntnis Kohle, vol. 8, 1928, pp. 234-255.

[86] Baukloh, W. and Edwin, B., [Effect of Temperature and Pressure on the Decomposition of Carbon Monoxide and the Mechanism of Carbon Deposition]: Arch. Eisenhüttenw., vol. 16, 1942, pp. 197-200.

[87] Körber, F., Wiesner, H., and Fischer, W., [Thermal Decomposition of Carbon Monoxide on Iron and its Alloys and Mixtures with Carbon]: Arch. Eisenhüttenw., vol. 17, 1943, pp. 43-52.

clearer picture of the thermal decomposition of carbon monoxide on iron. They studied the decomposition of carbon monoxide streaming over powdered soft iron and over mixtures of powdered soft iron with graphite and cementite (in the form of crude iron powder) at temperatures from 300° to 1200°C. Considerable decomposition of carbon monoxide by powdered soft iron was observed to start around 900°C. However, comparison with the equilibrium concentrations of the Boudouard curve indicates that this decomposition is to be attributed not to the catalytic action of the solid phase, but to chemical reaction between carbon monoxide and iron. Addition of graphite had no effect on the action of powered soft iron. However, when cementite was added to the catalyst, carbon dioxide formation showed a sharp maximum between 500° and 600°C., the amount of gas depending on the amount of catalyst used. Because of their much smaller active surface, steel samples produced considerably less decomposition than powdered or pressed iron.

Results obtained with various catalysts in isothermal reactions are revealing. In the presence of pig iron powder containing cementite, considerable carbon dioxide was evolved as soon as the operating temperature was reached, and a final value of about 65 percent of carbon dioxide was approached. However, when powdered soft iron was used, an induction period of several hours was always needed for the carbon dioxide content to attain the same final value.

FORMATION OF HIGHER CARBIDES BY ACTION OF CARBON MONOXIDE ON IRON

Hilpert and Dieckmann[88] studied the course of carbon

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[88] Hilpert, S. and Dieckmann, T., work cited (footnote 9).

deposition on Fe_2O_3 at about 800°C. The results showed that the decomposition of carbon monoxide is catalyzed by the iron carbide, Fe_3C. Carburization of this carbide is assumed to give carbides with a higher carbon content, such as Fe_2C or FeC, which decompose with elimination of carbon. The authors believe that their theory is supported by the manner in which steels (quenched at 900°C. and tempered at 200° to 600°C.) behave on acid decomposition. Thermomagnetic study of the carburized product showed a Curie Point of 200°C. The magnetic transition point (Curie Point) is defined in this paper as the point of inflection on the specific magnetization-temperature (thermomagnetic) curve. At that time the recorded data concerning the magnetic transition point of the iron carbide, Fe_3C, showed considerable variation, thus leaving the authors in doubt as to the homogeneous nature of the product.

In an article on the carbon monoxide-carbon dioxide equilibrium obtaining during the decomposition of carbon monoxide in iron, Falcke[89] concurred with the Hilpert and Dieckmann theory on the formation of higher iron carbides, but without contributing any experimental evidence. Hilpert and Dieckmann received further support of a purely hypothetical nature from Schenck[90], who assumed that higher carbides possess an

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[89] Falcke, V., [Reactions of Iron Oxide with Coal and of Carbon Monoxide with Iron]: Ztschr. Elecktrochem., vol. 22, 1916, pp. 121-133.

[90] Schenck, R., [The Relationships between Carbon and Oxygen]: Stahl u. Eisen, vol. 46, 1926, pp. 665-682.

unusually high vapor pressure of carbon to explain their high reactivity.

In contrast, Fischer and Bahr[21] were able to establish the existence of a higher iron carbide experimentally; by graphic determination of the amount of carbidic carbon in their carburization curves they found the formula Fe_3C_4. In evaluating the experimental results the iron combined with oxygen was assumed to be FeO. By reducing the carburized iron with hydrogen at 400°C., they arrived at the formula, Fe_2C. This discrepancy is attributed to the thermal instability of Fe_3C_4, which is said to decompose at higher temperatures:

$$Fe_3C_4 = Fe + 3C + Fe_2C.$$

Mittasch and Kuss[22] likewise showed plausible experimental reasons for the formation of higher iron carbides. A nitrogen-hydrogen mixture acting on ferrous cyanide at 400°C. yielded a carbide to which they assigned the formula, Fe_2C. The compound is believed to decompose rapidly into iron, cementite, and carbon. Decomposition with sulfuric acid at 60°C. yielded a mixture consisting of 75 percent of hydrogen and 25 percent of hydrocarbons, calculated as methane.

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[21] Fischer, F. and Bahr, H., [High-Carbon Carbides of the Iron Group]: Ges. Abhandl. Kenntnis Kohle, vol. 8, 1928, pp. 255-269. C.A., vol. 25, 1931, p. 2932.

[22] Mittasch, A. and Kuss, E., [Synthesis of Ammonia with Catalysts Made from Complex Iron Cyanides]: Ztschr. Electrochem., vol. 34, 1928, pp. 159-170.

Gluud, Otto, and Ritter[23] investigated more thoroughly the formation of a higher iron carbide from iron oxide, using a current of carbon monoxide at low temperature, then passing a stream of hydrogen at 275°C. and atmospheric pressure over the surface, and determining the carbidic carbon as methane. The decarburization curves led the authors to postulate the formation of the carbide, Fe_2C. The same result was obtained when the authors distinguished free carbon from carbidic carbon in their carburization curves. According to these curves, 10 to 12 parts of carbon are associated as the carbide with 100 parts of iron. Bahr and Jessen[24], upon repeating the work of Gluud and Ritter, found that the decarburization temperature should be carefully controlled. According to these authors, free carbon on iron oxide was hydrogenated at temperatures as low as 280°C., whereas free carbon deposited on pure iron reacted with hydrogen only at 320°C. Experiments in decarburization with hydrogen always produced 7 to 8 percent of carbidic carbon. Consequently the amount of carbon hydrogenated was always greater than that corresponding to the carbon content of cementite, but less than that corresponding to Fe_2C. At 225°C., however, metallic iron could be carburized to a point corresponding to Fe_2C; no further carbon was

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[23] Gluud, W., Otto, K. V., and Ritter, H., [Formation of Fe_2C During Reduction of Iron Oxide with Carbon Monoxide at a Low Temperature]: Ber. Deut. chem. Gesell., vol. 62, 1929, pp. 2483-2485.

[24] Bahr, H. A. and Jessen, V., work cited (footnote 50).

then taken up. At higher carburization temperatures, Bahr and Jessen again obtained products containing 7 to 8 percent of carbidic carbon. At temperatures above 400°C. the carbon content decreased to that of Fe_3C.

Tutiya[95] suggested that carbon monoxide decomposition on iron catalysts is accompanied by the formation of a higher iron carbide. In fact, he considers this compound to be the sole product of the carburization of magnetite at low temperatures. No cementite, ferrous oxide, and iron were found. At 280° to 320°C., carbiding of Fe_3O_4 by carbon monoxide yielded a mixture of Fe_3C and Fe_xC. As the carburization temperature was increased, the amount of cementite was increased at the expense of the higher carbide. From the point of view of the problems discussed in the present work, it is significant that at 270°C. the Fe_xC carbide is formed not only from iron and iron oxides but also from cementite.

Hofmann[96, 97] studied the formation of carbon, iron oxide, and iron carbide during carburization. Using oxygen-free carbon monoxide and extremely pure iron, prepared from iron pentacarbonyl,

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[95] Tutiya, H., work cited (footnote 44).

[96] Hofmann, U., "Carbon Deposition from Carbon Monoxide and Benzine on Iron": Ber. Deut. chem. Gesell., vol. 61, 1928, pp. 1180-1195.

[97] Hofmann, U. and Groll, E., work cited (footnote 42).

this investigator found that when carbon monoxide was passed over iron at temperatures up to 560°C., magnetite was always present, together with carbon, cementite, and very small amounts of iron. From 560° to 655°C. the solid phase contained principally ferrous oxide and carbon, very little cementite, iron, and magnetite. The presence of the oxides was established by X-ray analysis and by determination of the oxygen content. Above 655°C. oxides were no longer found, but cementite was always present. An oxygen-free product was obtainable at 655°C. only at an extremely high rate of flow. At high rates of flow, the carbon dioxide produced during the carbiding reaction was carried away so rapidly that its concentration did not reach the value necessary for the iron-magnetite or iron-ferrous oxide equilibrium. Under these conditions Hofmann found only iron and cementite in the product.

It was determined, moreover, that whenever free carbon is deposited, cementite is present in the solid phase. However, decomposition of cementite accompanied by elimination of carbon at temperatures below 450°C. appears extremely unlikely, since cementite is not decomposed at this temperature in an atmosphere of nitrogen. A purely catalytic acceleration of the reaction,

$$2CO = CO_2 + C,$$

also appears unlikely. The properties of the carbon deposited from carbon monoxide on iron at low temperature indicate that elimination of carbon occurs (through slight super-saturation) from a primary iron carbide. The size of the carbon crystallites thus obtained is quite different from the size of lustrous carbon which forms at the same temperature by simple thermal decomposition of benzine vapor.

This assumption of a higher carbide receives additional support from the fact that X-ray analysis of iron preparations which were treated with carbon monoxide at temperatures below 400°C. (for example at 320°C.) showed interference lines indicative of an unidentified crystal lattice. The majority of these lines coincided with those obtained by Brill and Mark[98] for the decomposition of ferrous cyanide. In accord with Mittasch[99], the lines were thought to be those of an unknown carbide. Hofmann believed this to be the higher iron carbide first described by Hilpert as an intermediate in carbon formation. Above 400°C. no lines of this carbide were observed, very probably because of its lack of stability in this region. The iron which may be liberated (with formation of free carbon) by decomposition of the higher carbide, appears to react again rapidly, since X-ray analysis of the solid phase showed the iron content to be very low below 655°C. It is interesting to note that at low carbiding temperatures no ferrous oxide is formed, and that the interference lines observed for iron oxide are those of magnetite. In accord with observations made by Schenck, the limits of stability of ferrous oxide are between 560° and 660°C.

In his experiments on the role of catalysts in heterogeneous

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[98] Brill, R. and Mark, H., work cited (footnote 30).
[99] Mittasch, A. and Kuss, E., work cited (footnote 92).

catalysis, Göthel[100] used the change in the electric resistance of powdered metal catalysts during reaction. It was observed that carburization of powdered iron catalysts was accompanied by an increase in electric resistance, which decreased again upon treatment with hydrogen. This increase in resistance was explained by carbide and oxide formation. The action of a carbon monoxide-hydrogen mixture also increased the resistance. Göthel arrived at an interpretation of the fundamental process of carbon monoxide decomposition, according to which carbon monoxide is chemisorbed by iron. The carbon-to-oxygen bond of these surface compounds was believed to be loosened so that adjacent carbon monoxide molecules react with each other to form carbon dioxide. The carbide thus formed was assumed to be Fe_2C.

THERMOMAGNETIC STUDY ON CARBURIZED IRON

Thermomagnetic studies of ferromagnetic substances have been used successfully in the determination of cementite, particularly in mixtures of iron and iron oxides. Early work in this field included the determination of iron and cementite in iron synthetic ammonia catalysts by Mittasch and Kuss[101], and the above-mentioned work by

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[100] Kröger (editor), [Surface Catalysis]: Hirzel, Leipzig, 1933.

[101] Mittasch, A. and Kuss, E., work cited (footnote 92).

Hilpert.[102] Magnetization curves, plotted as a function of temperature, showed that decomposition of complex iron cyanides resulted in the formation of cementite and iron. Magnetic studies by Körber, Wiemer, and Fischer[103] of the products obtained by carburization of iron catalysts are more directly concerned with the formation of such catalysts. From the thermomagnetic curve which showed an inflection point above 250°C., the authors concluded that cementite was formed. The probable catalytic effect of this carbide on the decomposition of carbon monoxide was indicated by the fact that the amount of carbide remained constant in spite of the formation of large amounts of carbon. However, the question remained as to whether carbon is deposited by way of higher carbides or directly from carbon monoxide. The thermomagnetic curves gave no evidence of the formation of other carbides. In addition, magnetic studies of the carburization of iron powder at 500°C. showed that all but 3.5 percent of the iron was converted to Fe_3C.

More recently Lange and Mathieu[104, 105] used the thermomagnetic

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[102] Hilpert, S. and Dieckmann, T., work cited (footnote 9).

[103] Körber, F., Wiemer, H., and Fischer, W. A., work cited (footnote 87).

[104] Lange, H. and Mathieu, K., [The Progress of Austenite Transformation in the Undercooled State of Iron-Nickel-Carbon Alloys]: Mitt. Kaiser-Wilhelm Inst. Eisenforsch., Dusseldorf, vol. 20, 1938, pp. 125-134, 239-246. C.A., vol. 32, 1938, p. 7878^6.

method to study steels. Magnetic saturation was determined with remarkable accuracy by means of a suitable magnetic balance, thus making the quantitative determination of the carbide and ferrite content of steels readily possible.

An interesting variation of the magnetic method is the procedure reported by Westerhoff[106/], in connection with work on changes in magnetic properties of catalysts used for heterogeneous catalytic reactions. This method is based on the fact that the ferromagnetic catalyst forms part of a tuned electric circuit which is coupled with a second one having a constant frequency. Any change in the permeability of the catalyst is accompanied by a change in the self-induction, and consequently a change in the frequency of its circuit.

The magnetic studies in the present work are concerned with iron and its ferromagnetic compounds. The known magnetic transition points of these substances are given in table 6.

105/ Mathieu, K., [Measurements of Specific Magnetization and Their Use in Problems of the Metallurgy of Iron]: Arch. Eisenhüttenw., vol. 16, 1943, pp. 415-423.

106/ Kröger (editor), [Surface Catalysis]: Hirzel, Leipzig, 1933.

Table 6.–Curie Points of iron and its ferromagnetic compounds

Substance	Curie Point, °C.	Investigator	Year
Fe	750	P. Curie	1894
	785	Jensen	1914
	769	Honda	1914
	768	Lange	1938
Fe_3C	180	Wologdine	1909
	215	Honda	1917
	215	-	1928
	215	Mittasch	1928
	210	Tammann	1922
	205	Lange	1938
Fe_3O_4	570	Huggett	1928
	510	Ischiwara	1917
	575	Takagi	1913
	565	Mathieu	1938
Fe_2O_3 (cubic)	500	Hilpert	1909
	650	Abraham	1925
	600	Chevallier	1927
	675	(Huggett (Chaudron	1928
$K_2O.Fe_2O_3$	150	Hilpert	1909
$CuO.Fe_2O_3$	455	(Forestier (Chaudron	1925

SUMMARY

Definite information is available concerning the equilibria between the gas and solid phases during the decomposition of carbon monoxide by iron and iron oxides. On the other hand, interpretations of the reactions occurring in the solid phase are not consistent. In evaluating the experimental results, it is convenient to differentitate among carbide reactions at high (above 900°C.), medium, and low (below 320°C.) temperatures.

The range of medium temperatures (400° to 500°C.) is characterized by the deposition of large amounts of free carbon, whereas the conditions existing at lower temperatures favor carbide formation. Below 900°C., iron is generally thought to catalyze the decomposition of carbon monoxide in either one or both of two possible ways: (1) surface catalysis of the decomposition of carbon monoxide by iron, and (2) formation of intermediate, unstable higher iron carbides from carbon monoxide, which decompose to yield free carbon. Iron carbide and/or metallic iron can be considered the active catalytic agent. The theory of catalytic higher carbides was at first hypothetical in character, but has since received support from the observation of unfamiliar interference lines in X-ray patterns of iron preparations treated with carbon monoxide at low temperatures. Formation of iron carbides higher in carbon content than cementite is also suggested by the easily reducible carbon obtained by hydrogen reduction of iron preparations which had been carburized at low temperatures. However, the evidence available cannot be considered as proof of the existence of higher iron carbides. It should be noted, for instance, that activated carbon, located in the interstices of the iron lattice, reacts with hydrogen at low temperatures to yield methane. The problem of whether the product obtained upon carburization at low temperatures is a single carbide or mixture of carbides deserves further consideration. As long as this question remains unsolved, there is no justification for the derivation of carbide formulas from carburization and decarburization curves. Although the results of magnetic studies have proved the formation of cementite from the decomposition of carbon monoxide over iron, they have as yet produced no information about the formation of higher carbide nor about the mechanism of carburization.

EXPERIMENTAL PART

One of the principal objects of the present work was to establish a theoretical basis for the empirically determined conditions governing the Fischer-Tropsch synthesis on iron catalysts. With this in view, the behavior of iron catalysts during carburization and synthesis was studied by acid decomposition, reduction with hydrogen, and thermomagnetic analysis. A relationship was sought between chemical composition and activity of the catalyst in the gasoline synthesis, with particular emphasis on the formation of carbides. The mechanism of the Fischer-Tropsch process and the formation of free carbon on iron catalysts during pretreatment and medium-pressure synthesis were considered in the light of the results obtained.

CHEMICAL STUDY

Carburization of Iron Catalysts Prior to Medium-Pressure Synthesis

Method and Apparatus

The iron catalysts studied in the first part of this work were prepared in large batches in the usual way by precipitating a hot iron nitrate solution with sodium carbonate. The precipitate was washed and alkalized with potassium carbonate, and then oven-dried at 105°C. After screening, a particle size of 1-5 millimeters was collected. The iron catalysts were treated with carbon monoxide in a standard aluminum block oven (figure 2) which consisted of an aluminum

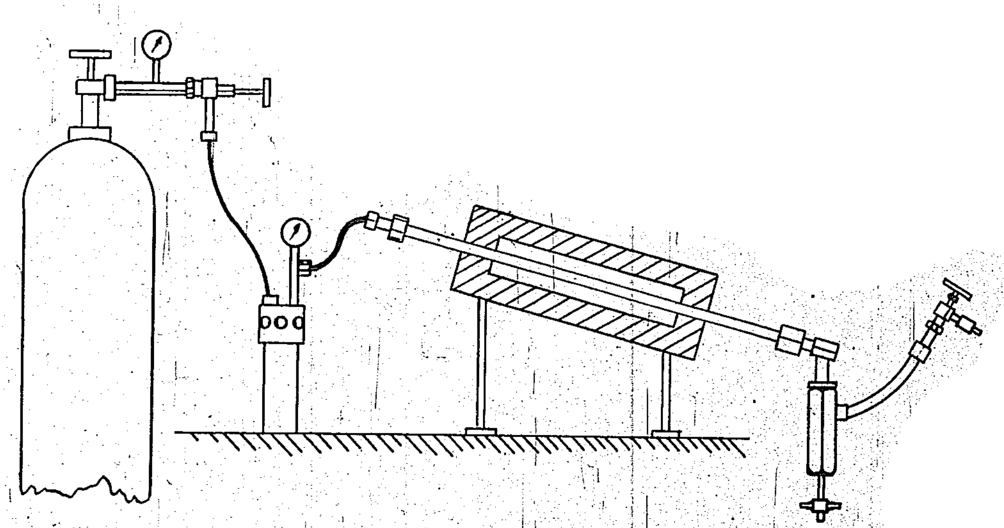

Figure 2.—Apparatus for carburization of iron catalysts.

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heating block containing a copper-lined iron tube. This tube was used for experiments at high and low pressures.

An amount of catalyst corresponding to 10 grams of iron was placed in an iron boat and spread out over a length of 30 centimeters. The boat was placed in the center of the copper-lined iron tube. The system was flushed with carbon monoxide, and then heated under a carbon monoxide pressure of 0.1 atmosphere. Temperature was maintained at 325 ± 1°C., by means of a thermostat. At the conclusion of the experiment, the aluminum heating block was cooled with wet cloths to reduce the temperature to below 200°C. within a few minutes. Thus no significant additional carburization occurred either during heating or cooling.

The carburized iron catalysts were markedly pyrophoric in air but not in water. Consequently, boiled distilled water was drawn through the cooled tube, thus making it possible to expose the catalyst to air without danger. The catalyst was stored in closed flasks under boiled distilled water. Since highly active catalysts evolved hydrogen on standing, it was necessary to use them immediately.

Acid Decomposition of Iron Catalysts Carburized Under Various Conditions

Method and Apparatus

A number of methods are reported in the literature regarding the separation of carbidic carbon from free carbon by acid decomposition of the carbide. Decomposition of the carburized iron catalysts with hydrochloric acid was carried out in the apparatus shown in figure 3.

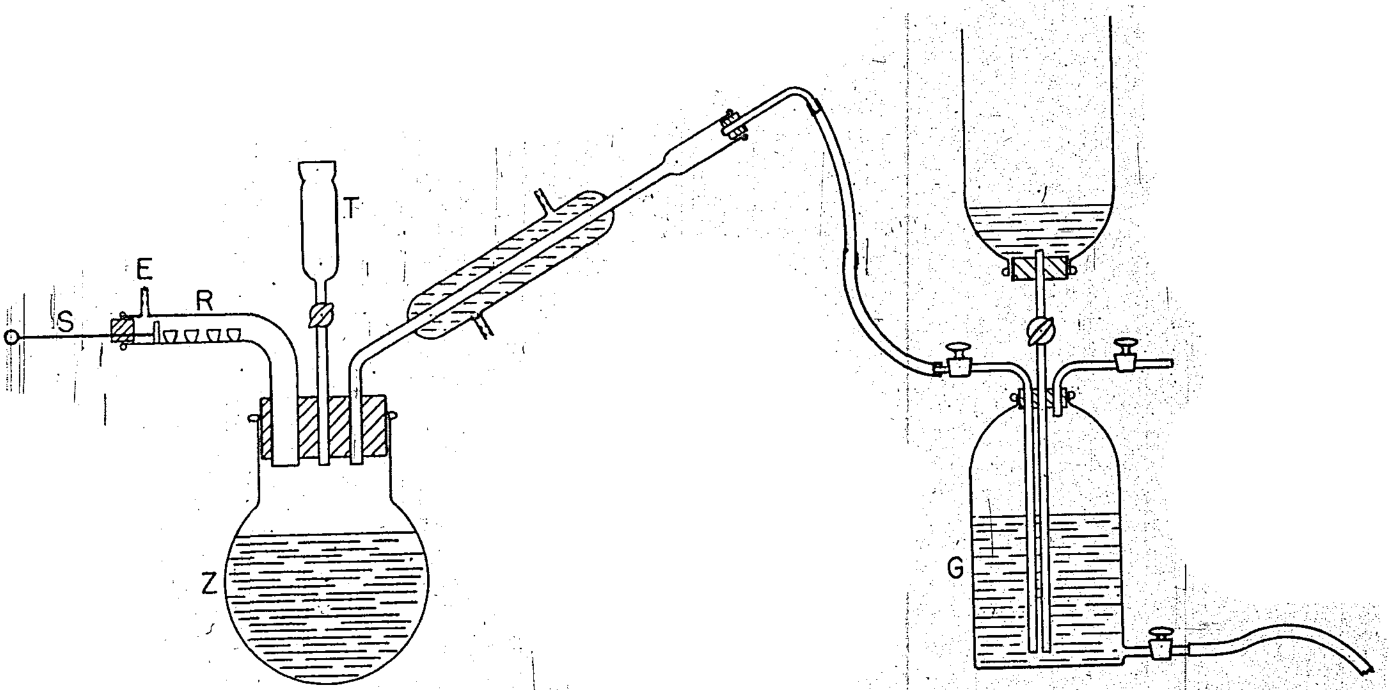

Figure 3.– Apparatus for acid decomposition of iron catalysts.

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During decomposition, carbidic carbon produced gaseous hydrocarbons and the residual carbon was assumed to correspond to the amount of free carbon initially present in the catalyst.

Conflicting data on the reaction of cementite (Fe_3C) with acids are reported in the literature. According to Hilpert[107] cementite in steels is completely hydrogenated in the presence of strong acids. The carbonaceous deposits which originate from the decomposition of steels tempered at 200 to 600°C., are attributed to the decomposition of higher carbides. Schenck and Stenkhoff[108] have shown that acid decomposition of cementite can proceed according to two different reactions:

$$(1)\quad Fe_3C + 6H^{+} = 3Fe^{++} + CH_4 + H_2$$

$$(2)\quad Fe_3C + 6H^{+} = 3Fe^{++} + C + 3H_2$$

The course of the reaction is determined by the concentration of the acid, temperature, and concentration of ferrous ions. Reaction (2) occurs with weak acid and a high concentration of ferrous ions. Reaction (1) is favored by a lower concentration of ferrous ion and strong, hot acid.

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[107] Hilpert, S. and Dieckmann, T./work cited (footnote 9).

[108] Schenck, R. and Stenkhoff, R., work cited (footnote 26).

Work by Mittasch and Kuss[109] justifies the assumption that decomposition of cementite (prepared at 1550°C.) may be effected according to equation (1).

The experiments described below were carried out in decomposition flask Z (figure 3), containing one liter of 5N hydrochloric acid which was heated to boiling in a stream of nitrogen. The catalyst was placed in little glass dishes which were introduced into the glass tube R. A plunger, S, pushed the catalyst containers successively into the decomposition flask. This procedure corresponded to the conditions of acid decomposition of cementite used by Schenck. Since the amount of iron used was only two or three grams, the formation of an undesirable concentration of ferrous ions was avoided and an excess of acid assured. Decomposition was very rapid and generally completed in a few seconds. The flasks were then filled with distilled water from the dropping funnel, T, almost to the opening of the inlet tubes, and the product gas was swept into the gasometer, G, by a stream of nitrogen (introduced through tube E).

In addition to nitrogen introduced as described above, the product gas contained hydrogen and hydrocarbons in varying amounts. Carbon, originating from iron carbide and hydrogenated during acid decomposition, was determined by combustion of the hydrocarbons; in the following discussion it will be referred to as carbidic carbon. The elementary carbon was filtered off from the iron solution, dried, and

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[109] Mittasch, A. and Kuss, E., work cited (footnote 92).

burned. The residue contained small amounts of iron which could not be eliminated even by prolonged treatment with acid. The iron was determined by titration.

Free Carbon

When carburized iron catalysts undergo acid decomposition, free and carbidic carbon are always present. A study was made of the quantity of free carbon formed under different carburization conditions. The effect of the rate of flow of carbon monoxide on the formation of free carbon was examined first. In each case an amount of catalyst equivalent to 10 grams of iron was treated with 100 liters of carbon monoxide at 325°C. and 0.1 atmosphere pressure, the standard conditions of pretreatment. The carbon monoxide was first purified by passage through two columns containing soda lime and activated charcoal. The results obtained from this series of experiments are given in table 7.

Table 7.-Effect of rate of flow of carbon monoxide on the formation of free carbon

(Temperature, 325°C.; CO pressure, 0.1 atmosphere; Fe, 10 grams)

Experiment number	Rate of flow (liters per hour)	Carburization time (hours)	Free carbon grams
1	100	1.0	0.56
2	40	2.5	.95
3	4	25.0	2.21

Table 7 shows that the quantity of elementary carbon increased as the rate of flow decreased, that is, as the contact time was prolonged. Similar results were observed when the throughput (liters of carbon monoxide per hour per gram of iron) was held constant and the pressure varied. The lower the pressure, the shorter was the contact time between catalyst and carbon monoxide, and the smaller the amount of free carbon deposited. In an experiment similar to experiment (3) in table 7, carburization was carried out at 1 atmosphere instead of 0.1 atmosphere; 4.32 grams of carbon per 10 grams of iron was obtained.

Table 8 shows the effect of carburization temperature on free carbon deposition.

Table 8.-Effect of carburization temperature on the formation of free carbon

(Rate of flow, 4 liters CO/hour/10 grams Fe; pressure, 0.1 atmosphere; carburization time, 25 hours)

Experiment number	Temperature, (°C.)	Free carbon, (grams)
1	175	0.00
2	225	.07
3	275	.89
4	325	2.21
5	425	10.02

No carbon deposition occurred at 175°C., but the catalyst turned black. Ferric oxide, Fe_2O_3, was reduced to magnetite even below 200°C. As the temperature was increased, the amount of carbon deposited increased to 10.02 grams of carbon per 10 grams of iron at 425°C. The free carbon was large-grained and hard up to 325°C.; at 425°C. it was obtained in a fine, sooty powder. According to Hofmann,[110] the difference in properties

[110] Hofmann, U., work cited (footnote 96).
Hofmann, U. and Groll, E., work cited (footnote 97).

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of carbon deposited at different temperatures is determined by the orientation of the individual crystallites and by their regular increase in size as the temperature rises.

Table 9 shows the formation of free carbon as a function of time.

Table 9.—Effect of carburization time on the formation of free carbon

(Rate of flow, 40 liters CO/hour/10 grams Fe; pressure, 0.1 atmosphere; temperature, 325°C.)

