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

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PREFACE

By L. J. E. HOFER[5]

This document contains many 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 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.

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 Oil Mission teams at the Kaiser Wilhelm Institut für