Experiment number	Carburization time (minutes)	Free carbon (grams)
1	4.5	0.017
2	9	.11
3	18	.28
4	37.5	.41
5	75	.49
6	150	.95
7	600	1.83
8	1500	3.23

It will be seen from experiment 1 (table 9) that free carbon formed after only 4.5 minutes of carburization. This carbon had a flaky, voluminous appearance, whereas it was hard and granular after a longer period.

Figure 4 shows graphically the results listed in table 9. The rate of carbon formation reached a constant value after about 2.5 hours, the formation of free carbon being proportional to the carburization time. Even after 25 hours of carburization, and after 1000 liters of carbon monoxide had flowed over the catalyst, there was no perceptible decrease in free carbon formation.

Next, the effect of activity of the catalyst upon the formation of free carbon was examined. Three iron catalysts of different origin were treated for 2.5 hours at 325°C. and 0.1 atmosphere with 40 liters of carbon monoxide per 10 grams of iron per hour. Catalyst Z 7 contained 0.81 gram of elementary carbon per 10 grams of iron, catalyst Z 4 contained 1.07 gram of carbon, and catalyst Z 3 contained 1.75 gram of carbon as shown in table 10. In the synthesis (15 atmospheres, 235°C.), all three catalysts showed satisfactory conversion (80-90 percent) of carbon monoxide on the first day of operation. After 6 to 10 days, conversion began to decrease for catalysts Z 7 and Z 4, but the activity of catalyst Z 3 was still unchanged after 35 days.

Table 10.-Effect of catalyst activity on the formation of free carbon

(Rate of flow, 40 liters CO/hour/10 grams Fe; time, 2.5 hours; pressure, 0.1 atmosphere; temperature, 325°C.)

Catalyst	Free carbon, (grams)	Period during which catalyst showed full activity in synthesis (days)
Z 7	0.81	6-10
Z 4	1.07	6-10
Z 3	1.75	35+

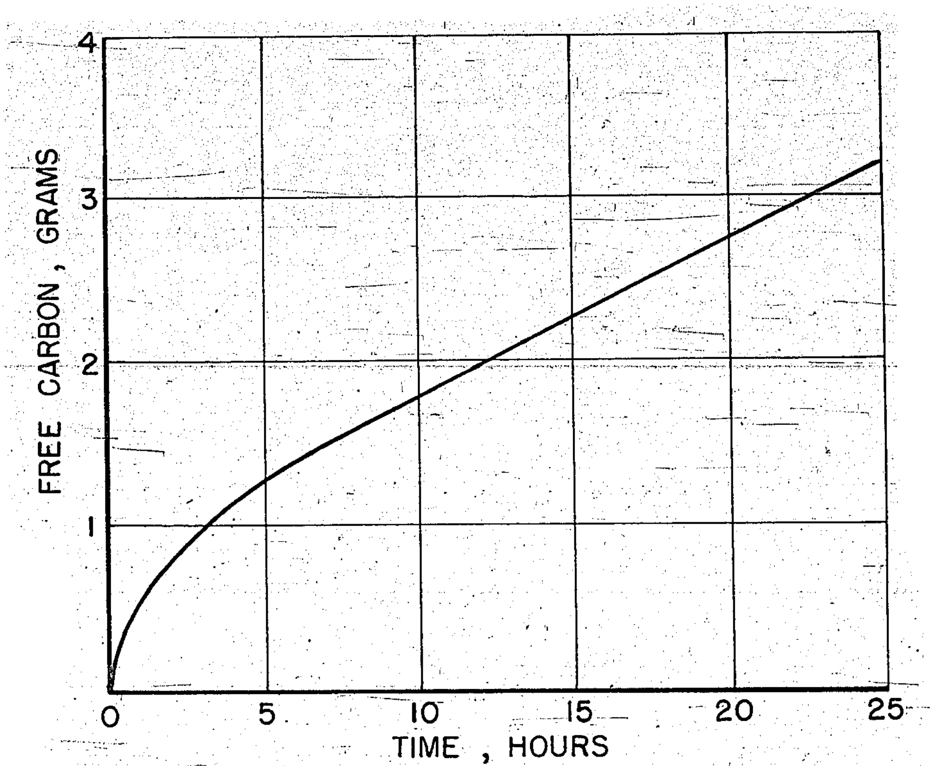

Figure 4.— Free carbon deposition on alkalized iron catalyst at 325° C. and 0.1 atmosphere, 40 liters of CO per hour per 10 grams of Fe.

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Carbidic Carbon

The gas produced during acid decomposition of carburized catalysts was measured and calculated at standard conditions. In one sample unsaturated hydrocarbons were determined with concentrated sulfuric acid; hydrogen and saturated hydrocarbons were determined by fractional combustion. In a second sample, combustion of all the hydrocarbons was carried out in oxygen over a copper oxide catalyst at bright red heat, and the carbon dioxide evolved was determined.

An experiment was performed in which the total carbon content of a carburized catalyst was determined both by acid decomposition and by combustion in a current of oxygen. In the former case, the sum of free carbon obtained by acid decomposition and of carbidic carbon obtained by combustion of gaseous hydrocarbons was 0.448 gram per gram of iron. The total carbon obtained by combustion of the catalyst in oxygen amounted to 0.423 gram per gram of iron. These results were in satisfactory agreement within the limits of experimental error and showed that no liquid hydrocarbons were formed during acid decomposition.

The procedure for investigating the formation of free carbon was also used to study the effect of various carburization conditions on the formation of carbidic carbon. An amount of catalyst equivalent to 10 grams of iron was treated with a current of carbon monoxide in a standard aluminum block oven under various conditions of rate of flow, temperature, pressure, and time. The effect of activity of the catalyst upon the formation of carbide was also studied.

Table 11 shows that the effect of the rate of flow of carbon monoxide on the formation of carbidic carbon was similar to that observed for free carbon (see table 7); however, combined carbon reached a maximum value for a flow rate of 40 liters per hour, while the formation of free carbon continued to increase (table 7, experiments 2 and 3).

Table 11.—Effect of rate of flow of carbon monoxide on the formation of carbidic carbon

(Temperature, 325°C.; CO pressure, 0.1 atmosphere; Fe, 10 grams)

Experiment number	Rate of flow, liters/hour	Carburization time (hours)	Carbidic carbon, (grams)
1	100	1	0.263
2	40	2.5	.436
3	4	25	.454

The following series of experiments show the effect of temperature on carbidic carbon (table 12 and figure 5).

Table 12.—Effect of carburization temperature on the formation of carbidic carbon from carbon monoxide

(Rate of flow, 4 liters CO/hour/10 grams Fe; CO pressure, 0.1 atmosphere; carburization time, 25 hours)

Experiment number	Temperature, (°C.)	Carbidic carbon,[a] (grams)
1	175	0.003
2	225	.004
3	275	.358
4	325	.454
5	425	017

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[a] By acid decomposition

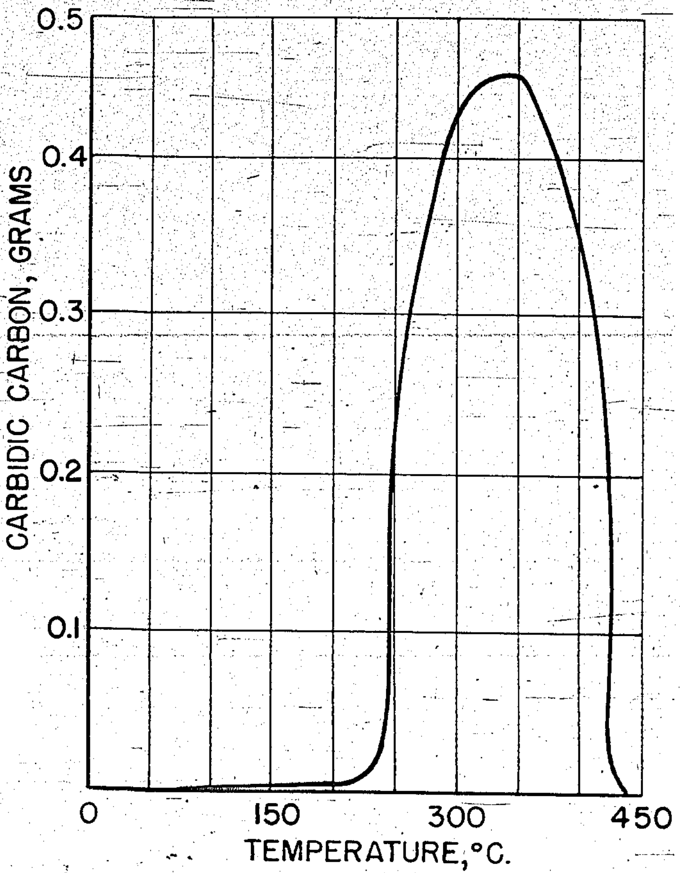

Figure 5.—Carbide formation on alkalized iron catalysts during 25 hours carburization at 0.1 atmosphere, 4 liters of CO per hour per 10 grams of Fe.

L-588

The amount of carbidic carbon was still very small at 225°C., reached a maximum value at 325°C., and decreased abruptly at 425°C. These results show that, in the course of 25 hours, carburization produced considerable amounts of carbidic carbon only in a relatively narrow temperature range.

Table 13 shows the relationship between the formation of carbidic carbon and contact time. Perceptible amounts of carbidic and free carbon were formed in the first 4.5 minutes of carburization. There was still little carbon after 9 minutes. After 150 minutes, carburization was almost complete under these conditions. In 1500 minutes carbidic carbon content increased only slightly. Prolonged carburization would be detrimental to activity in the synthesis since the free carbon which continues to form would block the active centers.

Column 6 of table 13 shows the ratio of hydrogen to carbon dioxide. Under the conditions chosen, the acid decomposition of cementite should proceed quantitatively according to the two following equations:

$$(1)\quad n\,Fe_3C + 6n\,HCl = 3n\,FeCl_2 + C_nH_{2n} + 2n\,H_2$$

$$(2)\quad n\,Fe_3C + 6n\,HCl = 3n\,FeCl_2 + C_nH_{2n+2} + (2n-1)\,H_2$$

Accordingly the hydrogen to carbon dioxide ratio should never exceed 2:1. Actually, (according to table 13) exhaustive treatment with carbon monoxide resulted in a ratio of 2.5:1. The explanation will be discussed in connection with the thermomagnetic analysis.

Table 13.–Formation of carbidic carbon from carbon monoxide as a function of carburization time

(Rate of flow, 40 liters CO/hour/10 grams Fe; CO pressure, 0.1 atmosphere; temperature, 325°C.)

Carburization time (minutes)	Carbidic C (grams)	Free C (grams)	H_2 (cc)	CO_2 from hydrocarbons, (cc)	H_2:CO_2	Composition of evolved gas, volume percent: Unsaturated hydrocarbons "SKW"a/	Saturated hydrocarbons	O_2	CO	H_2	N_2
4.5	0.001	0.017	-	-	-	-	0.4	5.0	0	0.8	19.1
9	.002	.11	2.6	2.9	0.9:1	-	1.4	5.4	0	1.0	23.3
18	.019	.28	72	35.4	2.0:1	0.6	0.5	2.0	0	6.2	88.7
37.5	.085	.41	333	159	2.1:1	1.3	1.9	1.4	0	21.4	71.5
75	.201	.49	775	374	2.1:1	2.9	2.2	1.2	0	38.6	53.5
150	.436	.95	1960	813	2.4:1	4.3	4.9	0.7	0	57.5	32.4
600	.454	1.83	2110	844	2.5:1	3.6	3.6	1.7	0	55.7	34.8
1500	.457	3.23	2110	855	2.5:1	1.7	3.7	1.2	0	54.0	37.1

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a/ Determined with fuming H_2SO_4.

The data from table 13 summarizing the results of experiments on the formation of carbidic carbon as a function of the carburization time are graphically shown in figure 6. Comparison of figures 4 and 6 shows that the end of carbide formation could also be seen from the shape of the free carbon deposition curve. Once the carbide content reached a constant value the free carbon curve became linear.[111]

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[111] Editor's note. The end of carbide formation did not coincide exactly with the beginning of the constant rate of free carbon deposition. Dr. Pichler believed that this discrepancy was probably due to slight differences between the two samples used for these experiments.

The effect of varying the carbon monoxide pressure was studied (table 14); increase in pressure resulted in a decrease of carbidic carbon, in contrast to results obtained with free carbon.

Table 14.-Effect of pressure on the formation of carbidic carbon from carbon monoxide

(Rate of flow, 4 liters CO/hour/10 grams Fe; temperature, 325°C.; carburization time, 25 hours)

Catalyst number	CO pressure, (atmospheres)	Carbidic carbon (gram)	H_2 (cc)
1	0.1	0.45	2220
	1.0	.34	1570
	15.0	.10	540
2	0.1	.50	2330
	15.0	.33	1520

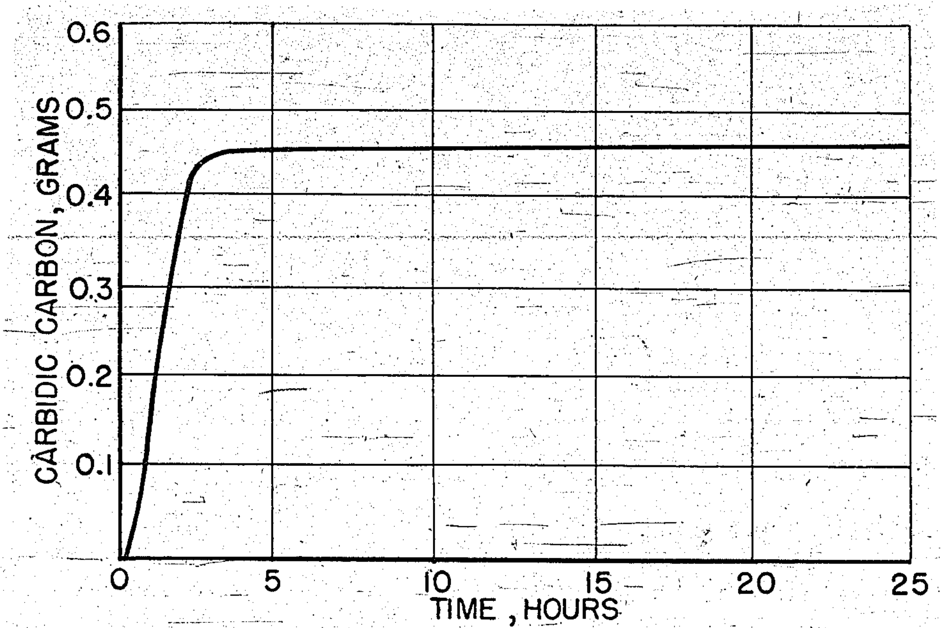

Figure 6.— Carbide formation on alkalized iron catalysts at 325° C. and 0.1 atmosphere, 40 liters of CO per hour per 10 grams of Fe. L-589

In order to characterize partially the hydrocarbons produced by acid decomposition of iron carbides, their carbon number was determined as follows. A sample of the gaseous hydrocarbon evolved was burned and the carbon dioxide measured. The volume of carbon dioxide produced by combustion of the saturated hydrocarbons was subtracted from this value. The difference, corresponding to the volume of carbon dioxide obtained by combustion of the unsaturated hydrocarbons, was divided by the volume of unsaturated hydrocarbons. The carbon number of the saturated hydrocarbons was determined similarly. Table 15 lists the carbon numbers obtained for different carburization times.

Table 15.-Effect of carburization time on the carbon number

Carburization time (hours)	Carbon number	
	Saturated hydrocarbons	Unsaturated hydrocarbons
1.25	2.2	4.7
2.50	1.7	4.5
10	1.9	4.3
25	1.7	-

The high carbon number for unsaturated hydrocarbons in table 15 indicated the probable presence of C_5 hydrocarbons. On the other hand, the carbon number of the saturated hydrocarbons was very low. There was apparently no correlation between carburization time and carbon number.

Oxygen Content of Carburized Catalysts

The next step in establishing the composition of carburized iron catalysts was to determine their oxygen content. The following solid phases can exist under carburization conditions: Fe_3O_4, Fe, Fe_3C, and C. In the presence of a carbon monoxide-carbon dioxide mixture the following reactions take place:

$$Fe_3O_4 + 4CO \rightleftharpoons 3Fe + 4CO_2$$

$$3Fe + 2CO \rightleftharpoons Fe_3C + CO_2$$

$$2CO \rightleftharpoons CO_2 + C$$

The amount of carbon dioxide present in the tail gas from carburization with carbon monoxide was determined. Table 16 shows the carbon dioxide to carbon monoxide ratios of the tail gas at different intervals.

Table 16.-CO_2 : CO ratio in the tail gas during carburization

(Rate of flow, 4 liters CO/hour; temperature, 325°C.; pressure, 0.1 atmosphere)

Time (minutes)	CO_2:(volume ratio)CO
25	1.92
55	.770
75	.794
115	.809
165	.794
305	.561
365	.458
425	.348
605	.144
1380	.073
1500	.069

After about 24 hours, the composition of the tail gas attained a constant ratio of carbon dioxide to carbon monoxide of 0.069:1. The equilibrium diagram for the system iron-carbon-oxygen shows that only Fe and Fe_3C are stable at 325°C. and in the presence of a gas of this composition.

The carbon dioxide to carbon monoxide ratio of the tail gas corresponded to the gas composition existing at the end of a 30-centimeter layer of catalyst. The carbon dioxide content decreased steadily towards the gas inlet so that these portions of the catalyst remained within the range in which free iron and iron carbide are stable.

The changes in carbon dioxide content of the carburization end gas are represented graphically in figure 7. The carbon dioxide content increased rapidly during the first 45 minutes and then decreased just as quickly to a value of 38.5 percent. This first rapid formation of carbon dioxide corresponded to the reduction of Fe_2O_3 to Fe_3O_4. It then increased again and reached a second maximum of 40.5 percent after carburization for 2 hours. This portion of the curve corresponds to the reduction of Fe_3O_4 to Fe and to the beginning of carbide formation (for a higher rate of flow, carbide formation had already started after a few minutes). Once reduction and carbide formation were completed, carbon dioxide formation reached a constant rate determined solely by the decomposition of carbon monoxide into carbon dioxide and free carbon.

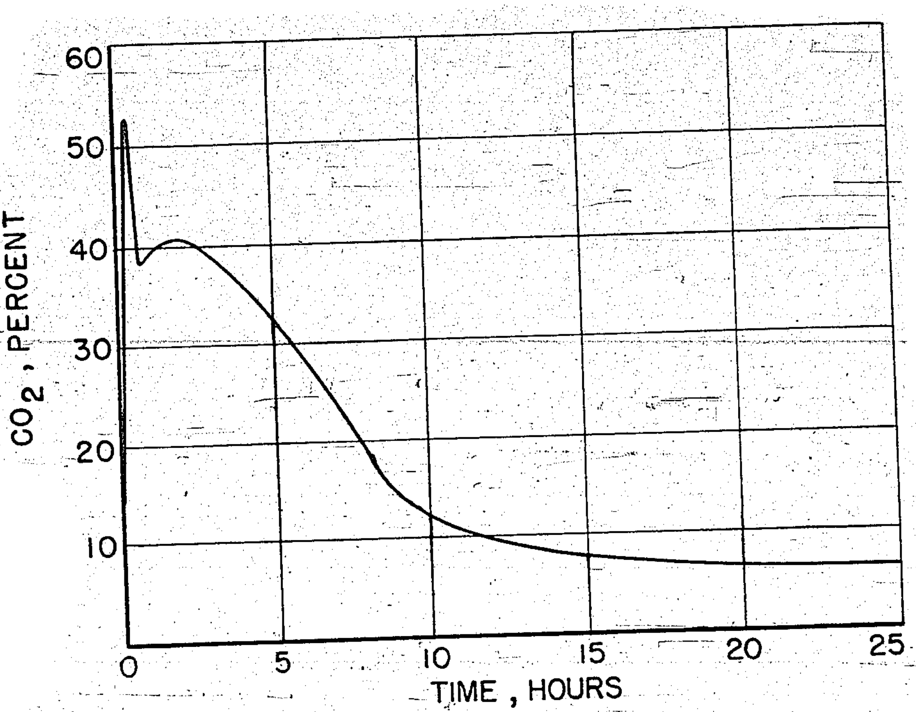

Figure 7.— Carbon dioxide content of the tail gas during carburization of an alkalized iron catalyst at 325° C. and 0.1 atmosphere, 4 liters of CO per hour. L-590

In the determination of the oxygen content of the catalyst, the following procedure was used: The catalyst was dried at 250°C. in a current of oxygen-free nitrogen by placing the catalyst container in a hard glass tube and heating it in an electric oven. After drying, the catalyst was reduced at 600°C. with hydrogen that had been freed of oxygen by passage over a copper spiral at 400°C. and had been dried in a series of columns packed with calcium chloride. Water formed by reduction of iron oxides was absorbed in a U-tube filled with calcium chloride, and weighed. To determine its iron content, the reduced catalyst was treated with hydrochloric acid until hydrogen evolution had ceased. The iron content of the filtrate was determined by titration.

To check the procedure, the oxygen content of an uncarburized iron oxide sample was determined. Analysis showed 0.3870 grams of iron and 0.1648 grams of oxygen. Thus 100 grams of iron were present for 42.6 grams of oxygen; and in ferric oxide there are 100 grams of iron for 43.0 grams of oxygen. This determination also proved that the dried, precipitated catalyst contained almost pure trivalent iron, present as ferric oxide or its hydrates.

The oxygen content was determined at intervals during carburization, to follow the course of catalyst reduction.

The low oxygen content of the catalyst after prolonged carburization (table 17 and figure 8) indicates that only 1 percent of the iron was still present as magnetite after carburization was completed and that reduction was virtually complete after 2.5 hours of

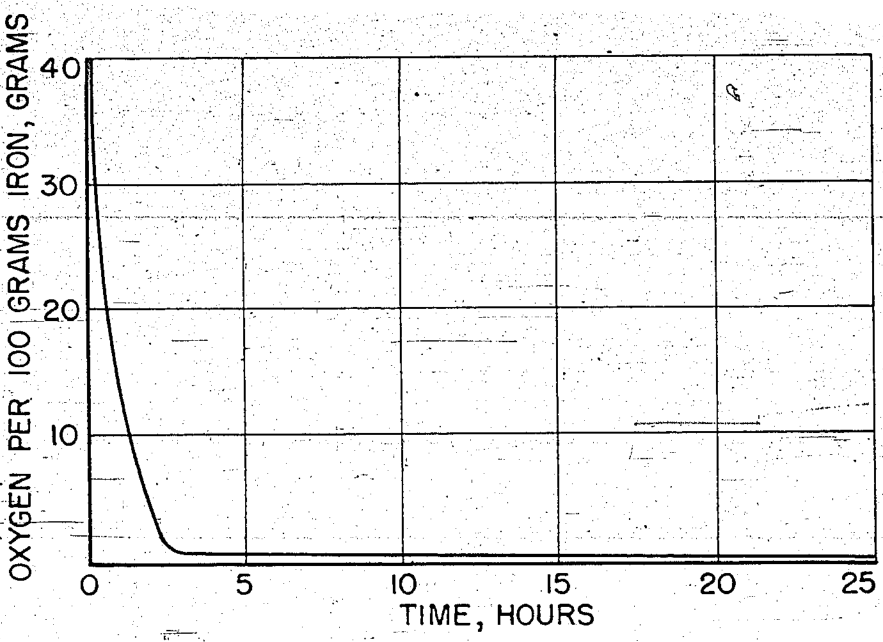

Figure 8.—Oxygen content of an alkalized iron catalyst during carburization at 325° C. and 0.1 atmosphere, 40 liters of CO per hour.

L-591

carburization. This is also shown by the fact that the carbidic carbon reached a maximum value after the same length of time (table 13 and figure 6).

Table 17.-Oxygen content of an iron catalyst as a function of carburization time

(Rate of flow, 40 liters CO/hour; temperature, 325°C.; pressure, 0.1 atmosphere)

Carburization time (minutes)	Oxygen content (grams per 100 grams iron)
0	42.60
9	30.95
37	18.95
150	0.59
600	.43
1500	.39

The influence of the rate of flow of carbon monoxide on the reduction of iron catalysts was studied by a method analogous to that used in determining carbidic and free carbon. One hundred liters of carbon monoxide was passed over the catalyst at two rates of flow (table 18). For the same amount of gas, the higher rate of flow effected

Table 18.-Oxygen content of an iron catalyst as a function of flow rate of carbon monoxide

(CO pressure, 0.1 atmosphere; temperature, 325°C.)

Rate of flow, liters CO/hour	Carburization time (hours)	Oxygen content (grams per 100 grams iron)
40	2.5	0.59
4	25	1.26

more extensive reduction. High rates of flow are thus necessary to prepare a catalyst virtually free of oxygen.[112]

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[112] According to Hofmann, a product from which all oxygen has been eliminated may be obtained by using high temperatures and high rates of flow.

Hydrogen Reduction of a Carburized Iron Catalyst

Exhaustive reduction with hydrogen at atmospheric pressure was used to determine the composition of the iron carbides formed. This method has been used often to determine carbide in carburized iron. It is based on the fact that carbidic carbon can be hydrogenated to methane at lower temperatures than can free carbon. According to Bahr and Jessen,[113] carbidic carbon obtained during the carburization of iron oxides can be hydrogenated at temperatures as low as 280°C. These authors found that 260° to 265°C. was best for hydrogenation of carbidic carbon, since the results they obtained at higher temperatures were scattered. Any hydrogenation of free carbon seemed unlikely at this temperature, while the removal of carbidic carbon proceeds sufficiently fast.

An alkali-promoted catalyst was treated with a stream of carbon monoxide (40 liters per hour) for eight hours in the aluminum block oven to ensure complete carbide formation. Then 0.8 liter per

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[113] Bahr, H. A. and Jessen, V., work cited (footnote 50).

hour of electrolytic hydrogen was passed over the catalyst at 263°C. and atmospheric pressure. Hydrogen and methane were collected in a gasholder. Hydrogenation was interrupted every 24 hours, and methane determined by passing the hydrogen-methane mixture over copper oxide at 280°C. until oxidation of the hydrogen was virtually complete. The residual gas was swept by carbon dioxide through a three-way stop-cock into a second gasholder. The methane content was determined by combustion, after removal of carbon dioxide.

This procedure not only gave more accurate results because of the concentration of methane, but permitted the determination of the rate of hydrogenation, as shown in figure 9. The experiment was interrupted after 408 hours, when 0.939 gram of carbon was reduced with hydrogen. The decarburized catalyst was dissolved with hydrochloric acid. The resulting gas contained no hydrocarbons, a proof of the complete hydrogenation of the carbidic carbon. The catalyst contained 10.060 grams of iron and 0.048 gram of oxygen. Assuming the oxide to be magnetite, 9.934 grams of iron combined with 0.939 gram of carbon, that is, a carbide containing 8.64 percent of carbon. This carbon content is lower than that of a carbide of formula Fe_2C (9.71 percent carbon), but appreciably higher than that of Fe_3C (6.68 percent carbon). Figure 9 shows the carbon content of Fe_2C and Fe_3C as dashed lines. The amount of carbidic carbon obtained by hydrogen reduction is indicated on the ordinate axis, and the hydrogenation time on the abscissa.

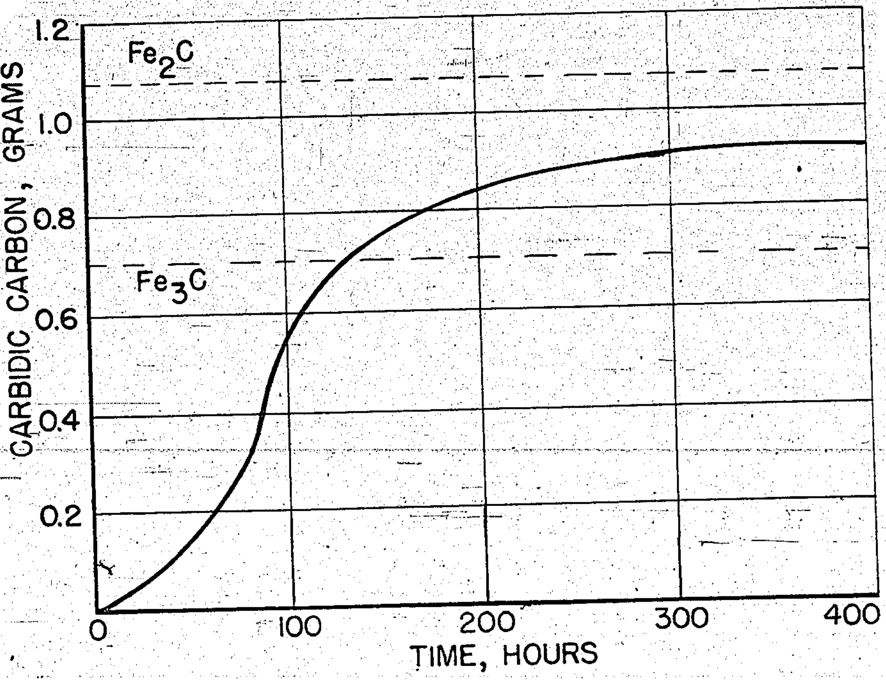

Figure 9.- Hydrogenation of 10.060 grams of a carburized, alkali-promoted (0.25% K_2CO_3) catalyst at 263° C. and atmospheric pressure, 0.8 liters of hydrogen per hour.

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(With 0.9 liter of hydrogen per hour, the rate of decarburization attained its maximum value only after about 90 hours.) The horizontal portion of the decarburization curve lies between the two dashed lines, that is, the carbide seems to be a mixture of cementite and an iron carbide with a higher content of carbon.

Acid decomposition of the catalyst, after removal of carbidic carbon, gave the following result:

Carbidic carbon (grams)	Free carbon (grams)	Hydrogen (cc)	Iron (grams)
0	1.4	3800	10

The large amount of hydrogen is explained by the absence of carbidic carbon which would have combined with a considerable amount of hydrogen upon reduction. Acid decomposition (without prior reduction) of a catalyst which had been carburized under the same conditions yielded 1.6 to 1.8 grams of free carbon per 10 grams of iron (see table 9), while only 1.4 grams of free carbon was present after hydrogenation.

Summary

Carburization during pretreatment of iron catalysts was studied by means of acid decomposition. The formation of free carbon was favored by a higher temperature, higher carbon monoxide pressure, and higher catalytic activity. Carbide formation stopped after a relatively short period of carburization, as indicated by the low oxygen content of the catalyst. Exhaustive carbide formation occurred only at low carbon monoxide pressures within a narrow temperature range around an optimum value of 325°C. Oxidation-reduction equilibria between gas and solid phase were not attained.

A carburized iron catalyst, reduced with hydrogen at atmospheric pressure and 263°C. until no more methane was formed, appeared to contain a carbide whose composition corresponded to the formula, $Fe_{2.28}C$. Acid decomposition yielded only half that value for carbidic carbon and produced hydrogen in excess of the calculated amount.

Effect of Carburization of Iron Catalysts upon Their Activity During Medium-Pressure Synthesis

Effect of Carbidic Carbon on the Activity of Iron Catalysts

It was stated in the introduction that the carbides formed by the action of carbon monoxide on the metals of the iron group may be considered as probable intermediates in the gasoline synthesis. After the conditions were examined under which such carbides are formed from iron catalysts, their behavior during synthesis was investigated. Carbon deposition during this process was studied concomitantly. Carburized alkalized iron catalysts were used. After operation under various conditions they were decomposed in the apparatus shown in figure 3. The deposit of high-boiling paraffins formed on the catalysts during synthesis was removed by exhaustive extraction with toluene. The extracted catalysts were washed with methanol to remove toluene, and then with water to remove methanol.

To determine whether any changes occur in the catalysts during extraction and washing, a used sample was decomposed with acid and compared with a second one which was extracted with toluene before acid decomposition. The results, as given in table 19, show that the effect of toluene extraction may be considered negligible.

Table 19.—Effect of toluene extraction on the analysis of a used iron catalyst
(Analysis by acid decomposition)

Sample	Carbidic carbon, (grams)	Free carbon, (grams)	Hydrogen, (cc)
Not extracted with toluene	0.430	5.75	2104
Extracted with toluene for 16 hours	0.426	5.85	1945

In the first part of this paper it was shown that the composition of the catalyst (that is, the relative amounts of chemically combined carbon, free carbon, and magnetite) depends largely upon the carburization procedure. Table 20 shows the advantage of carburization at low pressures. Moreover, a smaller amount of free carbon was formed at low carbon monoxide pressures.

Table 20.—Durability of catalyst as a function of carburization pressure

CO pressure during pretreatment	CO conversion
2 mm. Hg	Maximum yield still obtained after 3 weeks
15 atm.	Completely inactive after 3 weeks

The experimental results of table 12 show the marked effect of temperature on carburization. Table 21 shows the relative durability of iron catalysts carburized at temperatures ranging from 255° to 450°C.

Table 21.—Effect of carbiding temperature on the durability in the synthesis of an iron catalyst (copper-free)

(Synthesis conditions: temperature, 235°C.; pressure, 15 atmospheres; space velocity, 4 liters synthesis gas (NTP)/10 grams Fe/hour)

Experiment number	Carbiding temperature a/ (°C.)	Carbidic carbon content (grams per 100 grams Fe)	Period during which contraction was over 50% b/ days
1	255	0.6	2
2	285	3.8	10
3	305	4.2	24
4	315	4.4	50
5	325	4.6	365
6	355	4.2	20
7	450	0.1	c/

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a/ Carburization conditions: pressure, 0.1 atmosphere; space velocity, 4 liters CO/10 grams Fe/hour; time, 24 hours.

b/ This contraction represents the decrease in the volume of synthesis gas ($3CO + 2H_2$) resulting from the conversion of carbon monoxide and hydrogen into hydrocarbons. It was determined indirectly from the amount of nitrogen (which does not participate in the reaction) present before and after passage through the reactor. For almost complete carbon monoxide conversion, the maximum contraction obtained with iron catalysts was about 55 percent.

c/ Contraction never over 10 percent, heavy carbon deposition.

It will be seen from table 21 that preparations carbided at 255° and 450°C. were entirely unsuitable as catalysts. In the former case the initial contraction exceeded 50 percent, but decreased after two days; in the latter case the catalyst was almost inactive. Both catalysts contained only small amounts of carbidic carbon as determined by acid decomposition. The other catalysts all showed good initial activity, but their durability varied considerably. The catalyst which contained the largest quantity of carbidic carbon had the longest life.

To study the reasons for variations in catalyst activity, active catalysts (carburized as in experiment 5, table 21) were acid-treated after being operated for various periods. Table 22 presents data for 5 experiments in which conversion was still at a maximum after 7, 21, and 112 days.

Table 22.–Acid decomposition of catalysts active in synthesis

Experiment number	Operating time (days)	Contraction (percent)	Carbidic carbon (percent)	H_2 liters/100 grams Fe	O_2 grams/100 grams Fe
1	0	-	5.04	23.2	0.59
	7	52	2.34	10.5	-
2	0	-	4.94	21.9	-
	7	53	3.53	14.7	-
3	0	-	4.14	17.9	-
	7	50	3.78	11.1	-
4	0	-	5.04	23.3	-
	21	52	3.01	14.4	-
5	0	-	4.23	15.5	-
	112	50	3.76	14.2	1.6

In each case, catalyst samples were analyzed by acid decomposition at the beginning and at the end of the synthesis tests. All experiments showed that the amount of carbidic carbon of the catalysts as determined by acid decomposition decreased markedly after a few days of synthesis. After these few days, however, the value obtained for carbidic carbon showed no further decrease even after months of operation. The catalyst, which contained the highest amount of carbidic carbon prior to use in synthesis, that is, 5.04 grams per 100 grams of iron, reached the lowest value after 7 days (2.34 grams, experiment 1). The amount of hydrogen evolved during acid decomposition also decreased during the first days of operation and then remained approximately constant over a long period. The oxygen content of carburized catalysts, prior to their use in synthesis, was discussed in the section on carburization. In experiment 1 it was 0.59 gram per 100 grams of iron. After 112 days of operation (experiment 5) it had increased to 1.6 gram per 100 grams of iron. The catalyst apparently suffered some oxidation during synthesis.

Table 23 shows the data obtained by acid decomposition of catalysts whose activity had decreased for various reasons. In all four experiments diminished activity was associated with a decrease in the amount of carbidic carbon and an increase in the oxygen content. When the synthesis temperature was too high the carbon dioxide, which amounted to 50 percent or more of the tail gas, appeared to oxidize the catalyst. In experiment 2 in which the synthesis gas was rich in hydrogen and the operating temperature was unusually low, the water formed in the reaction was apparently responsible for the partial oxidation of the catalyst after a long operating period. A series of experiments with other catalysts with diminished activity showed a similar decrease in carbidic carbon to 1 gram or less per 100 grams of iron. A marked decrease in the amount of hydrogen evolved during acid decomposition was observed simultaneously. These results will be discussed further in the section on magnetic analysis.

Table 23.—Acid decomposition of catalysts with diminished activity

(Pretreatment: temperature, 325°C.; CO pressure, 0.1 atmospheres)

Experiment number	Synthesis conditions	Contraction (percent)	Carbidic carbon grams/100 grams Fe	H_2 liters/100 grams Fe	O_2 grams/100 grams Fe
1	548 operating days, S.G.[a] rich in CO, 15 atm., temp. progressively raised from 235° to 285°C. to maintain constant contraction	50	2.00	3.9	13.8
2	150 operating days, S.G.[a] rich in H_2, 15 atm., temp. 210°C.	35	1.00	4.2	15.7
3	21 operating days, S.G.[a] rich in CO, 15 atm., temp. 235°C., with eventual overheating to 400°C.	40	0.16	-	19.6
4	Normal catalytic activity decreased by prolonged overheating above 300°C.	40	0.54	-	28.2

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[a] S.G. = synthesis gas

Formation of Free Carbon in Iron Catalysts

The formation of free carbon on active unpromoted iron catalysts during the hydrocarbon synthesis has been a source of operating difficulties. Where horizontal reaction tubes were used in such a way that the catalyst did not occupy the entire volume of the tube, the synthesis proceeded for months and even years without interrupton. When the catalyst was contained in vertical reaction tubes so as to leave relatively little void space, an increase in the internal resistance of the catalyst was observed, resulting in obstruction of the reaction tube after operating intervals which depended upon synthesis conditions.

Table 24 shows the amounts of free carbon (as determined by acid decomposition of the catalyst) formed after various intervals of synthesis.

Table 24.-Formation of free carbon during synthesis

(Carburizing conditions: temperature, 325°C.; CO pressure, 0.1 atmosphere. Synthesis conditions: initial temperature, 235°C.; pressure 15 atmospheres; gas composition, $3CO + 2H_2$)

Experiment number	Operating time (weeks)	Temperature °C.	Contraction (percent)	Free carbon grams/10 grams Fe
1	0	-	-	1.75
	1	235	52	2.12
	3	235	55	2.37
2	0	-	-	1.85
	16	235	50	3.92
3	0	-	-	2.21
	78	235 to 285	55-45	7.97
4	0	-	-	1.75
	11	235	40	2.02

In all the experiments the quantity of free carbon increased with operating time. The increase in free carbon in experiment 3 may be caused to some extent by the increased temperature necessary for maintaining conversion. Contraction remained high in spite of dilution of the catalyst with imbedded carbon. In experiment 4, only

40 percent contraction was obtained during 11 operating weeks. Very little free carbon was formed owing to the low activity of the catalyst.

Table 25 shows the results of three experiments carried out with synthesis gas of different compositions. Since the conversion of carbon monoxide is more nearly complete at low temperatures with a hydrogen-rich synthesis gas than with a carbon monoxide-rich synthesis gas, an initial temperature of 190°C. was used in experiment 1. The carbon monoxide-hydrogen ratio of experiment 3 corresponded to the consumption ratio during synthesis. Consequently, it produced the maximum hydrocarbon yield in a single stage. In experiments 1 and 2 the gas had to be recycled and carbon monoxide added before each cycle.

Table 25.-Formation of free carbon as a function of synthesis gas composition

Pressure = 15 atmospheres

Experiment number	Temperature °C.	Operating time (days)	Synthesis gas ratio $CO:H_2$	Free carbon grams/10 grams Fe	Contraction (percent)
1	190	0	1:4[b]	2.21	-
	200[a]	60		1.88	30
2	210	0	1:2	2.21	-
	225[a]	151		2.51	35
3	235	0	3:2	1.85	-
	240[a]	112		3.92	50

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a/ Temperature required to maintain constant conversion.

b/ The low carbon monoxide content resulted in smaller contraction despite the high hydrogen content of the synthesis gas and low synthesis temperature which favor the formation of water rather than carbon dioxide.

These three experiments show that undesirable carbon deposits depend largely on the composition of the synthesis gas. In experiment 1 there was less free carbon present at the end of the experiment than at the beginning. This condition was similar to that found in an iron catalyst decarburized with hydrogen at 263°C., where less free carbon was found on acid decomposition after hydrogenation (see above). In experiment 3, a considerable amount of carbon was formed owing to the high carbon monoxide content.

Formation of carbon may therefore be avoided by use of hydrogen-rich synthesis gas and low reaction temperature. A series of parallel experiments showed that the composition of the catalyst is important. For instance, catalysts which were alkalized in order to increase the yield of solid paraffins formed more free carbon than non-alkalized catalysts.

Further study of iron catalysts used for medium-pressure synthesis showed that the disadvantages of carbon formation on promoted catalyst could be avoided by using technical water gas for the synthesis.

Summary

The composition of iron catalysts used in medium-pressure synthesis was studied by means of acid decomposition. The more carbide formed during carburization, the greater/was the activity of the catalysts during synthesis. Catalyst life also increased with higher carbide content. The large amount of carbide present after pretreatment decreased during the first days of operation to 0.2-0.4 gram of carbidic carbon per 10 grams of iron in an active catalyst. There was a

corresponding increase in the oxygen content to 0.1-0.2 gram per 10 grams of iron. The catalysts maintained this carbide-oxide equilibrium for months. Acid decomposition of catalysts whose activity had decreased (contraction less than 40 percent) showed at most 0.1 gram of carbidic carbon per 10 grams of iron, and a correspondingly high oxygen content.

Catalysts usually produced free carbon during medium-pressure synthesis; this tendency increased with higher operating temperature and with higher carbon monoxide-content of the synthesis gas. At low operating temperatures (such as may be used with especially active catalysts) and with hydrogen-rich synthesis gas, carbon formation could be completely eliminated in medium-pressure synthesis.

THERMOMAGNETIC ANALYSIS

Description of Magnetic Balance

The question of whether a single carbide or a mixture of carbides was formed during pretreatment could not be solved chemically. No indication was found as to the presence of free metal (known to be essential in cobalt and nickel catalysts) either during pretreatment or during synthesis. The large excess of hydrogen found upon acid decomposition (table 13) was another point still to be explained. It would have been unsatisfactory to attempt to determine the amount of carbidic carbon or a carbide formula from the carburization curve and from hydrogen reduction data. However, the ferromagnetic properties of iron, iron carbide, and magnetite offered an approach to the problem. The spacing of their magnetic transition points (Curie Points) is sufficiently far apart to make identification easy. A type of magnetic balance developed by Lange[114] was found to be suitable for measurements of this kind (figure 10).

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[114] Lange, H. and Mathieu, K., work cited (footnote 104).

The magnetic field was generated by a water-cooled electromagnet which produced a field gradient of 1750 oersteds per centimeter within the region of motion of the sample, with an operating current of 4 amps. The force of this field gradient was sufficient to indicate the Curie Point for a few milligrams of ferromagnetic substance. A small, water-cooled electric furnace with a non-inductive winding was installed between the poles of the electromagnet. Its temperature could be raised to about 900°C. by means of a resistance coil. The quartz tube of the furnace contained the thermocouple tube (sample holder support) to which the brass sample holder was fastened. The latter had a capacity of 0.3 to 0.4 cubic centimeter of material. The sample holder support was attached to the balance beam which was suspended from thin copper wires that could be adjusted so that the system formed by the balance beam, thermocouple, sample holder and its support swung freely in the quartz tube of the furnace.[115, 116]

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[115] Lange, H. and Mathieu, K., work cited (footnote 104).

[116] Editor's note. It was thought desirable to include a fuller description of the apparatus and procedure. The following information was supplied by Dr. H. Pichler from memory, and the drawing and numerical values are approximations. Details of the assembly between the magnetic poles are shown in figure 10a. The thin brass sample holder fitted tightly over the

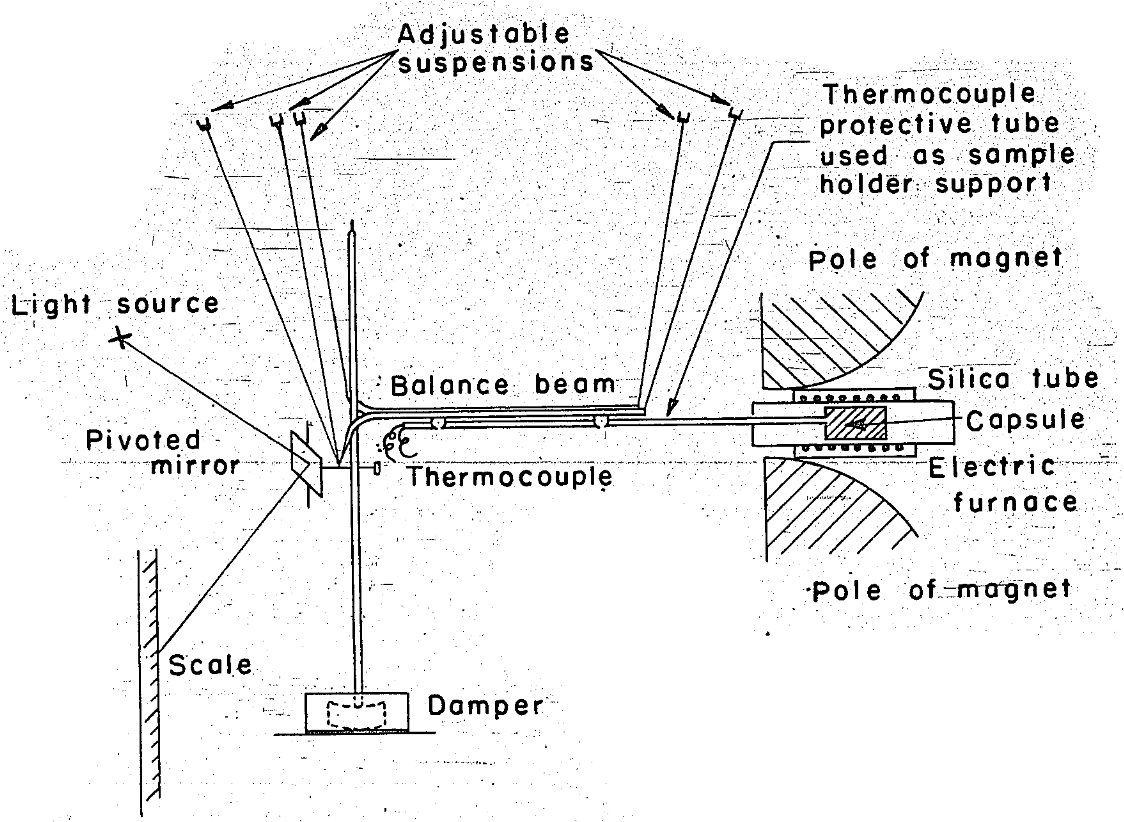

Figure 10.— Simplified schematic diagram of magnetic balance.

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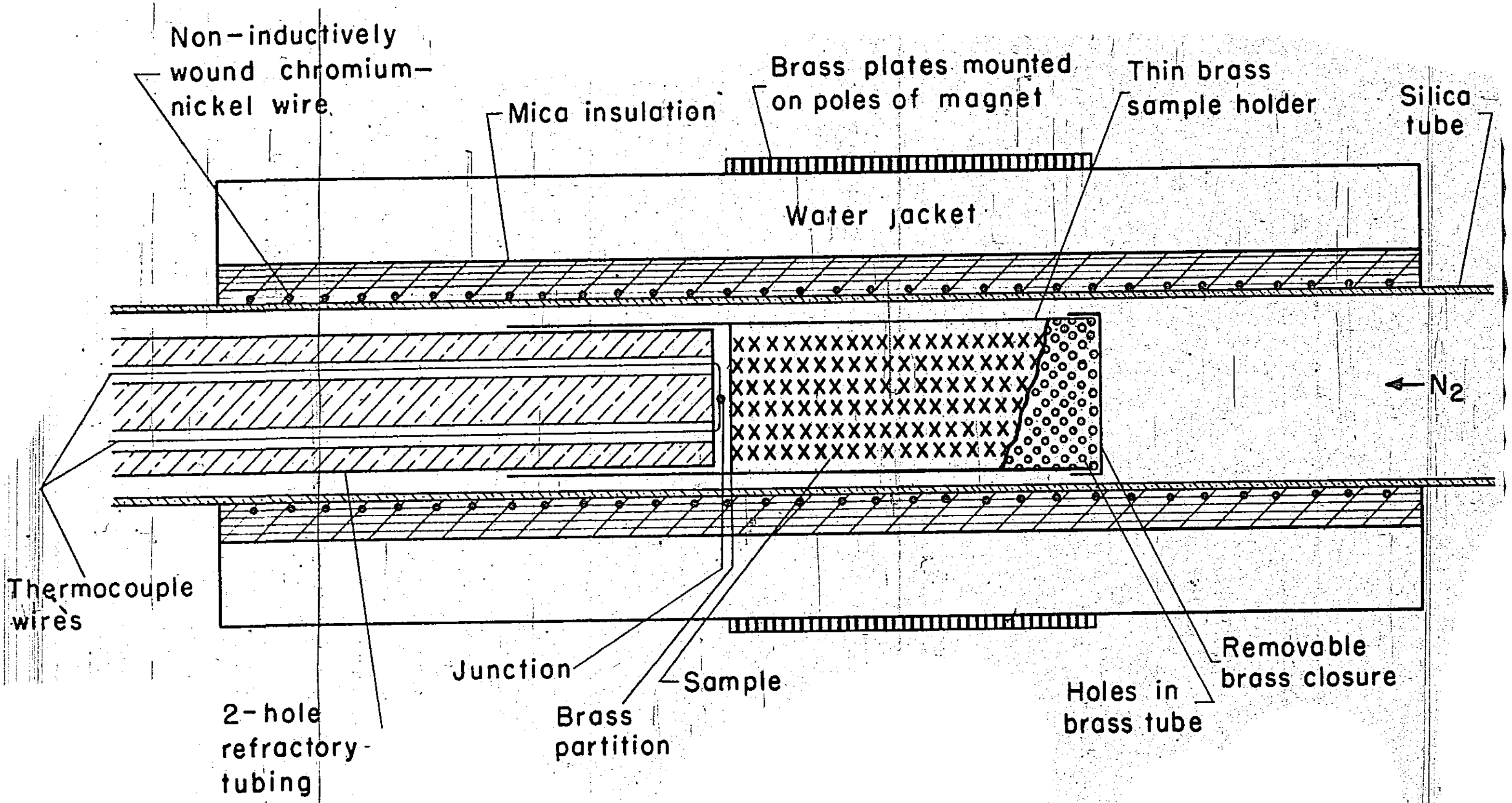

Figure 10A .— Detail of sample holder and water-cooled furnace.

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free-moving thermocouple tubing. The thermocouple junction was separated from the sample by a brass partition. The sample compartment was accessible from the end of the brass tube and could be closed with a brass cover. Numerous fine holes punctured the compartment walls to permit circulation of the nitrogen stream. The remainder of the assembly consisted of a silica tube, wound non-inductively with nichrome wire, and surrounded by a layer of mica insulation and by a double-walled brass tube containing cooling water. This water-cooled heater was fitted with brass plates and fastened to the poles of the magnet.

The brass sample holder had an overall length of about 4 cm. of which 1.5 cm. was slipped over the thermocouple tubing. The sample compartment was about 2.5 cm. in length and about 0.5 cm. in diameter. The clearance between the sample holder and the silica tube was about 2 mm.

The samples studied by Pichler and Merkel were always heated at a uniform rate from room temperature to 800°C. in about one hour, except where indicated otherwise. After 800°C. was reached, the furnace was turned off and the samples allowed to cool.

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The sample was pulled into the inhomogeneous field of the electromagnet. This attraction was counteracted by the force of the balance beam and pendulum. A damper made rapid readings possible. The deflection of the balance beam was indicated by a beam of light focused on a graduated scale by a rotating mirror. The magnification of the deflection could be adjusted.

Temperature was measured by means of a platinum-platinum-rhodium thermocouple whose junction was on the bottom of the sample capsule. Since the electric furnace was water-cooled and relatively short, a marked drop in temperature was observed within the quartz tube from the center outward; this decreased the accuracy of the measurements. The temperature values were therefore considered accurate to within ± 10°C.

Magnetic saturation was not determined, but the gradient of the magnetic field (in the range of movement of the sample) was determined as a function of the deflection of the beam of light. In a non-homogeneous field H, a sample of magnetic moment M, experiences a force P in the direction of the gradient:

$$P = M \text{ grad } H$$

The intensity of magnetization J (based on volume) is therefore

$$J = \frac{P}{V \text{ grad } H} \text{ Gauss}$$

If the measurements are based on weight, the specific magnetization is

$$\sigma = \frac{J}{S} = \frac{P\ 981}{g \text{ grad } H}$$

The gradient was determined by means of this equation with electrolytic iron ($\sigma = 218$) as a standard.

Deflection of beam of light, cm	Gradient Oersted/cm
36.3	1765
22	1755
17.6	1730
9.6	1730

These experiments showed that the gradient was constant within the range of movement of the sample. The deflections were therefore assumed to be proportional to the force, that is, to the magnetic moment of the sample. Thus, when the specific magnetization at saturation was known, the deflection was a measure of the quantity of ferromagnetic material present and accurate relative measurements could replace absolute measurements.

Preliminary Experiments

In the first experiment the sample holder was filled with precipitated ferric oxide which was heated to 500°C. in a current of nitrogen, and was then reduced in a stream of hydrogen. Figure 11 shows the magnetic moment as a function of the time during which the sample was exposed to hydrogen. At the beginning of the experiment the deflection was zero; in other words, ferric oxide showed no measurable magnetization (paramagnetic). During the first few minutes the magnetization increased sharply and then remained constant for several minutes, indicating a discontinuous reduction of ferric oxide. The first increase in magnetization undoubtedly resulted from reduction to (ferromagnetic) magnetite. Further reduction of magnetite to metallic iron proceeded more slowly after a short induction period, and the magnetization approached a final value asymptotically.

Figure 12 shows the thermomagnetic curve for electrolytic iron which was heated slowly to 800°C. The specific magnetization decreased slowly at first; at 600°C. the deflection had decreased from 50.5 to 40.0 divisions. Within the range of magnetic transition the decrease was very rapid. The Curie Point was about 790°C.; at 800°C. the deflection was only 8 divisions.

Formation and Stability of Higher Iron Carbides

Preliminary experiments with the magnetic balance were followed by investigation of the formation of iron carbides by carburization of iron and iron oxide.

Since it was thought that water might affect them at higher temperatures, catalysts which had been carburized in different ways were

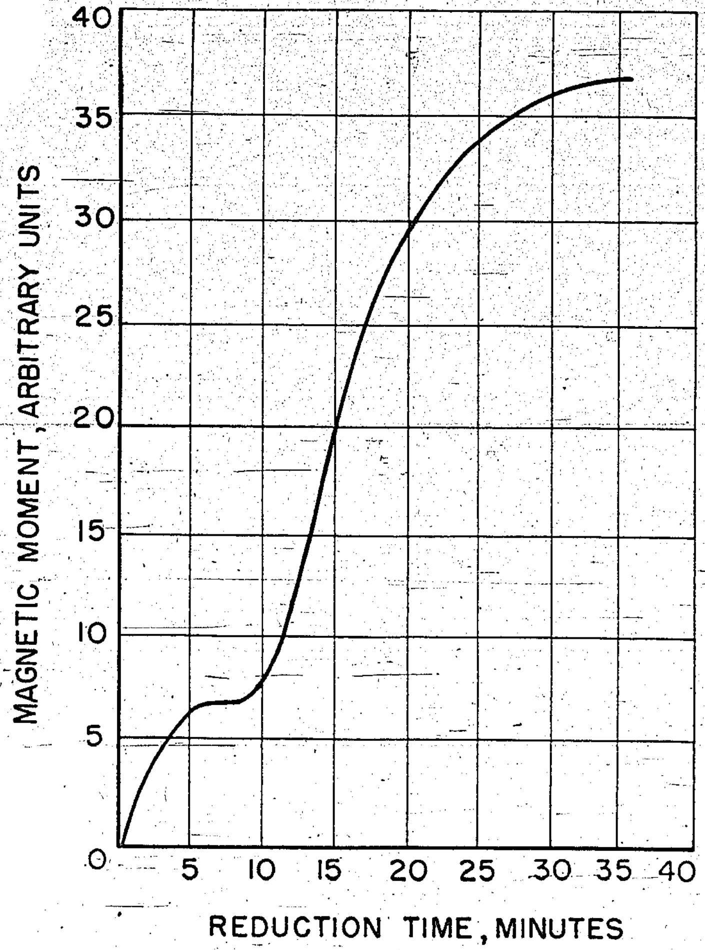

Figure 11.– Hydrogen reduction of Fe_2O_3 at 500°C. in the magnetic balance.

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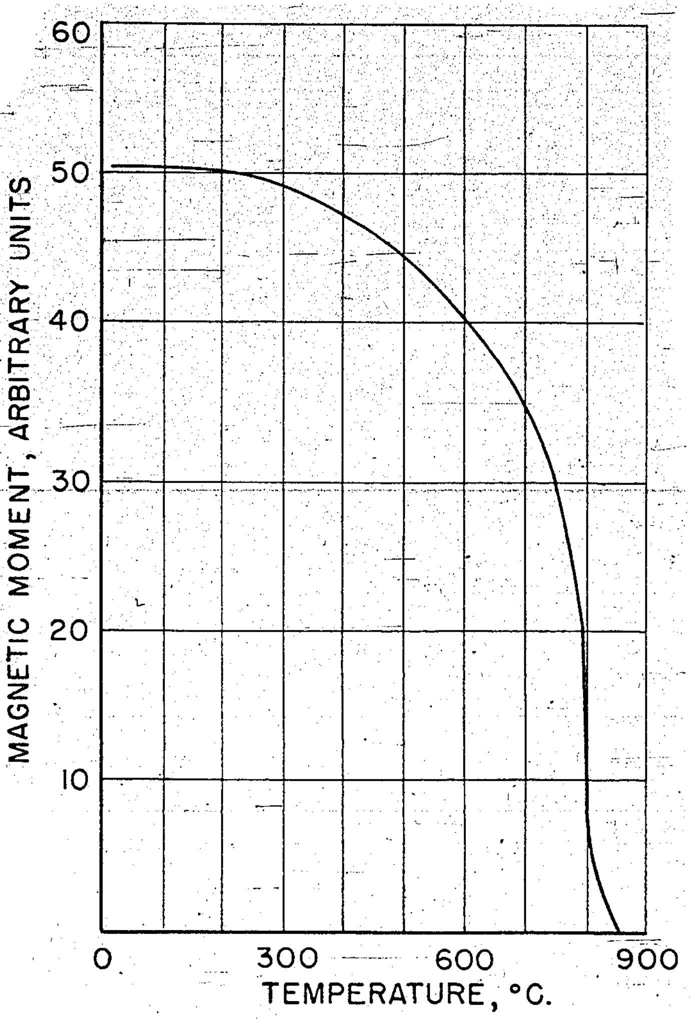

Figure 12.– Thermomagnetic curve of electrolytic iron.

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stored under n-hexane which was quite suitable because of its low boiling point and inert character. The hexane-saturated catalysts were placed in the sample holder which was introduced into the center of the electric furnace and adjusted there in such a way as to allow it to move freely. During the entire procedure a current of oxygen-free nitrogen flowed through the quartz tube of the furnace.

An iron catalyst of the type used in medium-pressure synthesis was carburized with carbon monoxide (325°C., 0.1 atmosphere, 4 liters of carbon monoxide per hour per 10 grams of iron). Figure 13, curve I, shows the thermomagnetic curve for such a sample. The Curie Point was 260°C. As will be seen from the following experiments, iron catalysts always exhibit this Curie Point during carburization or synthesis, the average value of which was 265°C., as found in a large number of experiments. Comparison with the Curie Points listed in table 6 shows that the ferromagnetic substance present was not identical with any known ferromagnetic iron compound and that this thermomagnetic curve probably shows a new iron carbide.

To obtain the data for curve I, figure 13, the catalyst was heated to 800°C. in a stream of nitrogen. The effect of this treatment became apparent from a redetermination of the thermomagnetic curve (shown in curve II, figure 13). It is clear that the ferromagnetic iron compound had undergone a change. The Curie Point in the second curve was 208°C., 50°C. below that of curve I. The close agreement with the cementite Curie Point (205°C., established by Mathieu on the same magnetic balance) showed that the iron carbide whose Curie Point is 265°C. is unstable at higher temperatures and changes to Fe_3C. A

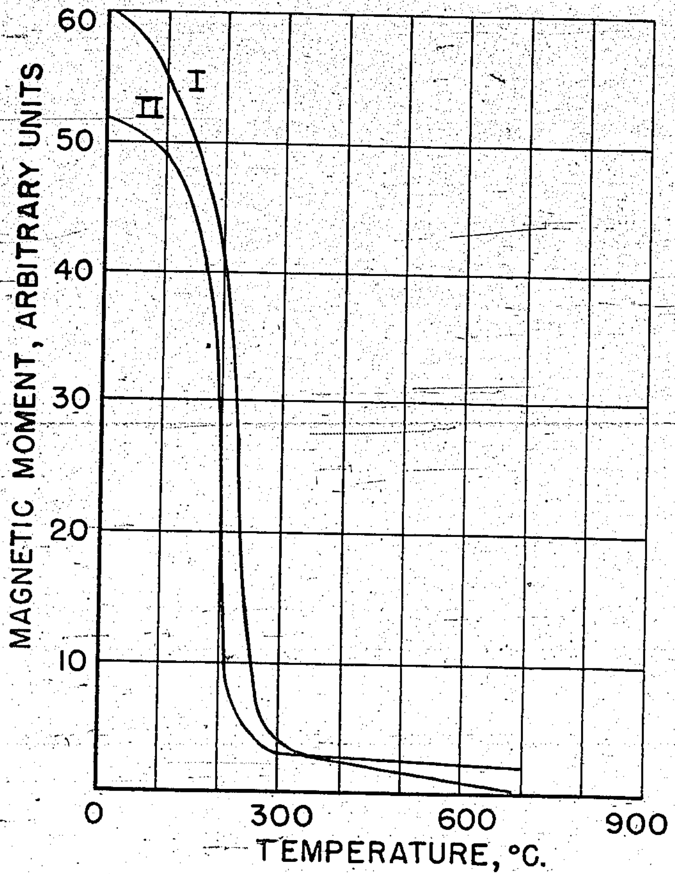

Figure 13.– Thermomagnetic curve of carburized, alkali-promoted iron catalyst; I after carburization, II after heating to 800°C. in nitrogen.

further difference in the thermomagnetic behavior of the two iron carbides was shown by the fact that the thermomagnetic curve of cementite (II) decreased far more slowly initially than that of the higher carbide (I).

Thermomagnetic analysis indicated the formation of a homogeneous iron carbide at a carburization temperature of 325°C.; its carbide content had been determined by hydrogen reduction. Although the formula $Fe_{2.28}C$ thus derived cannot be considered definite because of uncertainties inherent in the method, the values obtained indicated clearly that the new carbide was richer in carbon than Fe_3C, the only iron carbide whose composition is definitely known.

As observed by Bahr and Jessen, carburization (at 225°C.) of iron obtained by low temperature reduction of Fe_2O_3 yields a carbide whose carbon content corresponds closely to the formula Fe_2C. To study this carbide, two active iron catalysts (iron - 0.25 percent potassium carbonate, and iron - 1 percent copper - 1.5 percent potassium carbonate) were reduced with hydrogen at 250°C. for 240 hours (1 liter of hydrogen per hour per 20 grams of iron) and carburized at 220°C. for 219 hours (1 liter of carbon monoxide per hour per 20 grams of iron). Figures 14 and 15 show the thermomagnetic behavior of the two carburized catalysts. The action of carbon monoxide at 220°C. led to the formation of the iron carbide whose Curie Point is 265°C. However, this carbide did not form quantitatively, as it did at 325°C. Figure 14 shows a second Curie Point at 600°C. The average value obtained from a large number of experiments was 595°C. A comparison with table 6

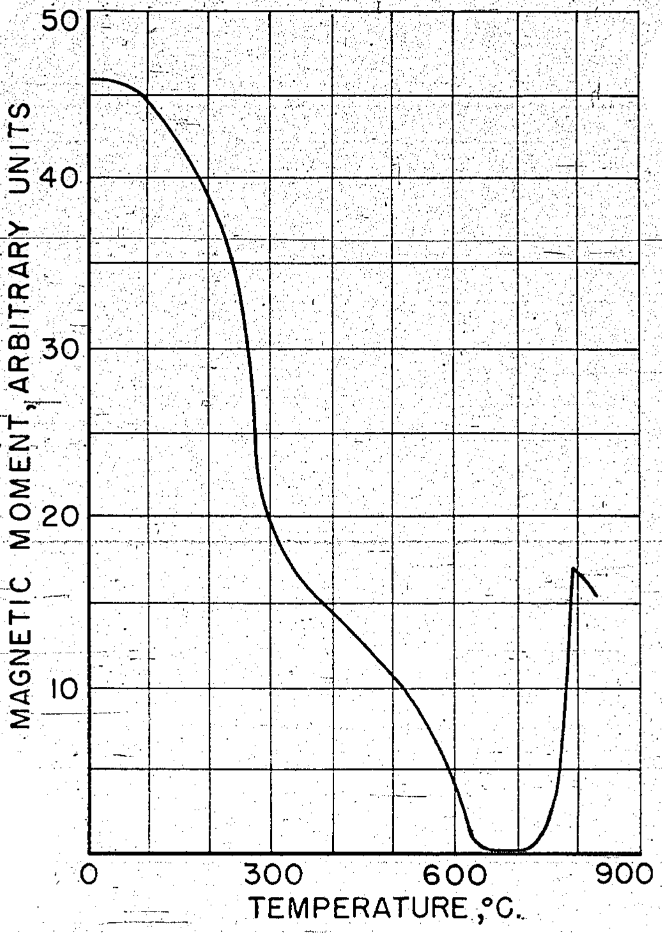

Figure 14.- Thermomagnetic curve of alkali-promoted (0.25 % K_2CO_3) catalyst, reduced for 240 hrs. at 250° C., 1 liter H_2 per hr. per 20 gm. Fe; carburized for 219 hrs. at 220° C., 1 liter CO per hr. per 20 gm. Fe.

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shows that this is the Curie Point of magnetite, Fe_3O_4, for which Curie Points from 565° to 595°C. are reported. The reappearance of the magnetization above 700°C. pointed to the formation of free iron from the reaction between magnetite and iron carbide.

The thermomagnetic curve of the iron - 1 percent copper - 1.5 percent potassium carbonate catalyst was different (figure 15). The decrease in magnetization occurred in three well-defined sections of the curve which fused at about 300° and 500°C. The first section corresponded to the new iron carbide (Curie Point 265°C.). The second (300° to 500°C.), with a Curie Point at 400°C. was new and did not correspond to any known ferromagnetic iron compound. Similar curves were obtained for a number of different catalyst samples. The carburization process was exactly that used by Glund and Ritter[117] and by Bahr and Jessen[118] The carbide formula, Fe_2C, derived by these authors does therefore probably not refer to a homogeneous substance.

Since the Curie Point corresponding to the new compound could not be established with certainty on samples carburized above 220°C. (for instance at 325°C.), it was assumed that low carburization temperatures are a necessary condition for its formation. Consequently another experiment was carried out with a highly active catalyst, Fe, Cu, K_2CO_3 (100:1:0.25) at an even lower carburization temperature (205°C.).

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[117] Glund, W. and Ritter, H., work cited (footnote 93).
[118] Bahr, H. A. and Jessen, V., work cited (footnote 50).

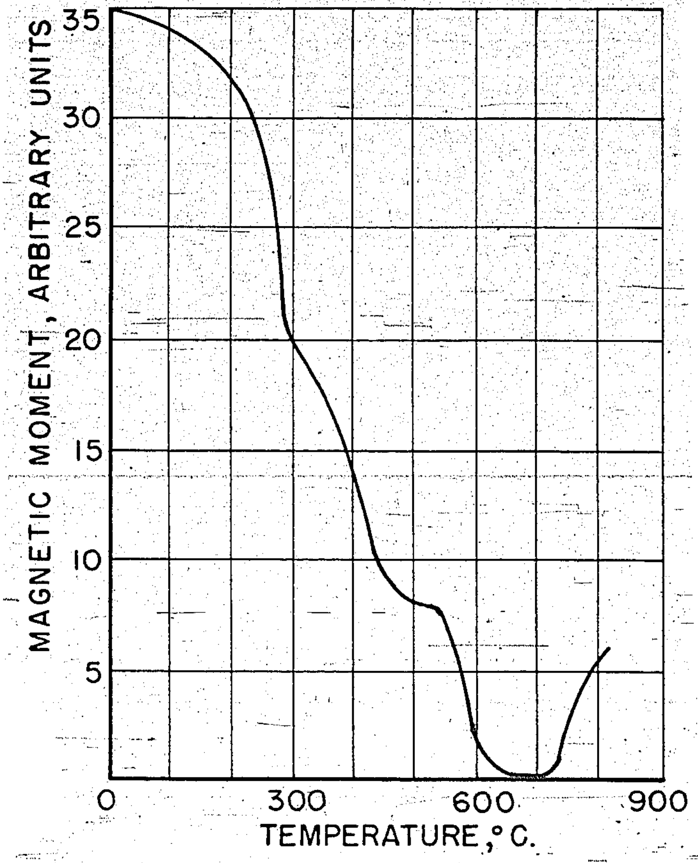

Figure 15.– Thermomagnetic curve of Fe, Cu, K_2CO_3 (100 : 1 : 1.5) catalyst, reduced for 240 hrs. at 250° C. with 1 liter H_2 per hr. per 20 gm. Fe; carburized for 219 hrs. at 220° C with 1 liter CO per hr. per 20 gm. Fe.

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The thermomagnetic curve for this experiment (figure 16) shows that a much larger quantity of this higher iron carbide was formed under these reaction conditions. This carbide, Curie Point 380°C., contributed the largest part of the total specific magnetization. The corresponding inflection in figure 15 was 20°C. higher. The difference between the two Curie Points resulted from the fact that in the first case only a small amount of the carbide was formed. The change in the magnetic force was too small at first to overcome the inertia of the balance, thus shifting the Curie Point towards a higher temperature. The carbide with the 265°C. Curie Point was also formed in appreciable amounts even at 205°C., as indicated by the first part of the curve of figure 16. The decrease in magnetization between 400°-600°C. was probably the result of decomposition reactions. It is interesting to note that extensive reduction and carburization of iron occurred even at these low carburization temperatures.

In order to determine the thermal stability of the Curie Point 380°C. iron carbide, the sample was heated to 800°C. in a second thermomagnetic analysis (figure 17). After the first heating to 800°C., the Curie Point 380°C. carbide had disappeared completely and had been replaced by cementite, Fe_3C, and by some metallic iron, as shown by the decrease in magnetization above 700°C. The part of the curve corresponding to the Curie Point 265°C. carbide was also absent, this compound was converted to cementite, as already noted in figure 13.

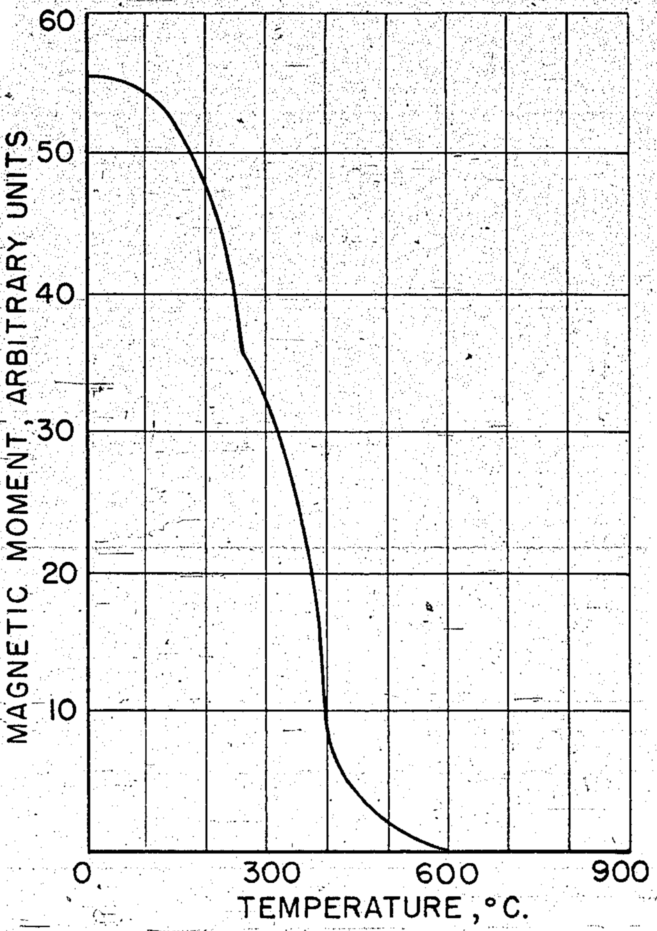

Figure 16.– Thermomagnetic curve of Fe, Cu, K_2CO_3 (100 : 1 : 0.25) catalyst, carburized at 205° C.

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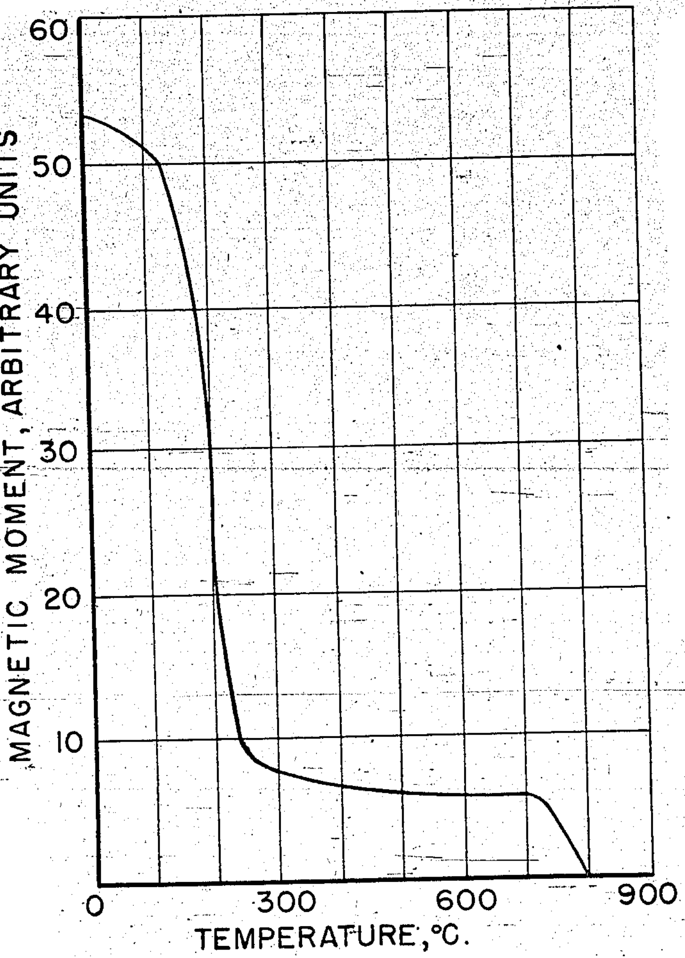

Figure 17.– Thermomagnetic curve of Fe, Cu, K_2CO_3 (100 : 1 : 0.25) catalyst, carburized at 205° C. and then heated to 800 °C., prior to thermomagnetic analysis.

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Figure 18 shows graphically the results of a systematic study of the thermal stability of the new iron carbides. Figure 18a represents the thermomagnetic curve of the catalyst after carburization at 205°C. The samples used for the experiments represented in figures 18b-f were heated in flowing nitrogen to 300°, 355°, 400°, 480°, and 510°C., respectively, and maintained at these temperatures for 0.5 hour. Thermal treatment at 300°C. produced little change in the carburized catalyst; however, the formation of metallic iron was perceptible (figure 18b). Treatment at 355°C. resulted in considerable decomposition of the Curie Point 380°C. carbide, whose presence was still clearly indicated by the virtually linear drop of the magnetic moment between 230° and 470°C. The unstable carbide was partially converted to the Curie Point 265°C. carbide (figure 18c). Treatment at 400°C. left only a small quantity of the Curie Point 380°C. carbide. The Curie Point 265°C. carbide remained unchanged, as shown by the Curie Point (figure 18d). At 480°C., the Curie Point 380°C. carbide disappeared completely. The amount of free iron increased considerably. The Curie Point 265°C. carbide also suffered changes as shown by the drop in the Curie Point to 230°C. (figure 18e). At 510°C., the Curie Point 265°C. carbide disappeared completely. In its place appeared cementite, which is the decomposition product of both the higher carbides. The amount of free iron increased still further (figure 18f).

The effect of a current of hydrogen at ordinary pressure on the two higher iron carbides was also determined. For this purpose, iron catalysts containing both the Curie Point 265°C. and the Curie

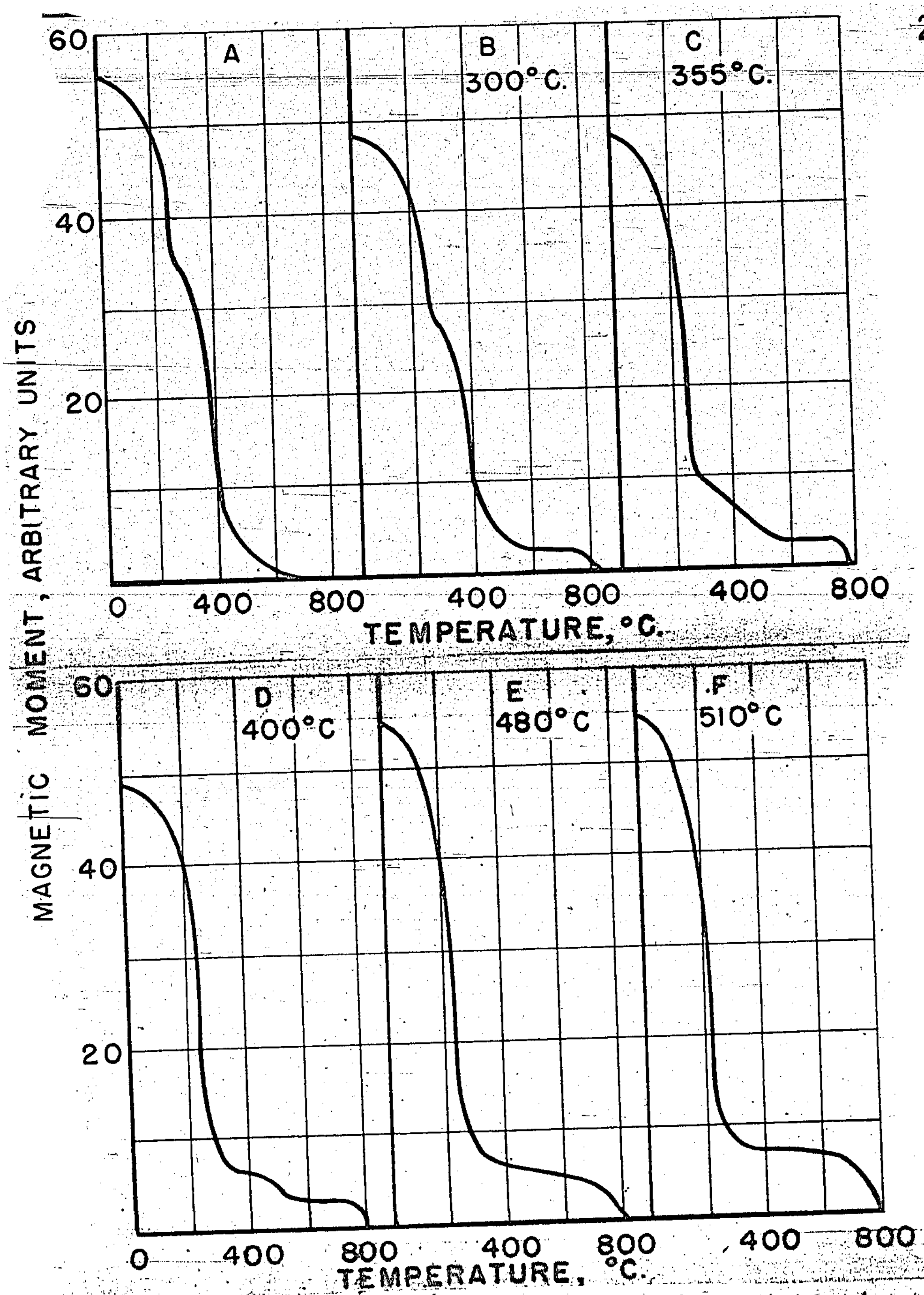

Figure 18.– Thermomagnetic curves showing thermal instability of higher iron carbides, obtained by carburization at 205°C. Samples B to F kept at indicated reaction temperature for 0.5 hr., prior to thermomagnetic analysis as shown (100 Fe, 1 Cu, 0.25 K_2CO_3 catalyst).

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Point 380°C. carbides were treated for three hours at 230° to 240°C. with a current of hydrogen in the sample holder of the magnetic balance. No change in magnetic moment was observed after this treatment nor after displacement of hydrogen by nitrogen.

Carburization of Iron Catalyst for Medium-Pressure Synthesis

The effect of carburization was studied on three catalysts that differed appreciably in activity and in the type of products synthesized. The procedure for preparation was the following: iron filings were dissolved in dilute nitric acid and the solution was neutralized and divided into three parts. The first fraction was heated to boiling and precipitated as usual with a sodium carbonate solution. It was then washed with hot water until the water was no longer alkaline, and dried in an oven at 105°C. This catalyst therefore consisted essentially of iron hydroxides. The second fraction of the iron nitrate solution was precipitated and washed in the same manner. It was then alkalized with 0.25 percent of potassium carbonate, based on the iron content. This was the so-called "standard" iron catalyst that was used for the first part of this work. Copper nitrate was added to the last portion of the iron nitrate solution before precipitation. After precipitation and washing as before, it was alkalized with potassium carbonate, so that it contained 1 percent of copper and 1.5 percent of potassium carbonate, based on iron.

Unpromoted iron oxide was unsuitable as a catalyst but useful for comparison with pure iron oxides for which carburization experiments were cited in the literature survey. The "standard" catalyst containing 0.25 percent of potassium carbonate and the catalyst containing 1 percent of copper and 1.5 percent of potassium carbonate differed not only in activity but also in the type of products synthesized. The former was a typical gasoline catalyst yielding principally liquid and light hydrocarbons. The latter yielded a larger amount of solid paraffins because of the presence of more alkali.

Carburization of Iron Oxide

The iron oxide obtained by precipitation was treated in an aluminum block oven at 325°C., with a current of carbon monoxide at 0.1 atmosphere and a flow rate of 8 liters per 10 grams of iron per hour (standard carburization conditions) for different intervals. Normal hexane was introduced into the catalyst tube after cooling for protection of the carburized product. After carburization for 12 hours, the sample gave the thermomagnetic curve shown in figure 19. The major part of the magnetization was due to magnetite, and above 700°C. to metallic iron (Curie Point 770°C.). The sample showed no ferromagnetism above 850°C.

After carburization for 25 hours, the magnetic curve showed that the amount of free iron had increased appreciably at the expense of magnetite (figure 20). The iron curve was again characterized by its sharp Curie Point. Iron carbide had also formed, as indicated by a slight decrease in magnetization between 250° and 300°C. Although most of the ferric oxide was reduced to free metal, the amount of carbide formed remained small, indicating that the production of free iron is not necessarily accompanied by carbide formation. Iron can remain

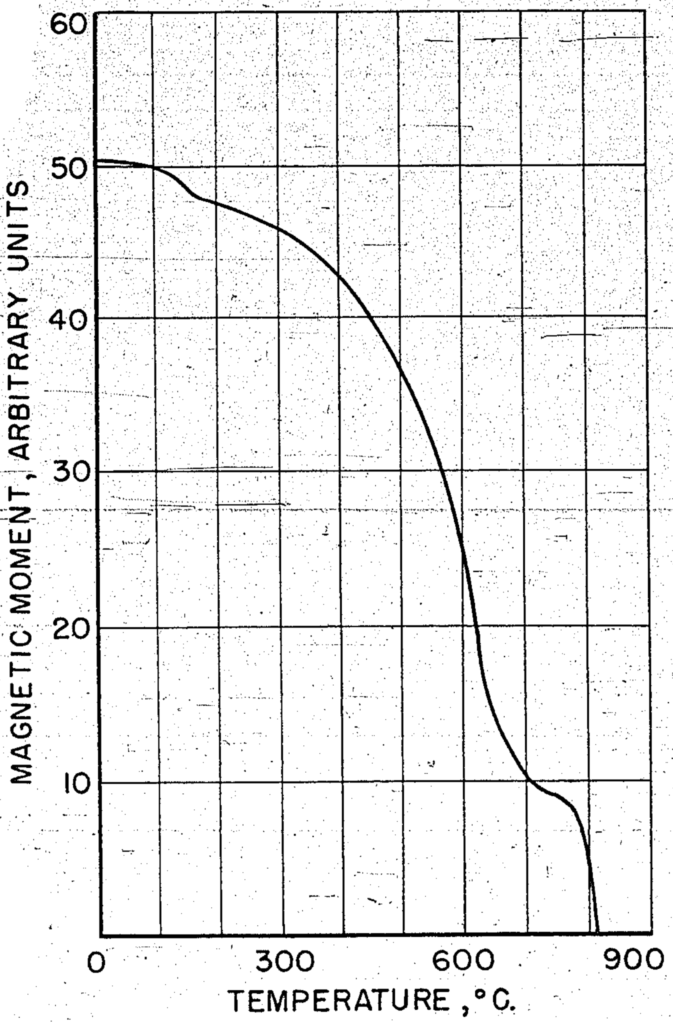

Figure 19.– Thermomagnetic curve of unpromoted iron oxide, after carburization for 12 hrs. at 325° C. and 0.1 Atm. 8 liter CO per hr. per 10 gm. Fe.

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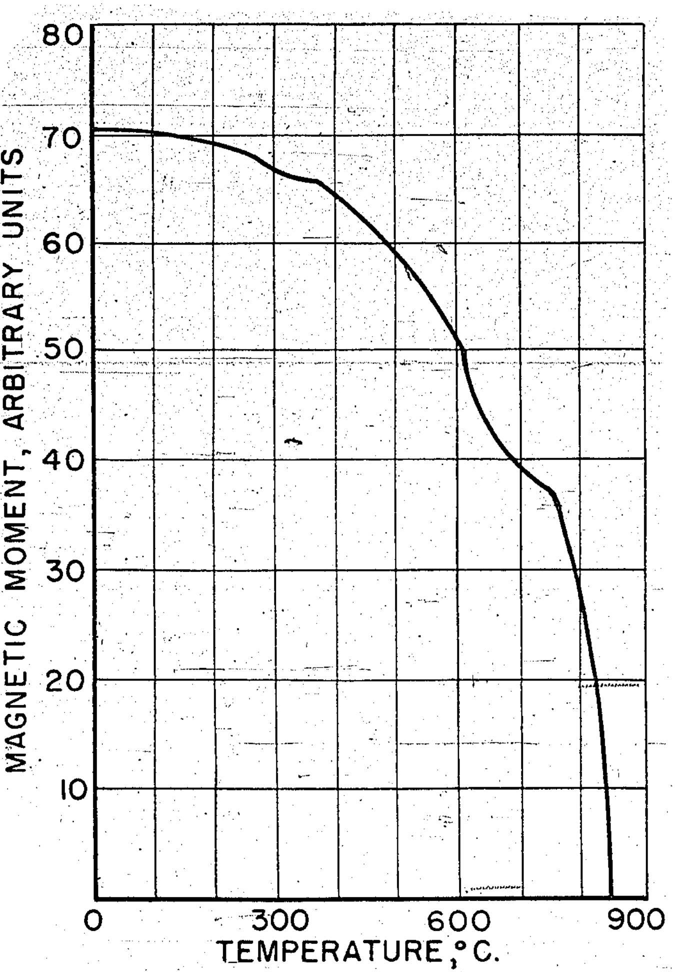

Figure 20.– Thermomagnetic curve of unpromoted iron oxide, after carburization for 25 hrs at 325°C. and 0.1 Atm., 8 liter CO per hr. per 10 gm. Fe.

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unchanged in an atmosphere of flowing carbon monoxide; the physical structure of the catalyst must create the conditions under which carbon (from carbon monoxide) can combine with iron to give iron carbide.

The same catalyst sample was cooled and subjected to a second thermomagnetic analysis to determine the effect of thermal treatment (figure 21). Comparison with figures 19 and 20 showed that the first heating caused extensive changes. This was particularly noticeable in the sharp drop of the initial magnetization from 70 divisions before heating to 27 divisions after heating. The magnetic moment (figure 21) remained unchanged up to about 440°C. Thereafter, it increased, then decreased in the magnetite region (Curie Point 600°C.) and finally dropped almost vertically in the region corresponding to metallic iron.

Carburization of an Alkalized Iron Catalyst

The "normal" iron catalyst containing 0.25 percent of potassium carbonate was carburized under the same conditions as the unpromoted iron catalyst. Figure 22 shows the results of carburization for 5 hours. The largest part of the magnetization was due to magnetite. The course of the curve between 200° and 300°C. indicated the formation of higher carbide, although the Curie Point remained rather vague. The curve shows an inflection as low as 150°C. which will be discussed later.

The effect of temperature on the magnetization of the catalyst after carburization for 12 hours is shown in figure 23. Formation of the Curie Point 265°C. carbide had increased to the point

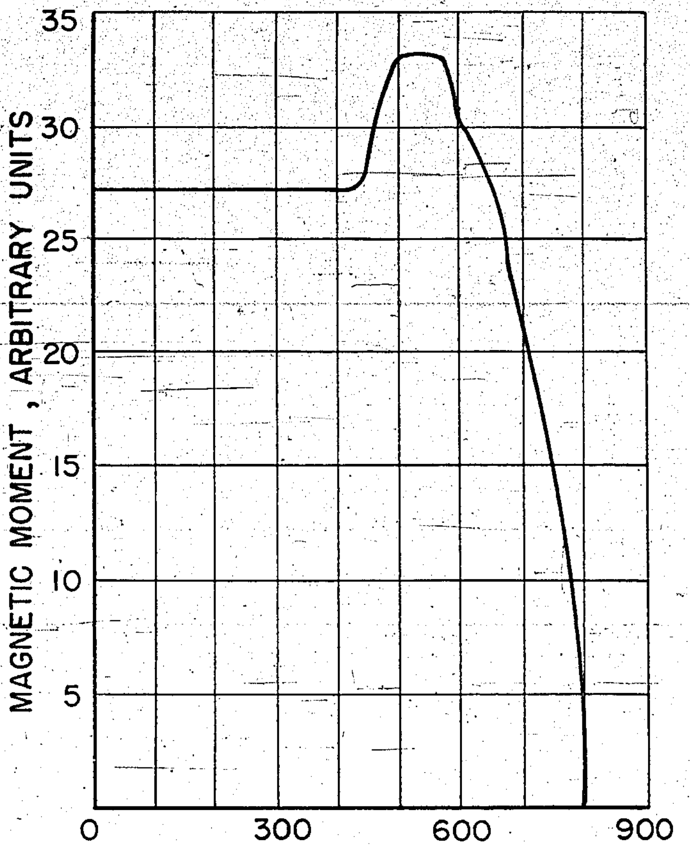

Figure 21. - Thermomagnetic curve, after heating to 800° C. of unpromoted iron oxide which had been carburized for 25 hours at 325° C. and 0.1 atmosphere, 8 liters of CO per hour per 10 grams of Fe.

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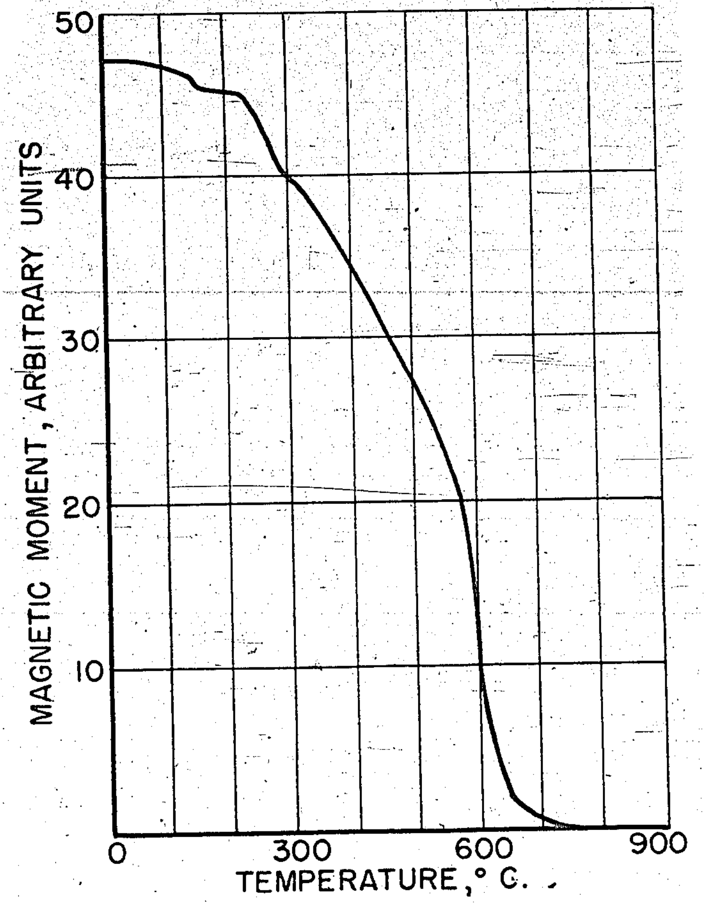

Figure 22.— Thermomagnetic curve of alkalized (0.25 % K_2CO_3) iron oxide, after carburization for 5 hours at 325° C. and at 0.1 atmosphere, 8 liters of CO per hour per 10 grams of Fe.

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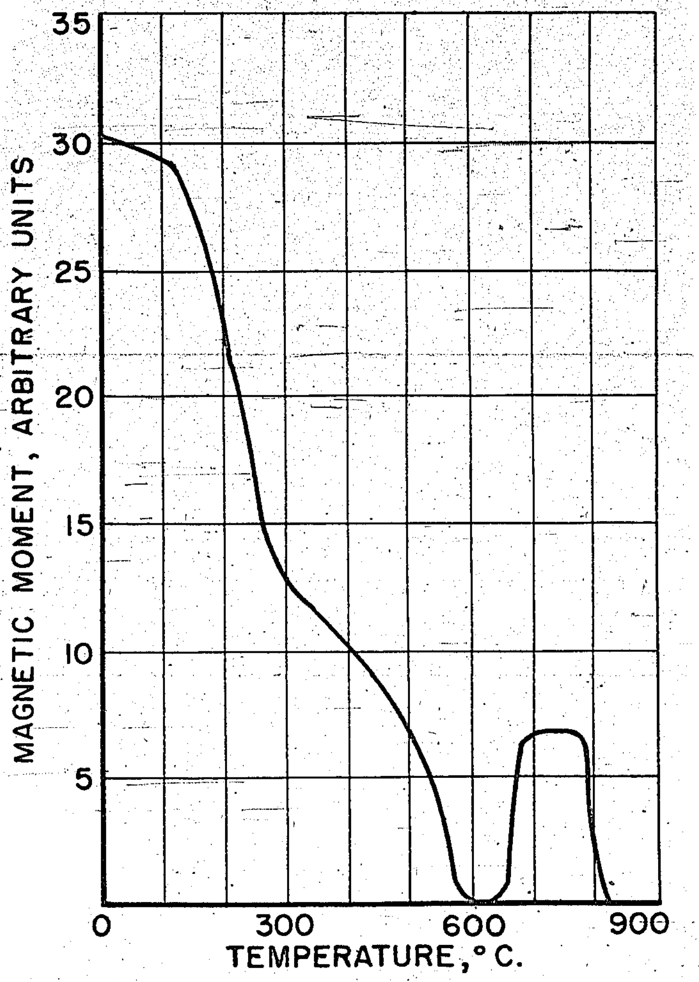

Figure 23.— Thermomagnetic curve of alkalized (0.25% K_2CO_3) iron oxide, after carburization for 12 hrs. at 325 ° C. and 0.1 Atm., 8 liter CO per hr. per 10 gm. Fe.

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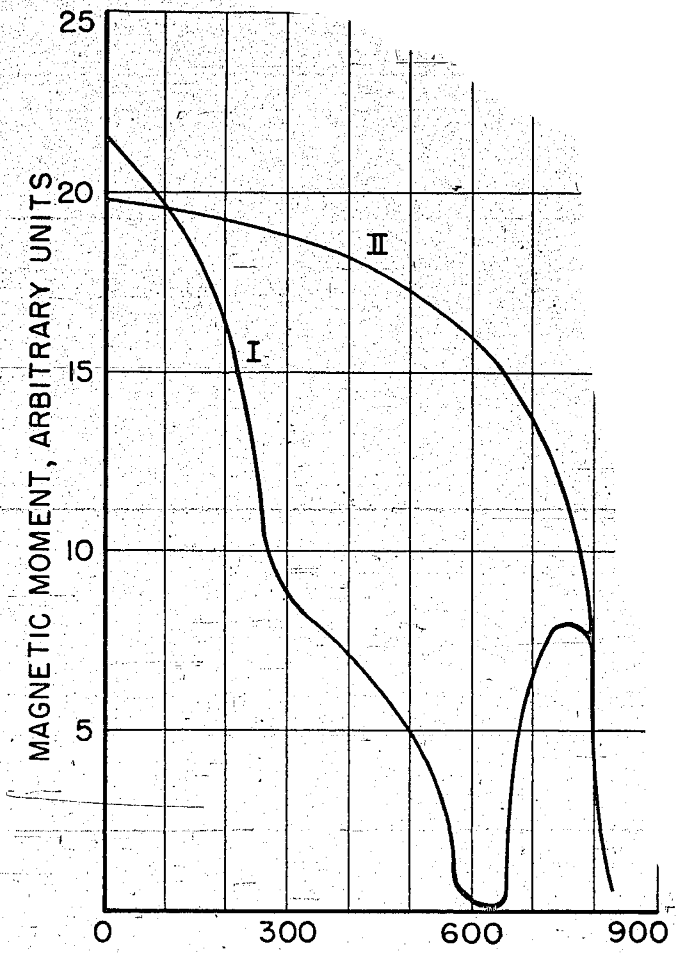
of accounting for almost 50 percent of the magnetization, the other 50 percent being due to magnetite. The magnetization increased again above 650°C., and the abrupt drop in the curve above 700°C. shows that metallic iron was formed.

The magnetic behavior of the catalyst after carburization for 25 hours is shown in curve I of figure 24. The proportion of iron carbide to magnetite had increased very little as compared with the previous experiment. Further reduction and carburization of this catalyst proceeded very slowly. Since the carbon dioxide content of the tail gas during pretreatment was lower than that for iron-magnetite equilibrium, this behavior must be attributed to the low reactivity of the catalyst under the carburizing conditions. Curve II, figure 24, shows the magnetization of the same sample after it had previously been heated to 800°C. The curve coincides with the curve of the first heating at higher temperatures. Carbide and oxide had reacted to yield free iron.

Carburization of an Alkalized Iron Catalyst Containing Copper

The iron-1 percent copper-1.5 percent potassium carbonate catalyst was similarly treated with carbon monoxide. Figure 25 shows the thermomagnetic curve after carburization for 0.5 hour. Comparison with figure 23 shows that carburizing the copper-containing catalyst for 0.5 hour is equivalent to carburizing the copper-free catalyst for 12 hours. This is a proof of the extremely high reactivity of the copper-promoted catalyst during carburization. Magnetite was reduced rapidly to carbide.



TEMPERATURE, °C.

Figure 24.– Thermomagnetic curves of alkalized (0.25% K_2CO_3) iron oxide, after carburization for 25 hours at 325°C. and 0.1 atmosphere, 8 liters of CO per hour per 10 grams of Fe. I freshly carburized sample; II after heating to 800°C.

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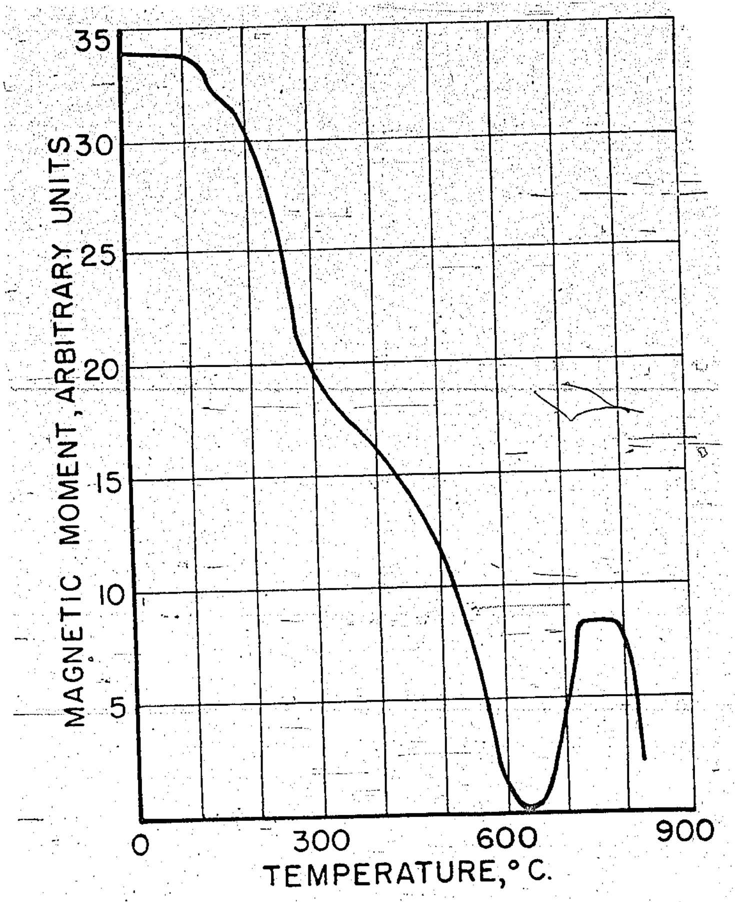

Figure 25.– Thermomagnetic curve of Fe, Cu, K_2CO_3 (100 : 1 : 1.5) catalyst, after carburization for 0.5 hour at 325° C. and 0.1 atmosphere, 8 liters of CO per hour per 10 grams of Fe.

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Figure 26 is the thermomagnetic curve after carburization for 5 hours. A comparison with the previous experiment shows that the composition changed appreciably. The largest fraction was the Curie Point 265°C. carbide, whereas the magnetic contribution of magnetite was very small. The course of the curve between 350° and 400°C. indicates the presence of the Curie Point 380°C. carbide. This result shows the pronounced tendency of this catalyst to form carbide. After the same period of carburization, the less active iron-0.25 percent potassium carbonate catalyst consisted almost entirely of magnetite. The iron oxide preparation contained little carbide even after carburization for 25 hours.

Figure 27 is the thermomagnetic curve for the same sample after heating to 800°C. The small amount of magnetite observed previously (temperature range 400° to 550°C., figure 26) was absent after heating. The magnetization disappeared below 400°C., that is, the catalyst consisted exclusively of cementite, which is paramagnetic at that temperature.

Another sample of the catalyst consisted almost entirely of the Curie Point 265°C. carbide after carburization for 12 hours (figure 28). Magnetite was no longer detectable. The decrease in magnetization starting at about 320°C. was probably due to the Curie Point 380°C. carbide whose ferromagnetism disappears above 450°C. Carburization for 25 hours and for 62 hours produced the same results as obtained in the preceding experiment (figure 29, curve I). Cementite again formed as a result of the first heating (curve II). Whereas the magnetization

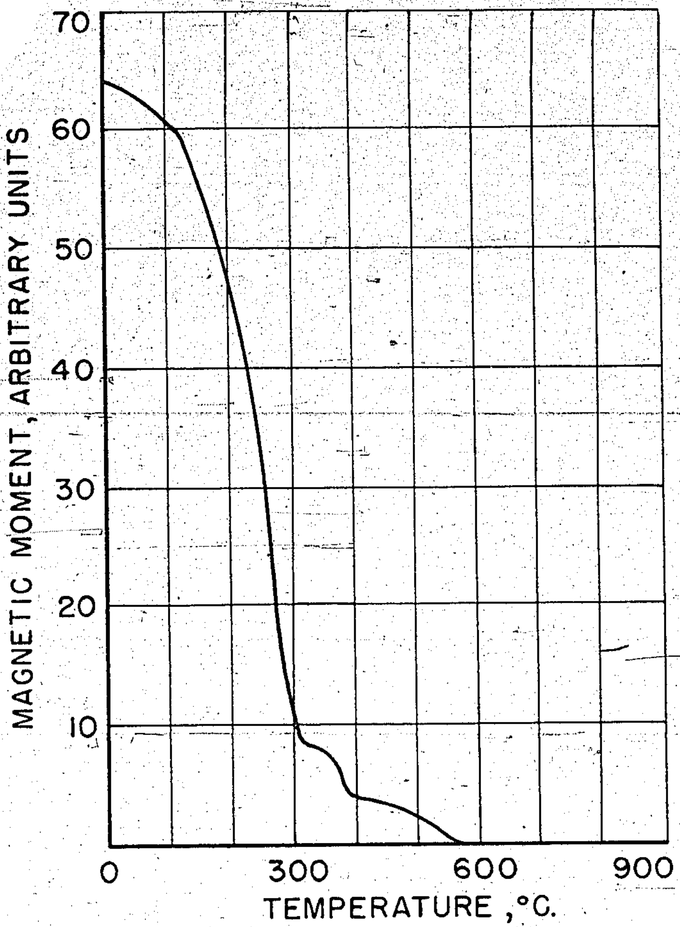

Figure 26.— Thermomagnetic curve of Fe, Cu, K_2CO_3 (100 : 1 : 1.5) catalyst, after carburization for 5 hours at 325° C. and 0.1 atmosphere, 8 liters of CO per hour per 10 grams of Fe.

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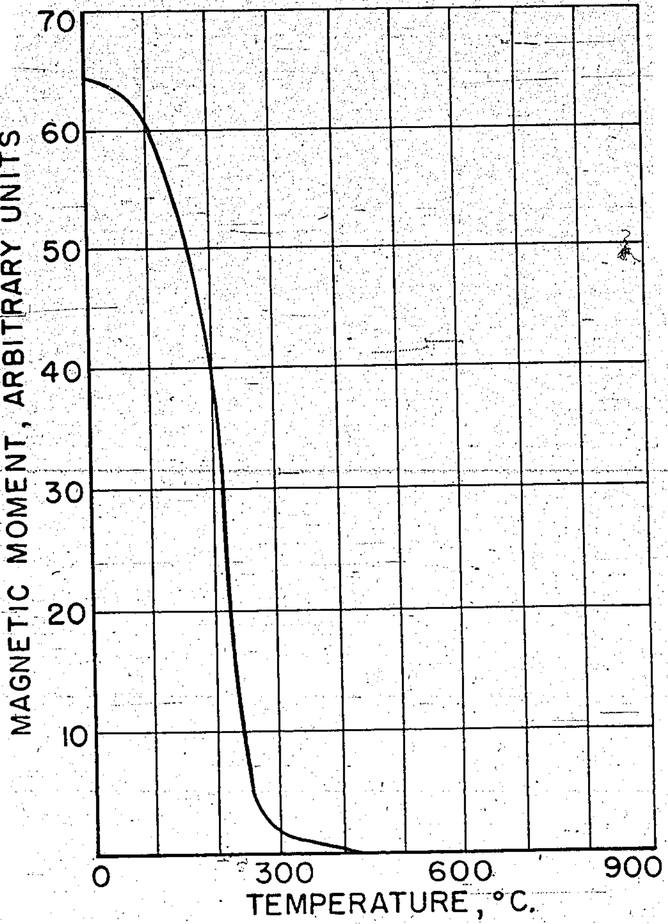

Figure 27.— Thermomagnetic curve, after heating to 800° C., of Fe, Cu, K_2CO_3 (100 : 1 : 1.5) catalyst which had been carburized for 5 hours at 0.1 atmosphere and 325° C., 8 liters of CO per hour per 10 grams of Fe.

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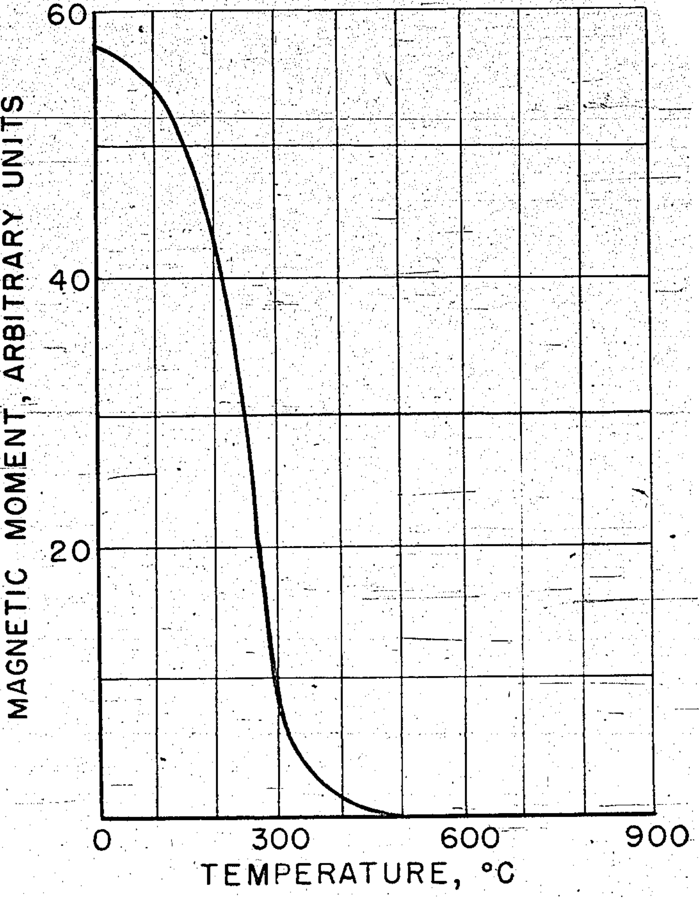

Figure 28.– Thermomagnetic curve of Fe, Cu, K_2CO_3 (100 : 1 : 1.5) catalyst, after carburization for 12 hours at 325° C. and 0.1 atmosphere, 8 liters of CO per hour per 10 grams of Fe.

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due to cementite disappeared at 350°C., the magnetization of the original product decreased only slowly above 350°C., indicating that in this experiment, too, the Curie Point 380°C. carbide was probably present in small amounts. Both curves in figure 29 show that the values of the specific magnetization of the two carbides are nearly the same because the deflections at room temperature were almost identical.

These copper-promoted iron catalysts were exceptionally reactive even when treated with synthesis gas (carbon monoxide:hydrogen = 1:2) at 100°C. Figure 30 shows the thermomagnetic analysis of an iron-1 percent copper-0.25 percent potassium carbonate catalyst, treated with synthesis gas at 100°C. for 24 hours. The fact that even at this low temperature hematite was reduced to magnetite shows that the data given in the literature for the minimum temperature at which carbon monoxide and hydrogen react with ferric oxide (180° and 280°C., respectively) are of limited value.

The results obtained by carburization of the three iron preparations can be summarized as follows: The action of carbon monoxide on precipitated iron catalysts at about 325°C. always resulted in a higher iron carbide, with a Curie Point at 265°C. There are also indications that a carbide with a Curie Point at 380°C. was formed. With active catalysts carbiding occurred even when only 100 liters of carbon monoxide per 10 grams of iron were used because of the relatively high carburization temperature and the low pressure.

Above their region of thermal stability, both higher iron carbides (Curie Point 265°C. and Curie Point 380°C.) were converted to

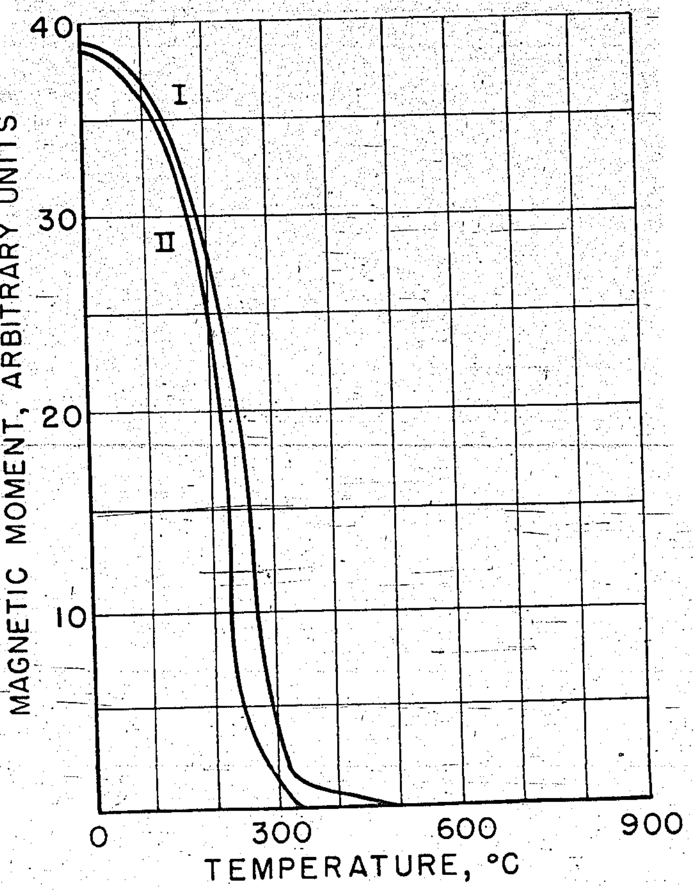

Figure 29.—Thermomagnetic curves of Fe, Cu, K_2CO_3 (100:1:1.5) catalyst, after carburization for 25 hours (also 62 hours) at 325°C. and 0.1 atmosphere, 8 liters of CO per hour per 10 grams of Fe. I, freshly carburized sample; II, after heating to 800°C.

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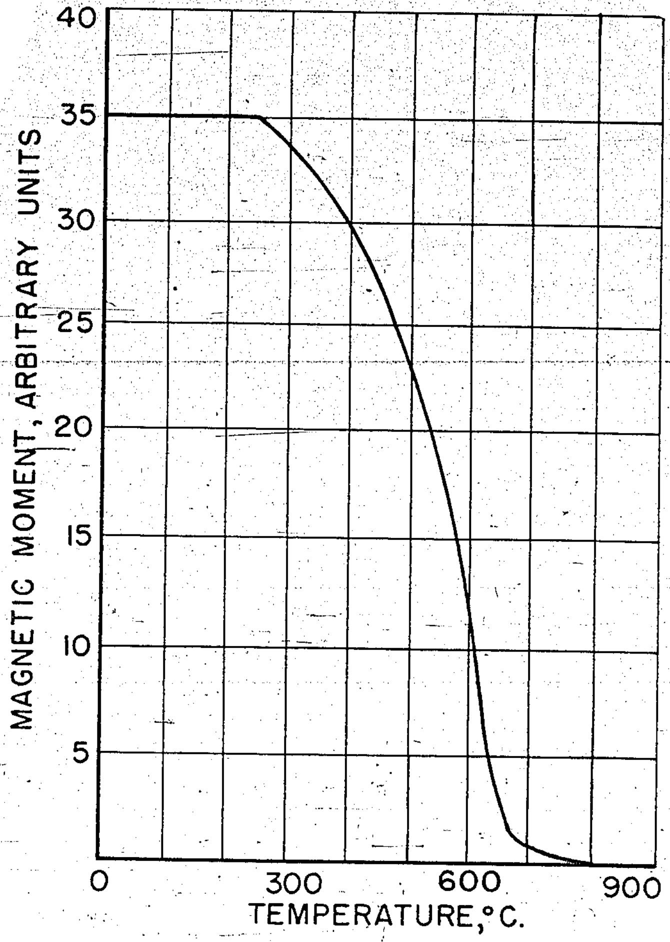

Figure 30.— Thermomagnetic curve of Fe, Cu, K_2CO_3 (100:1:0.25) catalyst, treated for 24 hours at 100°C. with synthesis gas (1 CO + 2 H_2 mixture).

L-613

cementite. In no instance was there any evidence that cementite had been formed directly as a result of carburization. Hofmann,[119] however, observed that cementite lines were always present in the X-ray pattern obtained from pure iron carburized within the same temperature range.

Thermomagnetic analysis clearly showed the effect of reactivity of catalysts on their carburization and final composition. A comparison of figures 19 (iron oxide without promoter, carburized 12 hours with carbon monoxide), 23 (iron catalyst with 0.25 percent K_2CO_3, carburized 12 hours with carbon monoxide), and 28 (iron-1 percent copper 1.5 percent K_2CO_3 carburized 12 hours with carbon monoxide) shows that iron oxide without promoter produced no detectable amounts of carbide, that alkali-promoted catalyst produced considerable amounts of carbide in the same period, and that the catalyst promoted with copper and alkali was converted to carbide almost quantitatively. In 25 hours of carburization of the pure iron oxide (figure 20) only traces of carbide could be detected, while the catalyst promoted with copper and alkali was about half converted to carbide in 0.5 hour of carburization (figure 25).

Copper-containing catalysts are characterized by a tendency to form a higher carbide which is virtually the exclusive carburization product. The high activity of these catalysts in the Fischer-Tropsch synthesis is apparently related to the process of carburization. This necessary pretreatment for medium-pressure synthesis converts the iron

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[119] Hofmann, U., work cited (footnote 96).
Hofmann, U. and Groll, E., work cited (footnote 97).

catalysts more or less completely to the Curie Point 265°C. carbide.

Behavior of Iron Catalysts During Hydrocarbon Synthesis

Medium-Pressure Synthesis

An iron catalyst containing a small amount of copper was carburized for 24 hours at 325°C. and 0.1 atmosphere with carbon monoxide (8 liters of carbon monoxide per hour per 20 grams of iron). It will be seen from figure 31 that the Curie Point 265°C. carbide was virtually the only ferromagnetic component. The catalyst was then used for synthesis at 235°C. and 11 atmospheres. Samples for thermomagnetic analysis were taken at intervals from the inlet side of the converters in a nitrogen-flushed sample collector while the synthesis gas was flowing to prevent contact with air. Since each removal diminished the original 10 grams of iron by about 1 gram, and since the throughput of synthesis gas was kept constant, the residual catalyst was increasingly overloaded.

After operating for 2.5 hours, (contraction 46 percent, figure 32) and even after 6.5 hours of operation (figure 33) the catalyst remained essentially unchanged. After 18-1/2 hours of operation, gas conversion corresponded to a contraction of 51.5 percent. The thermomagnetic curve shows that the catalyst was composed entirely of the Curie Point 265°C. carbide at this high activity (figure 34). The absence of magnetite indicates that it is not essential for gasoline synthesis. On the contrary, subsequent experiments showed that its

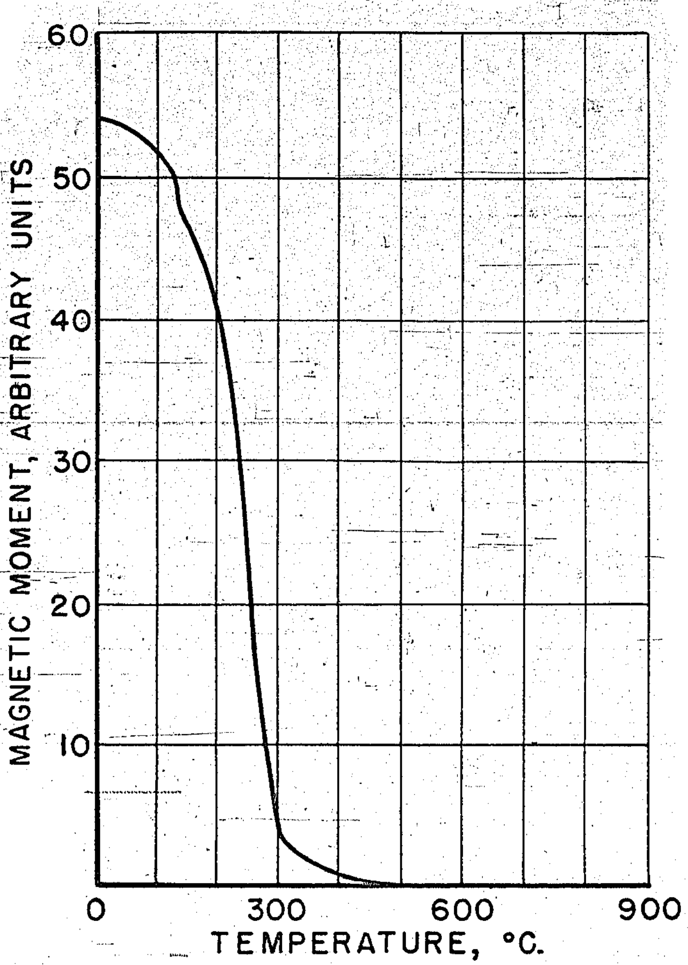

Figure 31.— Thermomagnetic curve of Cu- and alkali-promoted iron catalyst, carburized for 24 hours at 325°C. and 0.1 atmosphere, 8 liters of CO per hour per 20 grams of Fe.

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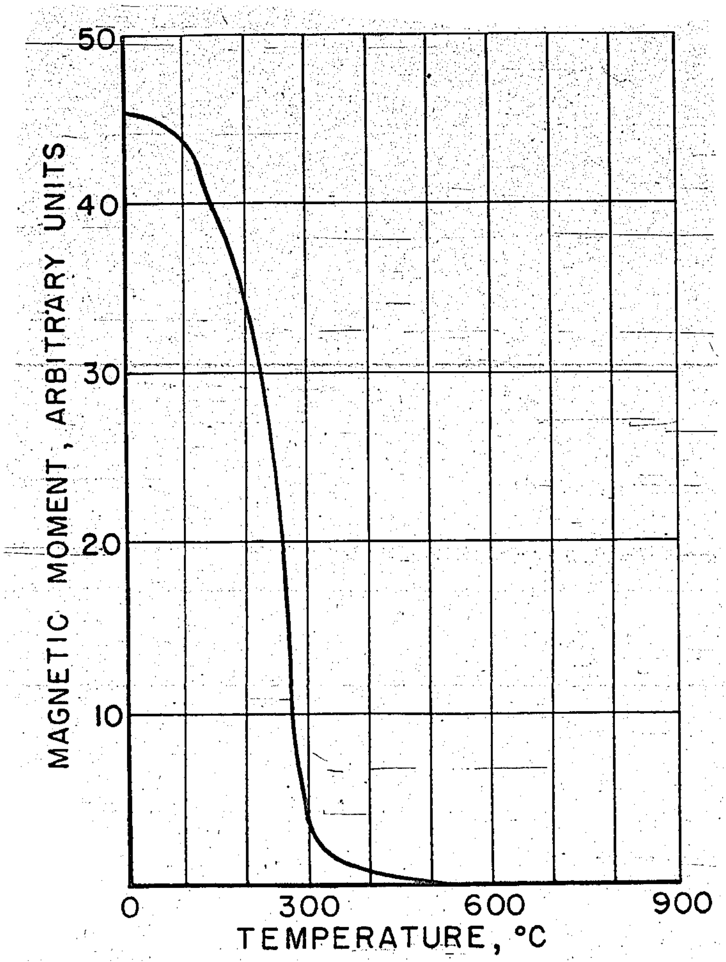

Figure 32.— Thermomagnetic curve of Cu-and alkali-promoted iron catalyst, carburized for 24 hours at 325° C. and 0.1 atmosphere, 8 liters of CO per hour per 20 grams of Fe; and used for synthesis for 2.5 hours at 235° C. and 11 atmospheres.

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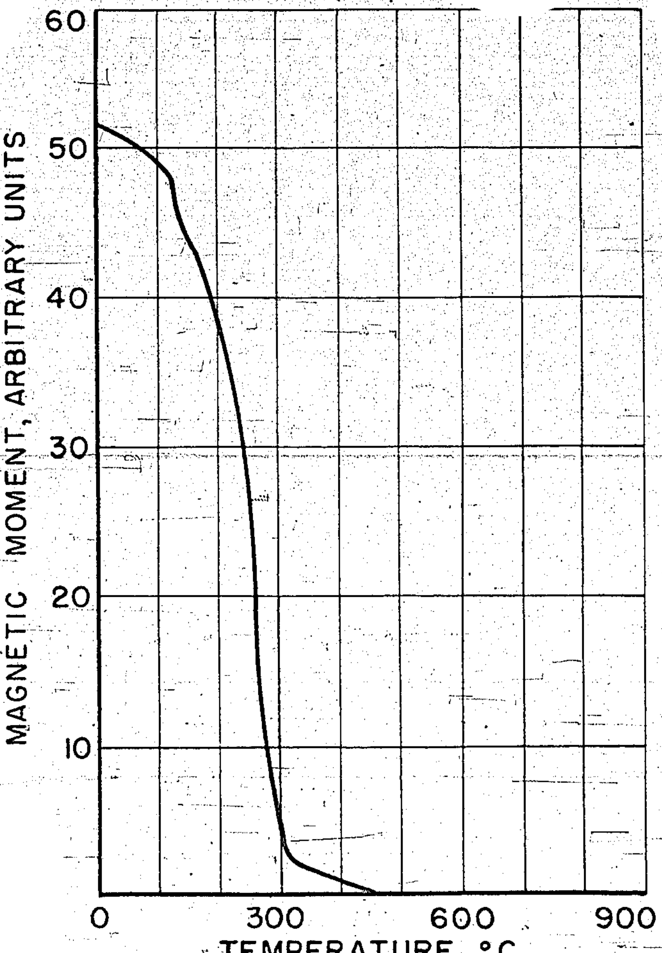

Figure 33.— Thermomagnetic curve of Cu-and alkali-promoted iron catalyst, carburized for 24 hours at 325°C. and 0.1 atmosphere, 8 liters of CO per hour per 20 grams of Fe; and used for synthesis for 6.5 hours at 235° C.—and 11 atmospheres.

L-616

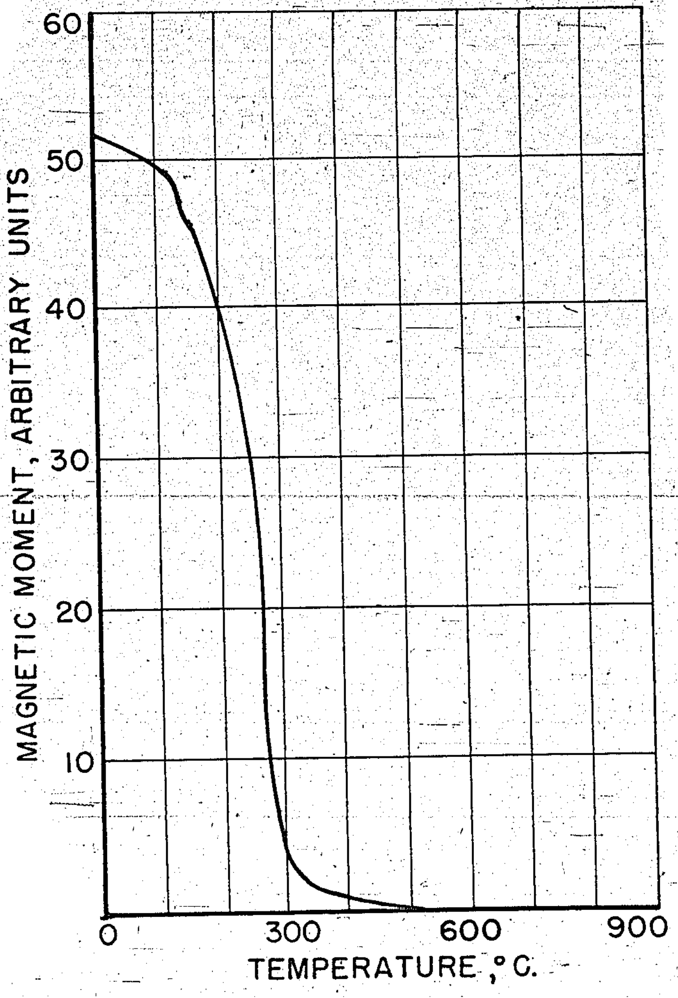

Figure 34.—Thermomagnetic curve of Cu- and alkali-promoted iron catalyst, carburized for 24 hours at 325° C. and 0.1 atmosphere, 8 liters of CO per hour per 20 grams of Fe; and used for synthesis for 18.5 hours at 235° C. and 11 atmospheres.

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presence hinders the synthesis. Figures 32 to 34 show that no free iron is formed during medium-pressure synthesis. The presence of the free metal for the synthesis is thus unnecessary.

Figure 35 shows the thermomagnetic behavior after 40 hours of operation. The contraction was 50 percent. The decrease in magnetization above 500°C. shows that magnetite was present. After 62 hours of operation the amount of magnetite increased considerably (figure 36). The oxidation of the catalyst resulted in reducing the contraction from 50 to 40 percent, the synthesis temperature having been kept constant. After 109 hours, the amount of magnetite increased considerably at the expense of the carbide as shown in figure 37. Oxidation was probably caused by the carbon dioxide formed during the reaction. The carbon dioxide of the tail gas increased to 40 percent during the first part of the experiment and then decreased with diminishing conversion.

This series of experiments also demonstrates the approximately linear relationship in medium-pressure synthesis between the activity of the catalyst and the amount of Curie Point 265°C. iron carbide present. There was no positive evidence of the presence of the Curie Point 380°C. carbide.

Thermomagnetic analysis showed that by extending the operating time the magnetite content was increased. However, the gradual increase in space velocity over the remaining portion of the catalyst made it impossible to evaluate the later results in terms of the usual synthesis conditions.

In the following series of experiments comparable operating conditions were maintained by using equal portions of a catalyst (which

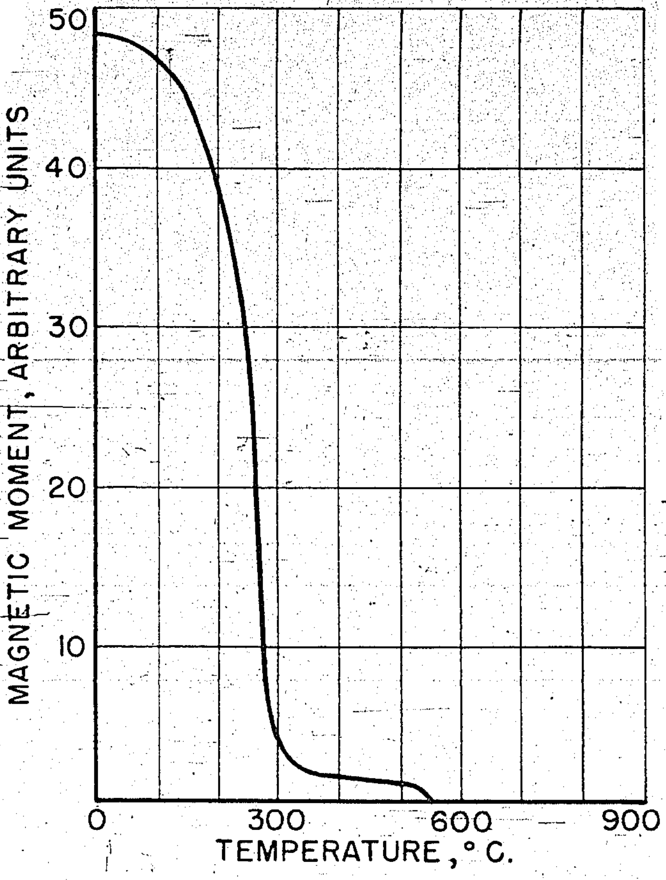

Figure 35.—Thermomagnetic curve of Cu-and alkali-promoted iron catalyst, carburized for 24 hours at 325°C. and 0.1 atmosphere, 8 liters of CO per hour per 20 grams of Fe; and used for synthesis for 40 hours at 235°C. and 11 atmospheres.

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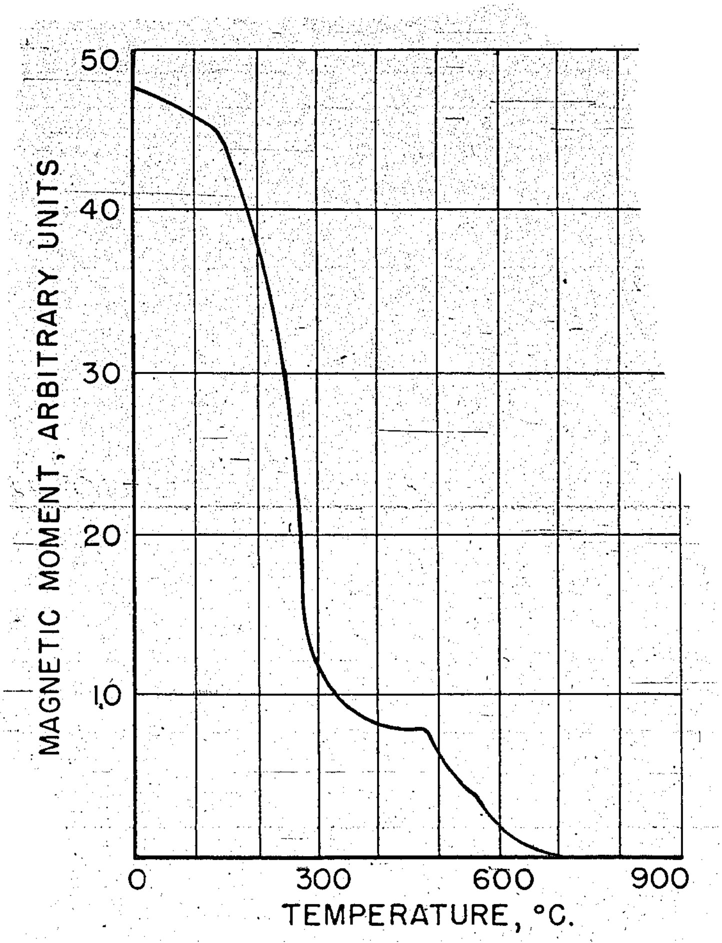

Figure 36.—Thermomagnetic curve of Cu-and alkali-promoted iron catalyst, carburized for 24 hours at 0.1 atmosphere and 325° C., 8 liters of CO per hour per 20 grams of Fe; and used for synthesis for 62 hours at 11 atmospheres and 235° C.

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had been carburized identically) in several converters. The experiments were interrupted at intervals and the ferromagnetic components of the catalyst determined. This method eliminated the disturbances due to changes in pressure and temperature which accompany the study of a single sample.

Batches of 40 cubic centimeters of catalyst were pretreated with water gas for 25 hours (325°C., 0.1 atmosphere). The rate of flow was 8 liters per hour, making the total volume of carbon monoxide passed over the catalyst 100 liters. The carburized catalysts were placed in operation at 215°C. and 12 atmospheres. After 54 hours of operation, contraction for one sample amounted to 49 percent. Here too, the synthesis gas had little effect on the magnetic behavior of the catalyst (figure 38).

In a second experiment (figure 39) the catalyst was operated for 410 hours under the same conditions as before. At the end of this time contraction had attained an approximately constant value of 40 to 41 percent. The curve corresponds to a catalyst containing chiefly the Curie Point 265°C. carbide.

It will be seen from figures 22, 25, and 31 to 34 that a new Curie Point appeared between 125° and 150°C. This phenomenon might be explained by the formation of potassium ferrite which has a Curie Point of 150°C., according to Hilpert.

Although no definite conclusions can be drawn from the data, it does appear now that the opinion of Lefebvre and LeClerc[120/] is

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[120/] Lefebvre, H. and LeClerc, G., work cited (footnote 12).

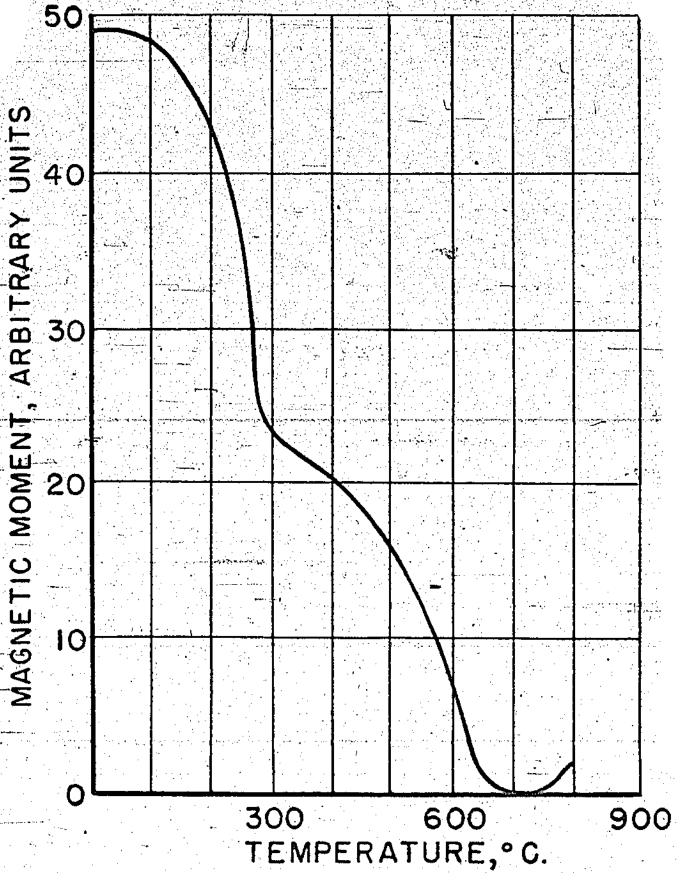

Figure 37.— Thermomagnetic curve of Cu- and alkali-promoted iron catalyst, carburized for 24 hours at 325° C. and 0.1 atmosphere, 8 liters of CO per hour per 20 grams of Fe; and used for synthesis for 109 hours at 235° C. and 11 atmospheres.

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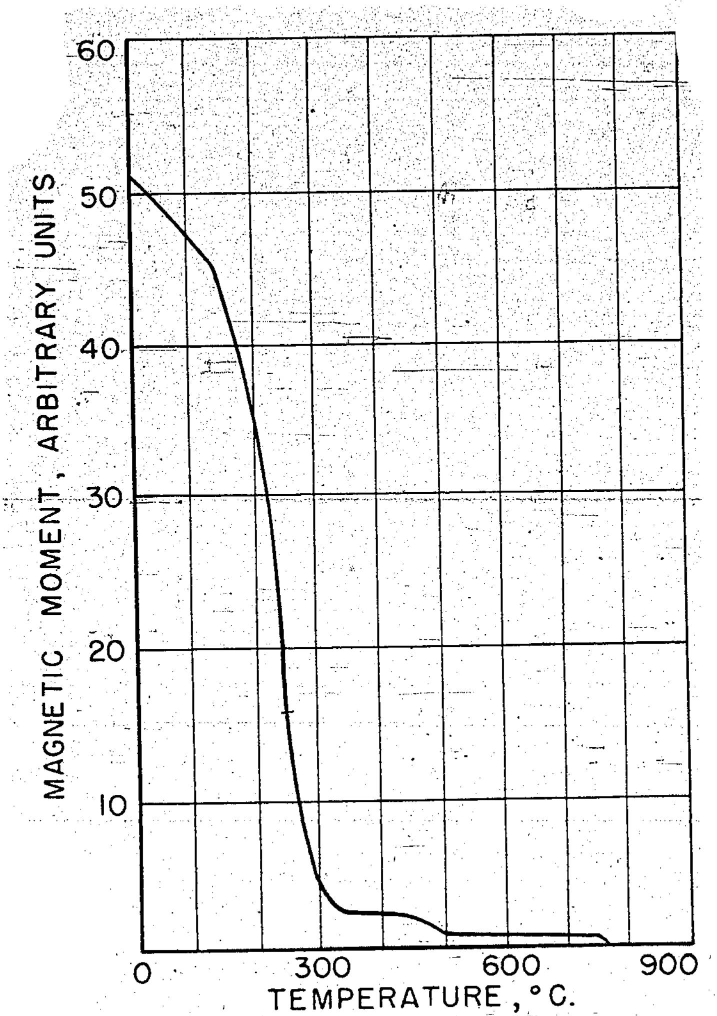

Figure 38.—Thermomagnetic curve of Cu-and alkali-promoted iron catalyst, carburized for 25 hours at 325° C. and 0.1 atmosphere, 8 liters of water gas per hour per 40 cubic centimeters of catalyst; and used for synthesis for 54 hours at 215° C. and 12 atmospheres.

L-621

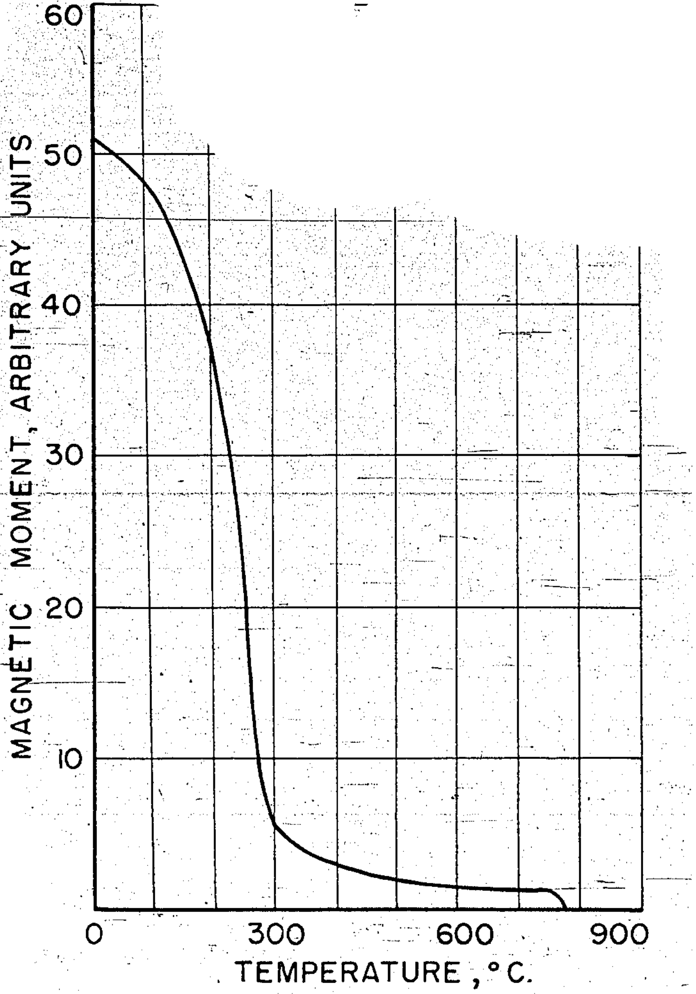

Figure 39.— Thermomagnetic curve of Cu-and alkali-promoted iron catalyst, carburized for 25 hours at 325 °C. and 0.1 atmosphere, 8 liters of water gas per hour per 40 cubic centimeters of catalyst; and used for synthesis for 410 hours at 215 °C. and 12 atmospheres.

L-622
4-8-48

incorrect; according to them catalytic activity during synthesis is to be attributed to cubic iron oxide which is stabilized by ferrite formation. The thermomagnetic curve which these authors ascribed to potassium ferrite is undoubtedly characteristic of carbide.

Atmospheric Pressure Synthesis

The production of especially active iron catalysts makes it possible to obtain good conversion of the synthesis gas even at atmospheric pressure, so that the carbon monoxide in water gas is converted almost quantitatively at 220°C. By adjusting the composition of the synthesis gas and the alkalization of the catalyst, this method can yield gasoline and oil having the desired boiling range, and white, high molecular-weight paraffin wax.

In atmospheric pressure synthesis, active iron catalysts form paraffins a few minutes after being put into operation. In order to study the state of a catalyst (Fe-Cu-K_2CO_3 = 100-20-1.5) just before synthesis starts a thermocouple was introduced into the center of the catalyst, which was heated in a flow of synthesis gas. The gas was shut off when the thermocouple indicated an exothermic reaction. The catalyst was blackened on the gas inlet side, whereas it still showed the brown color characteristic of ferric oxide on the outlet side. As will be seen from the thermomagnetic analysis (figure 40), the sudden reduction of ferric oxide to magnetite was accompanied by carbide formation, thus demonstrating the rapid carburization of active catalysts by synthesis gas at 225°C.

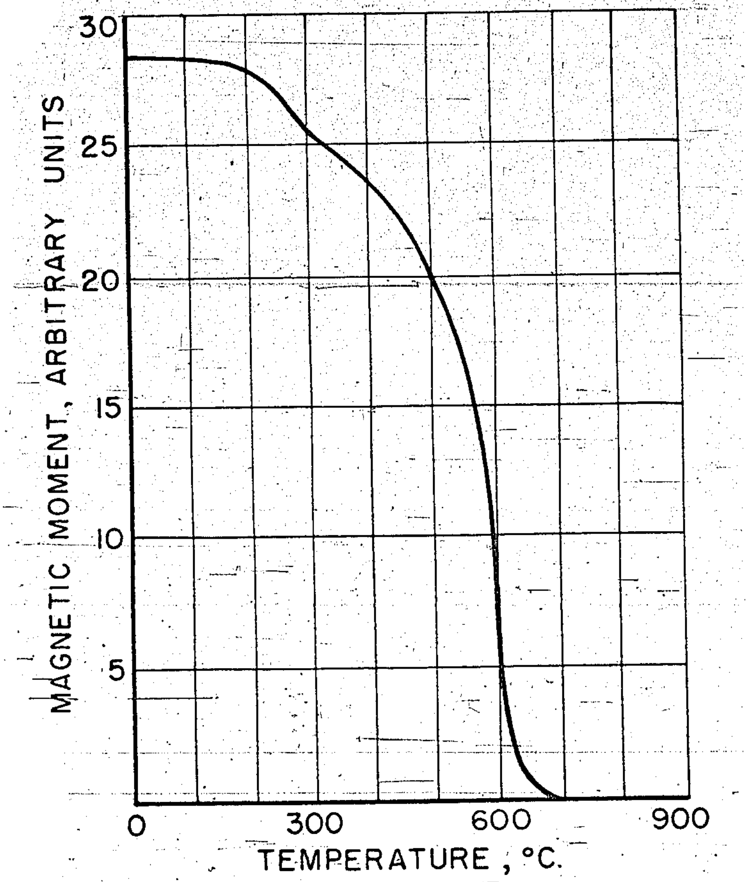

Figure 40.—Thermomagnetic curve of Fe, Cu, K_2CO_3 (100:20:1.5) catalyst heated in synthesis gas at 1 atmosphere until an exothermic reaction occurred.

L-623

Three types of iron catalyst were studied in various stages of carburization and synthesis at atmospheric pressure with synthesis gas ($2H_2 + 1CO$). An alkalized catalyst containing 0.25 percent of copper was used for the first group of experiments. This catalyst was not very active and was therefore carburized and simultaneously operated at 235°C. It produced little paraffin. The data on time, temperature of aluminum block oven, rate of flow of exit gas, contraction, and carbon dioxide content of the tail gas are tabulated in table 26 for the first six days of operation. Contraction rose sharply during the first hour and, after reaching a maximum value of 54 percent, decreased to 2.6 percent; the carbon dioxide content of the end gas was approximately proportional to the contraction. This first reaction was a reduction of the original oxide to magnetite. A second rise in the contraction (and parallel carbon dioxide increase) followed and reached a final value of 34 percent after several days. This was due to the reduction of magnetite, to carburization (decomposition of carbon monoxide and carbide formation), and to hydrocarbon synthesis. Samples for thermomagnetic analysis were collected periodically as before in a current of synthesis gas, in samplers which were flushed with nitrogen.

Figure 41 shows the thermomagnetic curve of the catalyst at the conclusion of 1.5 hours of operation. At this point contraction had reached its lowest value (2.6 percent). The catalyst evidently consisted of magnetite. The thermomagnetic curve after a total of 4 hours and 40 minutes is shown in ~~in~~ figure 42; magnetite was still the principal component, but the higher iron carbide became perceptible at 330°C. Contraction had risen to 16.1 percent. The catalyst reached

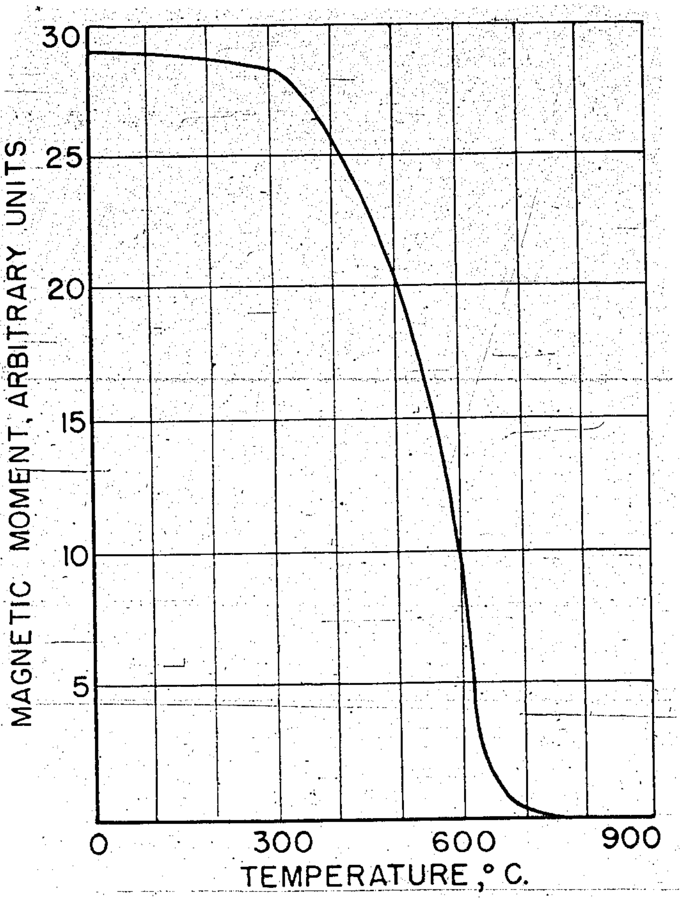

Figure 41.— Thermomagnetic curve of Cu- and alkali-promoted (0.25 % Cu) iron catalyst, after heating to 235 °C. in synthesis gas at 1 atmosphere (time, 90 minutes).

L-624

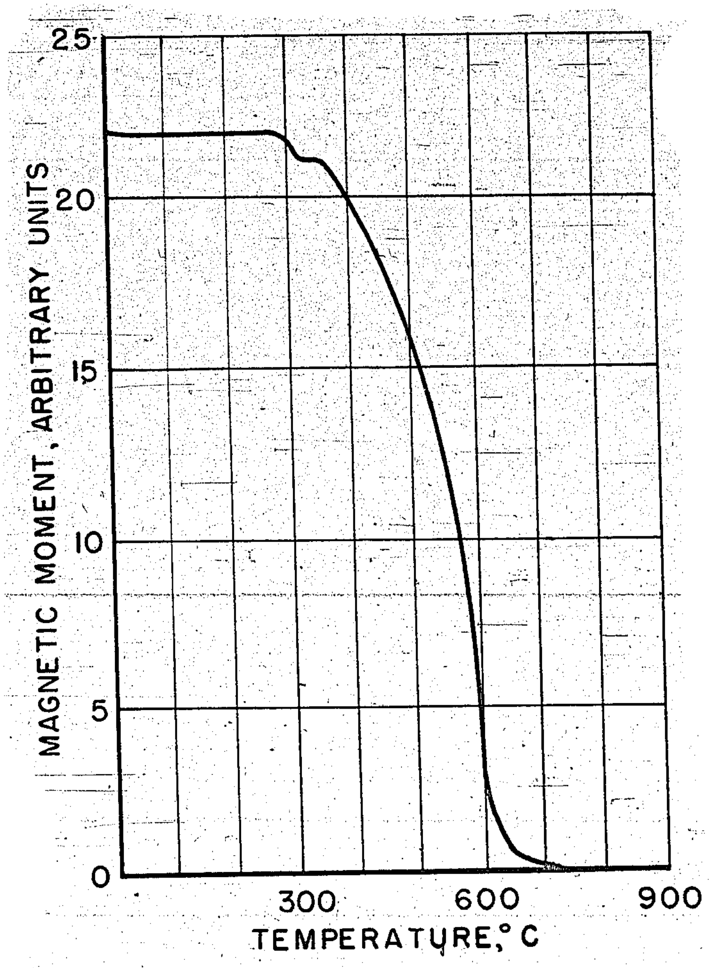

Figure 42.— Thermomagnetic curve of Cu-and alkali-promoted (0.25% Cu) iron catalyst, heated to 235 °C. in synthesis gas at 1 atmosphere and kept at that temperature (total time, 4 hours and 40 minutes).

L-625

Table 26.—Operation of a copper-containing iron catalyst at normal pressure

Date November	Time	Oven temperature (°C.)	Tail gas (liters per hour)	Contraction (percent)	Carbon dioxide in tail gas (percent)
23	8:55 a.m.	30	4.0	-	-
	9:00	56	3.9	-	-
	9:05	75	4.0	-	-
	9:10	91	4.0	-	-
	9:15	115	3.9	-	-
	9:20	128	3.84	-	-
	9:25	140	3.72	7.0	-
	9:30	162	3.48	13.0	4.2
	9:40	192	2.40	40.0	39.8
	9:50	214	1.95	51.3	-
	9:55	230	1.83	54.2	45.0
	10:05	232	3.55	11.3	10.8
	10:10	227	3.80	5.0	-
	10:25	231	3.89	2.6	5.4
	10:45	235	3.81	4.7	-
	11:00	231	3.78	5.5	6.0
	11:20	237	3.78	5.5	-
	11:40	236	3.72	7.0	6.7
	1:15 p.m.	236	3.31	17.1	-
	1:35	236	3.36	16.1	11.2
	2:30	237	3.36	16.1	10.4
	3:05	237	3.36	16.1	-
	3:45	237	3.36	16.1	-
	4:30	236	3.31	17.1	-
24	8:00 a.m.	237	2.82	29.6	17.1
	9:00	233	2.76	31.0	-
	10:30	233	2.76	31.0	17.4
	2:00 p.m.	234	2.64	34.0	-
25	10:00 a.m.	230	2.64	34.0	19.6
27	8:40 a.m.	230	2.64	34.0	17.7
28	8:30 a.m.	230	2.64	34.0	-

its maximum contraction after 49 hours of operation. Figure 43 shows that the amount of Curie Point 265°C. carbide had increased considerably. Figure 44 is the thermomagnetic curve of the catalyst after operation for 120 hours. The contraction remained unchanged, but the amount of higher carbide increased still more at the expense of magnetite. The horizontal portions (figures 43 and 44) at the lower temperatures and around 400°C. are unusual.

Thus, the first effect of synthesis gas at atmospheric pressure was to reduce and carburize the iron catalyst. As carbide formation increased, the contraction and the amount of carbon dioxide also increased and reached their maximum value when carbiding was complete. The first stage in atmospheric pressure synthesis corresponds therefore to carburization in medium-pressure synthesis, although no free carbon is formed. Because carburization is a separate, preliminary operation in medium-pressure synthesis, correlation between activity and carbide content of the two processes becomes possible only after carbide formation in the atmospheric pressure synthesis is complete.

In the second group of experiments with synthesis gas at normal pressure, an iron catalyst (Fe-Cu-K_2CO_3 = 100-20-0.25) was used at 235°C. This was more active than the preceding one. Several converters were operated simultaneously under the same conditions for different periods and samples were withdrawn and analyzed thermomagnetically.

A contraction of 14 percent was attained after 17 hours of operation. At this point the thermomagnetic curve (figure 45) clearly indicated the presence of higher carbide. However, the catalyst still

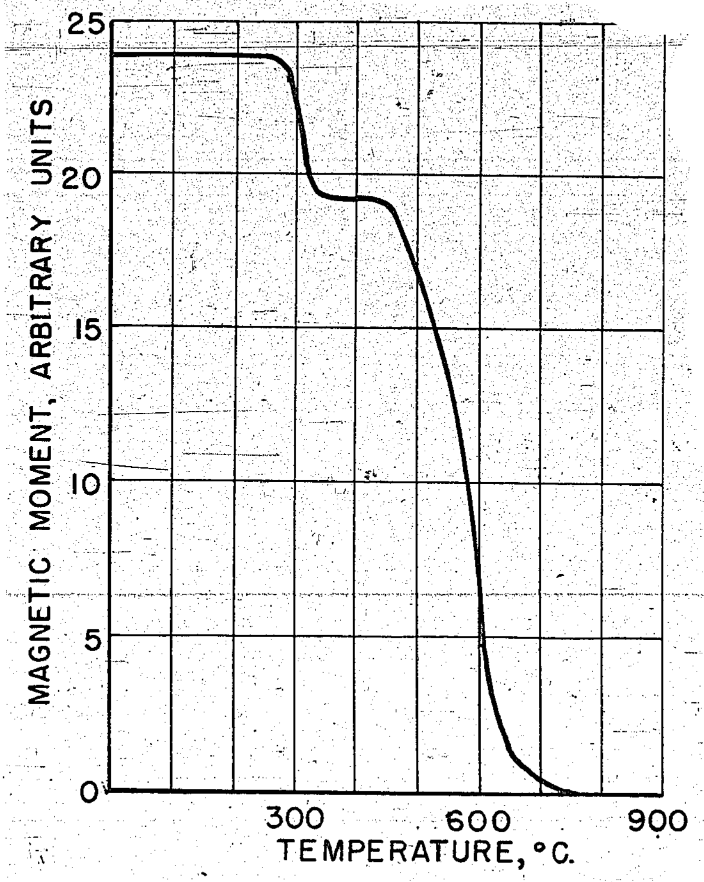

Figure 43.— Thermomagnetic curve of Cu- and alkali-promoted (0.25% Cu) iron catalyst, heated to 235°C. in synthesis gas at 1 atmosphere and kept at that temperature (total time, 49 hours).

L-626

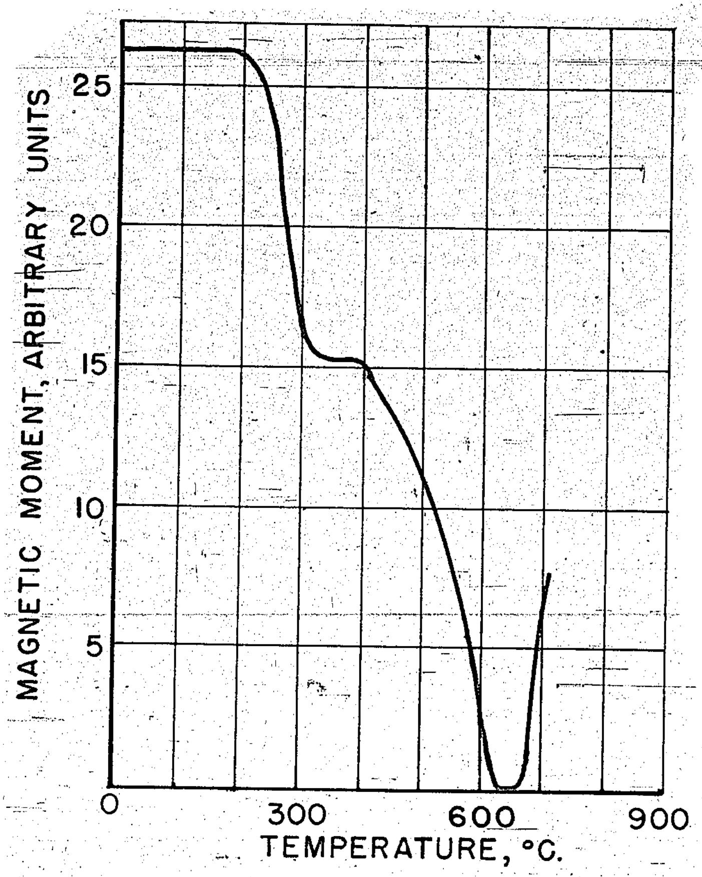

Figure 44.— Thermomagnetic curve of Cu- and alkali-promoted (0.25% Cu) ~~iron~~ catalyst, heated to 235° C. in synthesis gas at 1 atmosphere and kept at that temperature (total time, 120 hours).

L-627

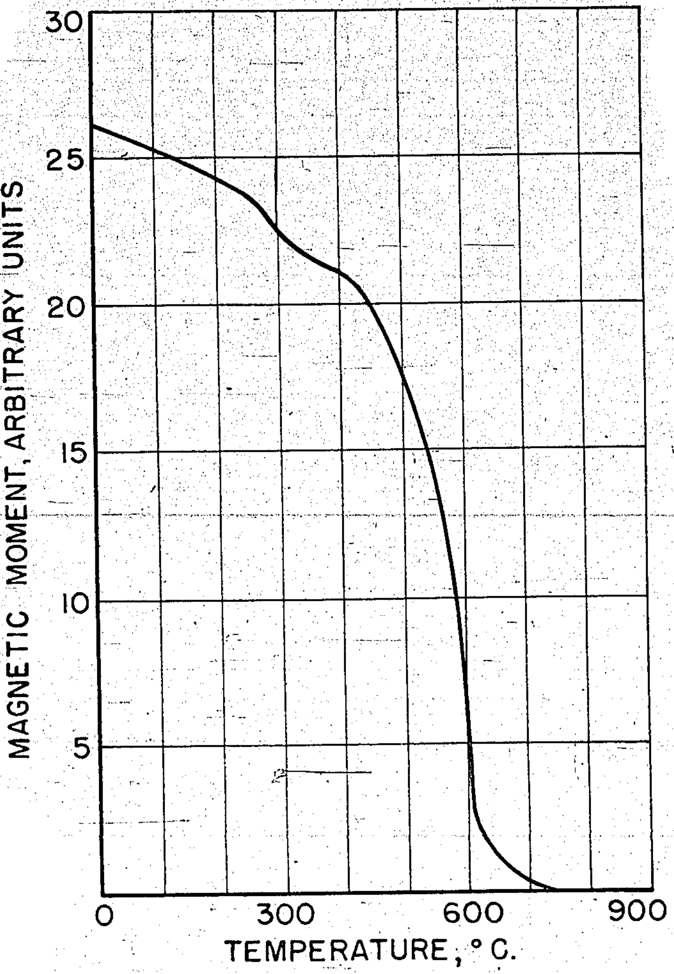

Figure 45.— Thermomagnetic curve of Fe, Cu, K_2CO_3 (100 : 20 : 0.25) catalyst, heated in synthesis gas at 1 atmosphere to 235°C. and kept at that temperature (time, 17 hours).

L-628

consisted mainly of magnetite. After 47.5 hours of operation (contraction 26.5 percent) the thermomagnetic curve clearly showed the Curie Point 265°C. carbide (figure 46). After 121 hours of operation the catalyst reached its maximum contraction, amounting to 30 to 31 percent. As shown in figure 47, there was only a slight change in the relative amounts of carbide and magnetite. However, the formation of the Curie Point 380°C. carbide in this experiment was evident from the Curie Point at about 390°C.

The relationship between activity and carbide content is clear from this group of experiments. Increased carbide formation was associated with increased contraction. The appearance of the Curie Point 380°C. carbide in the last experiment was accompanied by a rise in contraction from 26.5 to 31 percent.

In the third group of experiments an iron catalyst (Fe-Cu-K_2CO_3 = 100-20-1.5) was used (at 225°C.) which was considered to be the best catalyst for the Fischer-Tropsch process at atmospheric pressure. Since the catalyst was alkalized with 1.5 percent of potassium carbonate, large quantities of solid paraffins blocked the surface and periodic extraction with Diesel oil was necessary. Extraction resulted in an immediate rise in the carbon dioxide content, showing the reaction was resumed at once. Samples were collected at various intervals for thermomagnetic examination.

Figure 48 shows the thermomagnetic behavior of the catalyst after treatment for 24 hours with synthesis gas at 225°C. The gas throughput was 20 liters per hour per 40 cubic centimeters of catalyst.

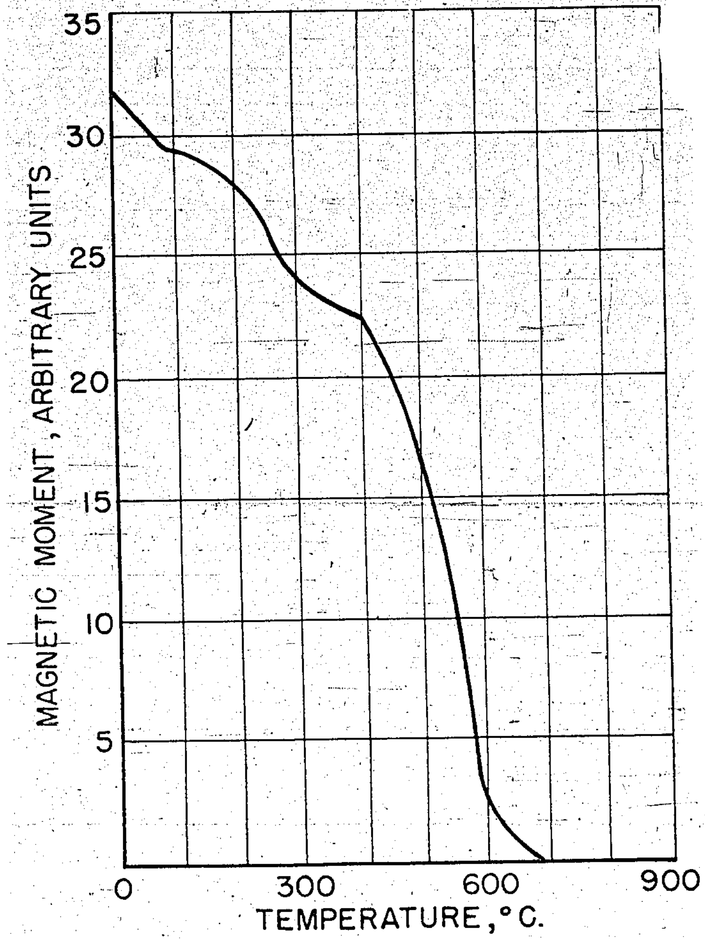

Figure 46. - Thermomagnetic curve of Fe, Cu, K_2CO_3 (100:20:0.25) catalyst, heated to 235° C. in synthesis gas at 1 atmosphere and kept at that temperature (time, 47.5 hours).

L-629

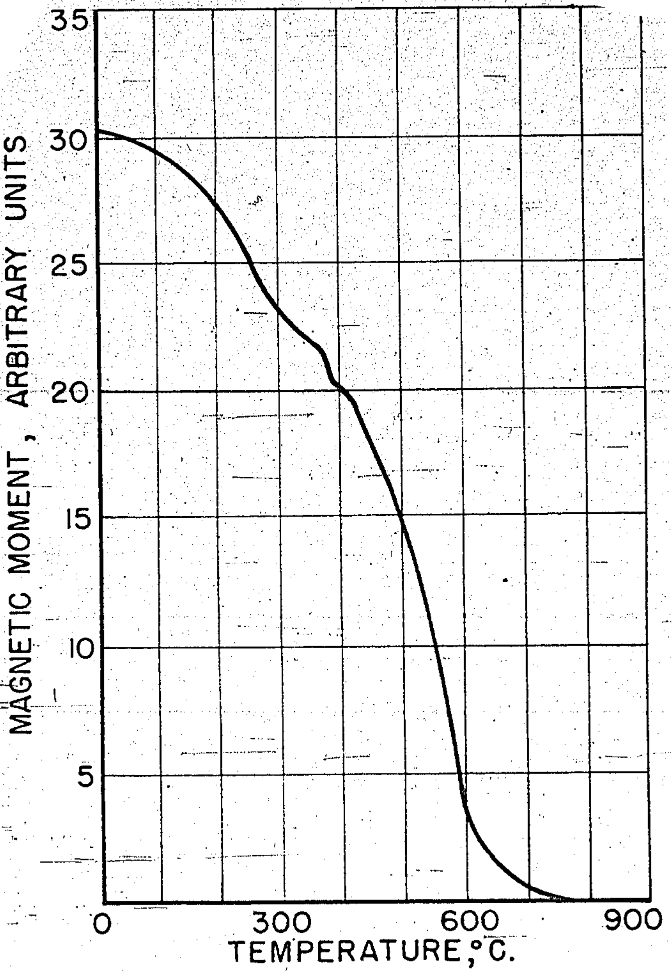

Figure 47. - Thermomagnetic curve of Fe, Cu, K_2CO_3 (100 : 20 : 0.25) catalyst, heated to 235° C. in synthesis gas at 1 atmosphere and kept at that temperature (time, 121 hours)

L-630

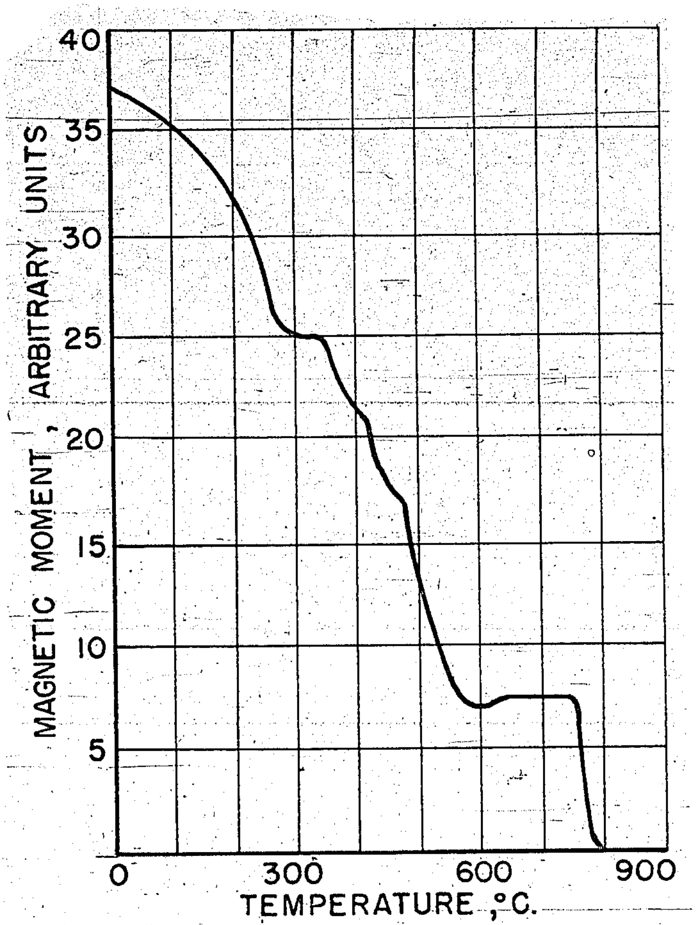

Figure 48. – Thermomagnetic curve of Fe, Cu, K_2CO_3 (100:20:1.5) catalyst, treated for 24 hours at 225° C. with synthesis gas (20 liters 1 CO + $2H_2$ gas mixture per hour per 40 cc. catalyst) L-631

4-8-48 L-631

An appreciable amount of paraffin and oil had been formed. The graph clearly shows the composition of the catalyst. The Curie Point 265°C. carbide was already formed at this time. It is interesting to note that after the elimination of the magnetization due to this carbide, the curve proceeded horizontally from 290° to 340°C., that is, magnetization was independent of the temperature. The second drop in magnetization shows a Curie Point at 395°C. which was the result of the formation of the Curie Point 380°C. carbide, as the following experiments demonstrate more clearly. The next well-defined inflection at 430° to 440°C. was probably due to the formation of copper ferrite whose Curie Point, according to Chaudron, is 455°C. The remaining drop in magnetization was due partly to magnetite, and above 600°C. to iron.

Figure 49 shows the effect of a three-day treatment with synthesis gas. The catalyst was extracted with Diesel oil before the end of the experiment. It is interesting to note that the amount of Curie Point 265°C. carbide remained virtually unchanged, as compared with the 24-hour experiment in this group. The Curie Point at 380°C. was more clearly defined, showing that the Curie Point 380°C. carbide content had increased. This probably explains the absence in figure 4 of the first horizontal section which appears in figure 48; the magnetization in this region was more temperature dependent now. As a result of increased carbide formation, the amount of free iron was also considerably greater than in the preceding experiment. After 6 days, during which time the catalyst was extracted twice with Diesel oil, the thermomagnetic curve shown in figure 50 was obtained. Here, too, the Curie Point at 380°C. is well-defined. The formation of free

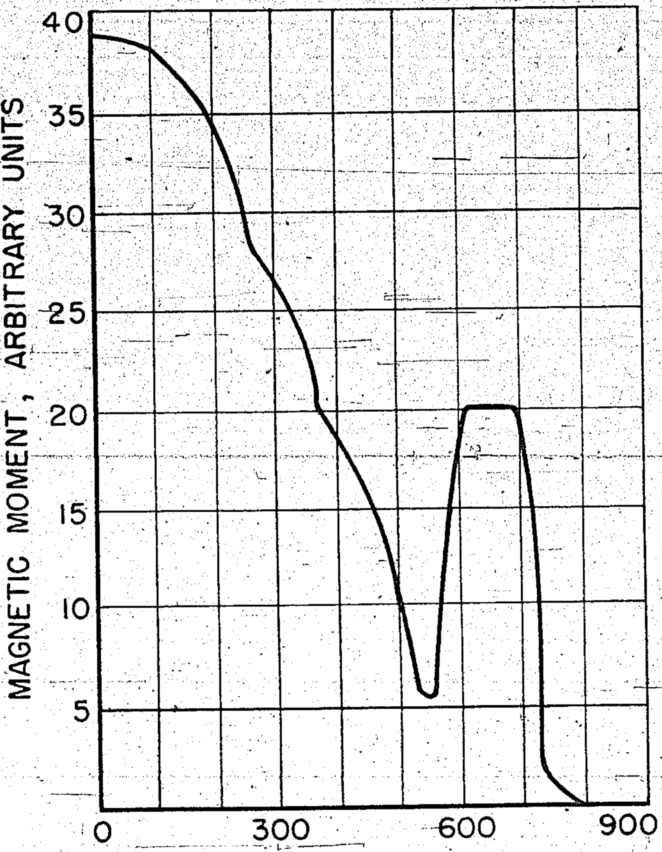

Figure 49.—Thermomagnetic curve of Fe, Cu, K_2CO_3 (100:20:1.5) catalyst, treated for 3 days at 225° C. with synthesis gas (20 liters 1 CO + $2H_2$ gas mixture per hour per 40 cc. catalyst)
L-632

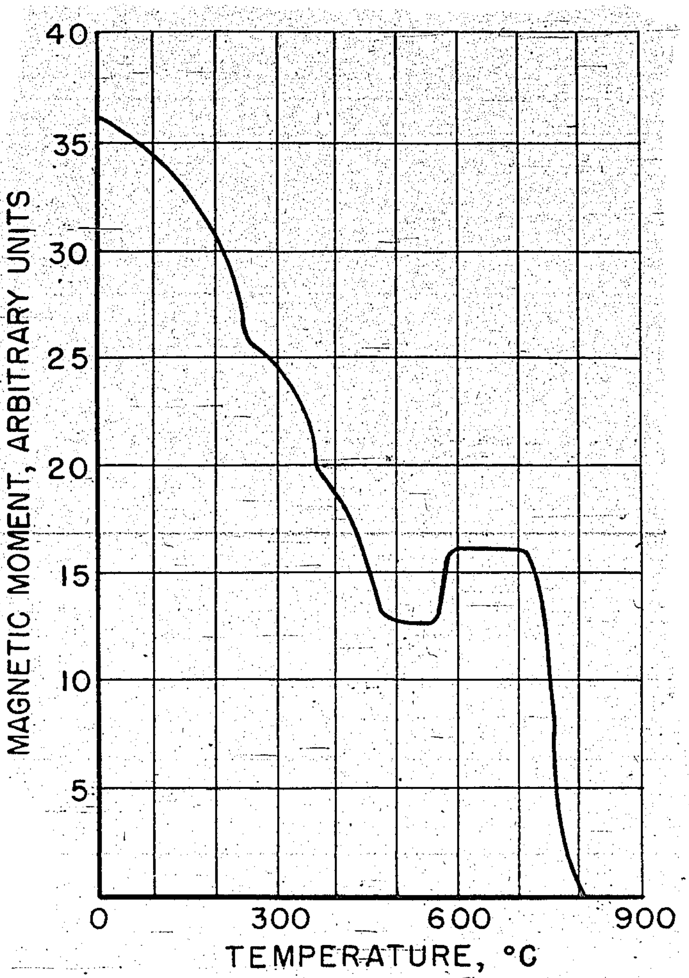

Figure 50. – Thermomagnetic curve of Fe, Cu, K_2CO_3 (100: 20: 1.5) catalyst, treated for 6 days at 225° C. with synthesis gas (20 liters $1 CO + 2H_2$ gas mixture per hour per 40 cc. catalyst)

L-633

iron began below 500°C. (flat portion of the curve). The carbide content of the catalyst shows virtually no change, as compared with the preceding experiment (figure 49).

In another experiment in this series, a catalyst was operated for 4 days with synthesis gas (20 liters per hour per 40 cubic centimeters of catalyst at 225°C. and 1 atmosphere), and was then operated with water gas (4 liters of water gas per hour per 40 cubic centimeters of catalyst at 220°C. and 1 atmosphere). Following the third extraction, the carbon dioxide content of the tail gas was over 30 percent, corresponding to about 36 percent contraction. After 2 days of operation with water gas, the catalyst gave the thermomagnetic picture shown in figure 51. It will be seen that the Curie Point 265°C. and the Curie Point 380°C. carbides were equally prominent. The amount of Curie Point 380°C. carbide had increased during synthesis with water gas over that formed during operation with synthesis gas.

Comparison of the three series of experiments on the effect of pretreatment with synthesis gas ($1CO + 2H_2$) on iron catalysts at atmospheric pressure shows the following: The catalyst used in the first series contained mainly magnetite, but also some higher carbide (Curie Point 265°C.). There was no evidence of the formation of the Curie Point 380°C. carbide. An operating temperature of 235°C. was necessary in this case to obtain satisfactory conversion. The carbon dioxide value on the fifth day amounted to 17.7 percent, showing that the catalyst was not very active.

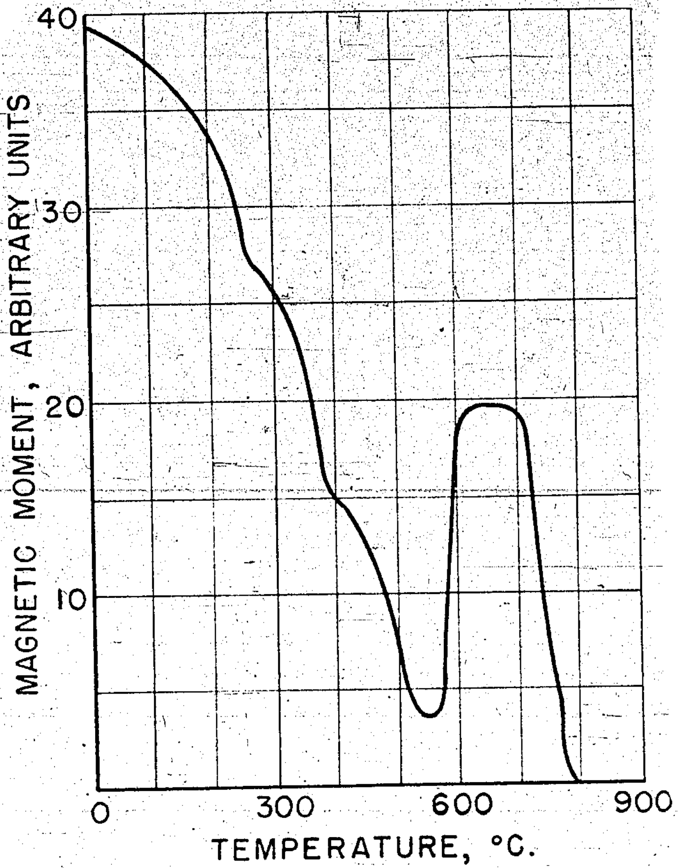

Figure 51.—Thermomagnetic curve of Fe, Cu, K_2CO_3 (100:20: 1.5) catalyst, treated for 4 days at 225° C. and 1 atmosphere of synthesis gas (20 liters 1CO + $2H_2$ gas mixture per hour per 40 cc. of catalyst) and then 2 days at 220° C. and 1 atmosphere of water gas (4 liters gas per hour per 40 cc. catalyst)

L-634

In the second series of experiments the higher activity of the catalyst containing 20 percent copper was apparent from the 31 percent contraction obtained at the same operating temperature. Figure 47 shows that the Curie Point 380°C. carbide was formed in addition to the Curie Point 265°C. carbide.

The third series of experiments was characterized by low operating temperature (220°C.), by high contraction, and by high content of Curie Point 380°C. carbide (figure 51). Under these conditions the catalyst converted the carbon monoxide in water gas quantitatively. The gas ratio was approximately 100 parts of carbon monoxide to 60 parts of hydrogen and contraction amounted to 36 percent.

With an iron catalyst of this type, pretreated as usual with synthesis gas (220° to 225° C., 1 atmosphere, 20 liters per hour), and operated at medium pressure (that is, 10 to 20 atmospheres) instead of atmospheric pressure, the optimum synthesis temperature dropped from 220° to 205°C., for the same conversion. This increased activity (as compared with iron catalysts pretreated at 325°C. with carbon monoxide, which require operating temperatures between 220° and 230°C. for the same pressures) was probably caused by the Curie Point 380°C. carbide, to which the characteristic properties of synthesis at atmospheric pressure are due. As already stated, there were only minor indications of the presence of the Curie Point 380°C. carbide in copper-free iron catalysts which were pretreated at 325°C. In this case the synthesis proceeded through the Curie Point 265°C. carbide, which required a higher synthesis temperature. The oxide content of catalysts was appreciably higher in atmospheric pressure synthesis than in medium-pressure synthesis (for the same activity). Thus, the oxide content alone is no measure of the activity of an iron catalyst.

Even a catalyst containing the carbide needed for satisfactory activity may prove inactive in the gasoline synthesis. Figure 52 shows the thermomagnetic curve of an iron catalyst in an experiment in which the carbon monoxide of the synthesis gas was converted almost quantitatively at normal pressure; it became almost completely inactive after extraction with Diesel oil containing sulfur. Chemical analysis showed that the catalyst had a high sulfur content. As a result, the active centers were rendered inoperative due to sulfide formation, though the structure remained unchanged. While the thermomagnetic curve offered no explanation of this behavior, the catalyst had already shown atypical behavior in the course of thermomagnetic measurement, when large quantities of oil vapor were evolved above 220°C. Figure 52 is unusual because the drop at 550°C. (corresponding to magnetite) is followed by a slight peak. Subsequently, there is a second rise followed by a drop with a point of inflection at 760°C. (Curie Point of α-iron).

Effect of Carbide Content on Catalyst Activity

Figure 53 is a thermomagnetic curve obtained with a highly active catalyst ($Fe-Cu-K_2CO_3$ = 100-20-0.25) which attained a contraction of 40% at atmospheric pressure and 235°C. Figure 54 is the thermomagnetic curve of the same catalyst after its activity had dropped to a contraction of 2 percent after prolonged operation. Figure 53 shows that high activity at normal pressure and 235°C. was characterized by large amounts of Curie Point 265°C. carbide and some Curie Point 380°C.

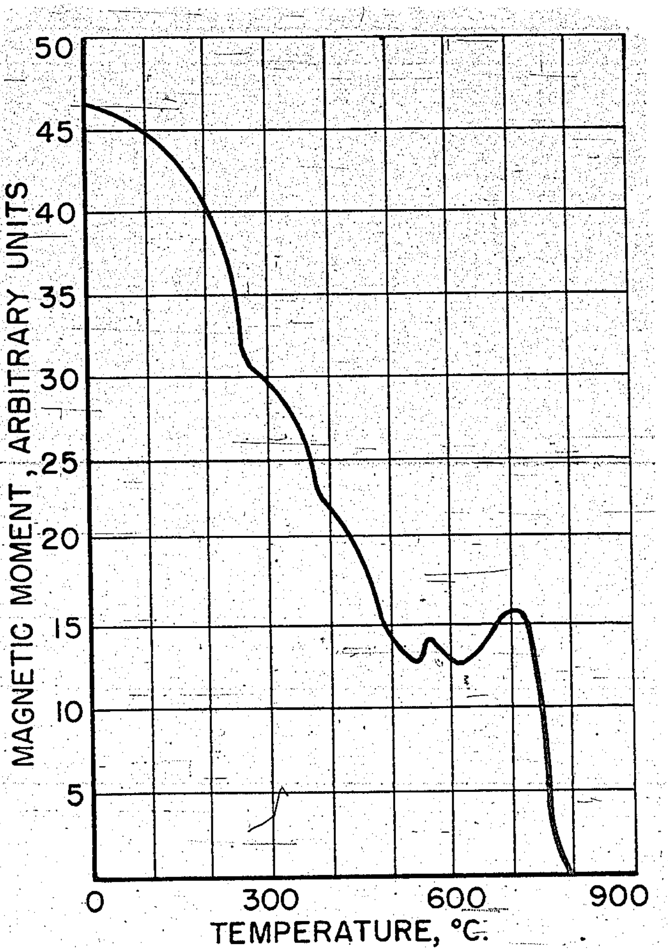

Figure 52.—Thermomagnetic curve of an active catalyst used for synthesis at atmospheric pressure and poisoned by extraction with sulfur-containing diesel oil. L-635

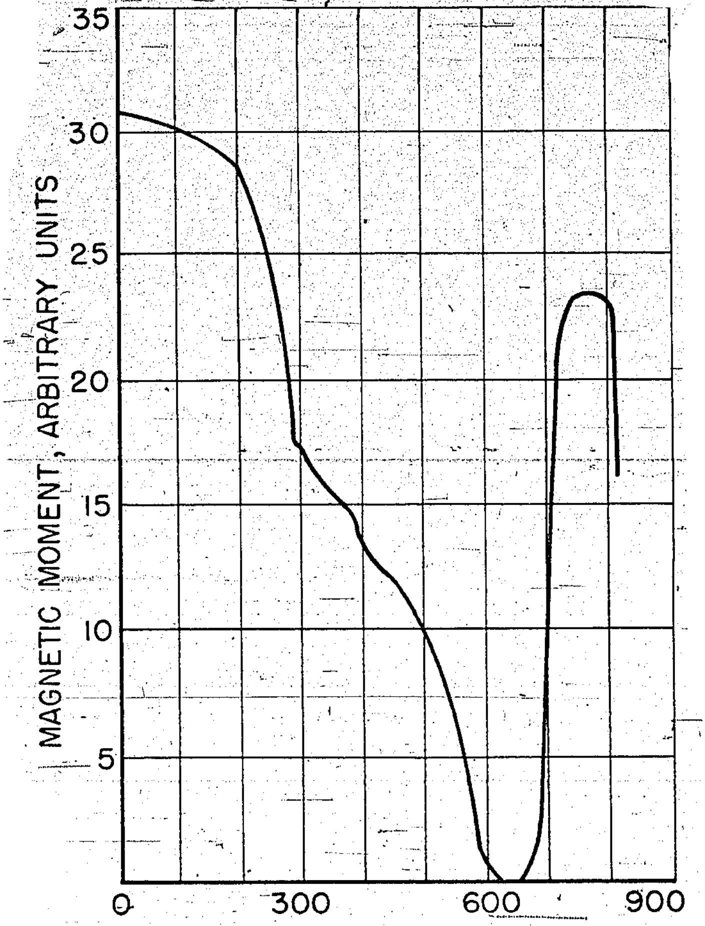

Figure 53.– Thermomagnetic curve of Fe, Cu, K_2CO_3 (100: 20: 0. 25) catalyst at high activity.

L-636

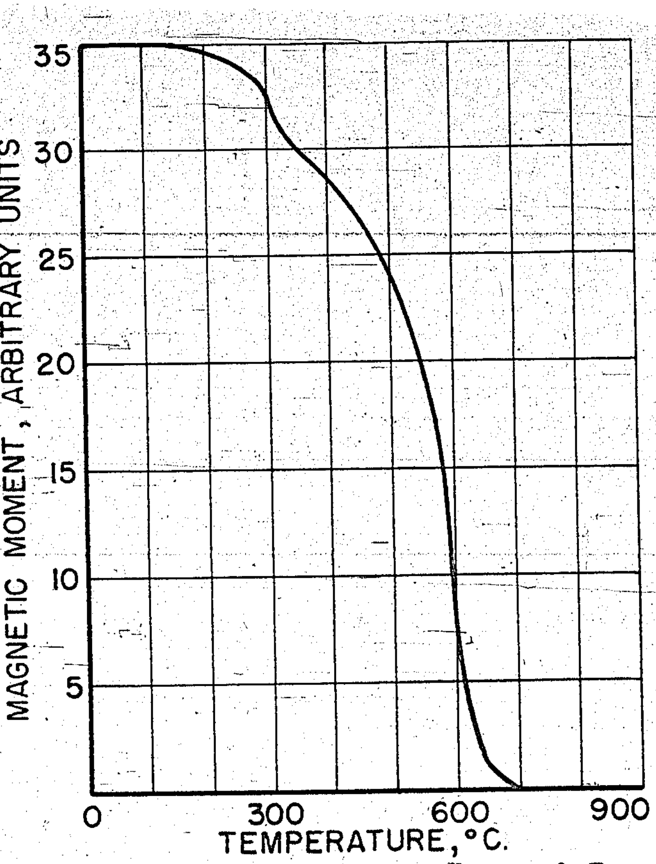

Figure 54 – Thermomagnetic curve of Fe, Cu, K_2CO_3 (100: 20: 0.25) catalyst at low activity. L-637

carbide. Magnetite was present in large amounts, as indicated by the Curie Point at 590°C. The amount of iron carbide in the inactivated catalyst was extremely small. The catalyst consisted chiefly of magnetite which was formed by oxidation of the carbides.

The following experiment again illustrates the need of iron carbide for the synthesis. An iron catalyst that gave a 30-percent contraction when operated at atmospheric pressure was reduced with hydrogen at 400°C. Synthesis gas was then passed over the reduced catalyst, which reached a contraction of 10 to 12 percent in the course of several days. It is apparent from the thermomagnetic curve that the catalyst consisted of metallic iron (figure 55). The catalyst was almost completely inactive for the gasoline synthesis in this state. Metallic iron is not capable of catalyzing the formation of hydrocarbons from carbon monoxide and hydrogen, and the iron formed by reduction at 400°C. could not be carbided at the prevailing synthesis temperature. It should be mentioned that iron catalysts which were reduced to the free metal by hydrogen at 250°C. reacted almost completely with carbon monoxide at 205°C. to yield higher iron carbides.

Summary

The outstanding characteristic of atmospheric pressure synthesis was that the catalysts formed both the higher iron carbides in approximately equal amounts with synthesis gas at 220 to 230°C. (assuming that the specific magnetization of the two carbides is of the same order of magnitude). The formation of the Curie Point 380°C.

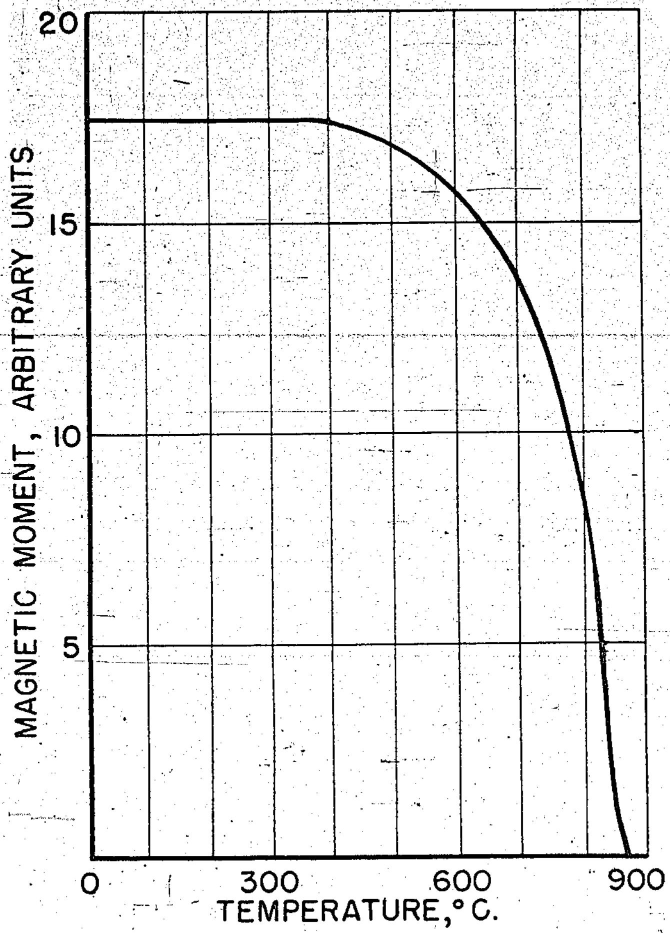

Figure 55. – Thermomagnetic curve of an active iron catalyst after reduction with H_2 at 400° C.

L-638

carbide was favored by the low reaction temperature and by the high copper content of the catalyst, as shown in earlier experiments on the formation of this carbide.

After operation for several days, the catalysts still contained appreciable amounts of magnetite, although free iron and iron carbide are stable in the presence of the synthesis gas used. This fact cannot be explained as resulting from the limitation of the reaction to the surface of the catalyst particles since it is known that variation of grain size between 1 and 5 millimeters has no effect on the activity. When the grain size exceeds 5 millimeters, the catalyst disintegrates quickly because of insufficient heat removal. Because of its large internal surface, the catalyst is completely penetrated by the synthesis gas.

These results show that it is useful to distinguish between two groups of iron catalysts:

(1) Copper-free iron catalysts which are pretreated with carbon monoxide at low pressure and 325°C., and are operated at pressures between 10 and 20 atmospheres;

(2) Iron catalysts with a high copper content which are pretreated with synthesis gas at atmospheric pressure and 225°C., and which can be used both in atmospheric-pressure and in medium-pressure synthesis.

The results obtained with iron catalysts during medium- and atmospheric-pressure synthesis show that in the former, the carbide-oxide equilibrium is established during synthesis by a decrease in the amount of carbide which had been formed during pretreatment, whereas the latter reach equilibrium by gradually forming the carbide during treatment with synthesis gas at 220° to 230°C.

As a result of the low operating temperature and pressure, formation of free carbon was completely eliminated during operation at atmospheric pressure.

The Mechanism of the Synthesis

These experimental results leave no doubt about the necessity of higher iron carbides in the Fischer-Tropsch process over iron catalysts. According to Fischer and Tropsch these compounds act as intermediates which are continually hydrogenated and regenerated, the first reaction product being (CH_2) radicals. Craxford[121] thought he could explain the synthesis over cobalt in such a manner by showing that cobalt catalysts react with carbon monoxide at synthesis temperature to yield a carbide which can be hydrogenated at atmospheric pressure and 140°C.

The stability of iron carbides at synthesis temperature, and the fact that metallic iron and cementite are not decomposition products in the synthesis, make it seem likely that other products are important in addition to the carbides whose presence has been demonstrated thermomagnetically. These products are probably unstable and perhaps are surface combinations. When carburization and hydrogenation proceed

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[121] Craxford, S. R., [Fischer-Tropsch Synthesis of Hydrocarbons and Some Related Reactions]: Brennstoff Chem., vol. 20, 1939, pp. 263-270.

simultaneously, (CH_2) radicals are formed and adsorbed as polymethylenes on the catalyst surface. With large amounts of chemisorbed hydrogen only methane is formed. If little hydrogen is present, predominantly straight-chain paraffins and olefins are desorbed, whose molecular size and degree of saturation are determined by the amount of chemisorbed hydrogen, by the contact time with the catalyst, and by the relative reducing and polymerizing activity of the catalyst.

DISCUSSION OF EXPERIMENTAL RESULTS AND SUMMARY

The composition of iron catalysts at various stages of pretreatment and synthesis in the Fischer-Tropsch process was determined by chemical and thermomagnetic analysis. During carburization of copper-free iron catalysts free carbon was formed continuously, its rate of deposition increasing with longer contact time, higher pressure, and especially with higher carburization temperature. This formation of elementary carbon probably continued during medium-pressure synthesis, especially in the presence of carbon monoxide-rich gas and at high operating temperatures. The thermomagnetic method revealed that copper-free iron catalysts, carburized at 325°C. prior to medium-pressure synthesis, were virtually completely transformed to a ferromagnetic higher iron carbide with a Curie Point of 265°C., whose formula corresponded approximately to Fe_2C.

Carburization of copper-promoted (20 percent Cu) iron catalysts at 220° to 230°C. prior to atmospheric-pressure synthesis yielded not only the Curie Point 265°C. carbide but also a second ferromagnetic iron carbide whose Curie Point was 380°C. Thus higher, iron carbides and their Curie Points have been detected by the thermomagnetic method; they could not have been found by the hydrogen reduction method. At the same time, the theory advanced by Fischer and Tropsch concerning the formation of higher carbides in these catalysts has been confirmed experimentally. At 205°C. iron was carburized largely to the Curie Point 380°C. carbide. However, the Curie Point 265°C. carbide was always present. Consequently, the formula Fe_2C derived by Gluud and Ritter, and by Bahr and Jessen, for an iron carbide prepared at 220°C., does not correspond to a homogeneous compound.

A systematic study of the thermal stability of the higher iron carbides showed that the Curie Point 265°C. carbide is the more stable of the two. It reverts to Fe_3C above 400°C. without any marked change in the specific magnetization at room temperature. The Curie Point 380°C. carbide is unstable above 300°C. and is ultimately also converted to cementite and free iron above that temperature.

Determination, by acid decomposition, of the carbidic carbon content of carburized iron catalysts always gave values that were only half those obtained by reduction with hydrogen at atmospheric pressure. This difference is explained by the formation of higher iron carbides whose decomposition by acid was not accompanied by quantitative hydrogenation of carbidic carbon, as in the case of cementite. Actually, almost half the carbon reverted to free carbon, which also explains the large amount of hydrogen evolved.

The higher iron carbides formed during carburization were stable during the synthesis. During carburization at 325°C. and during subsequent medium-pressure synthesis, the Curie Point 265°C. carbide was virtually the only carbide present. Carbide-oxide equilibrium was established during the first days of operation by partial oxidation of the large amounts of carbide that had been formed during pretreatment. Once equilibrium was established, active catalysts maintained their carbide content unchanged. A decrease in catalytic activity was marked by a drop in the carbide content and by an increase in the oxygen content. Thus, both acid decomposition and thermomagnetic analysis showed that the activity of iron catalysts in the Fischer-Tropsch process was higher when more carbide was formed during pretreatment.

Iron catalysts with a high copper content consisted of approximately equal amounts of Curie Point 265°C. and Curie Point 380°C. carbide during operation at atmospheric pressure. These carbided catalysts gave almost quantitative conversion of the carbon monoxide in water gas, with liquid and solid hydrocarbons as the principal products. When a catalyst thus carbided was operated at medium pressure (10 to 20 atmospheres) instead of atmospheric pressure, the optimum synthesis temperature dropped from 220°C. to 205°C. for the same conversion capacity. This increase in activity (compared with catalysts carburized at 325°C. with carbon monoxide) was probably due to the presence of the Curie Point 380°C. carbide which characterizes atmospheric pressure synthesis.

When the synthesis proceeded at a lower temperature there was no formation of free carbon during carburization and synthesis; at the end of the pretreatment process carbide formation and conversion capacity had reached their maximum values, and no further carbon appeared.

A current of hydrogen had little effect on the higher iron carbides in the temperature range of the synthesis.

In contrast to Hofmann's carburized pure iron which always contained cementite, iron catalysts carbided up to 325°C. had no Curie Point corresponding to cementite. But the thermomagnetic curves showed additional Curie Points at 130° to 140°C. and at 425°C., probably due to potassium ferrite and copper ferrite, respectively.

These results make it necessary to modify Fischer and Tropsch's interpretation of the mechanism of hydrocarbon formation on iron catalysts. It now seems probable that the higher iron carbides do not themselves act as synthesis intermediates, but that they are important for the structure of the catalyst and that in their presence other products, such as surface compounds, may be formed.

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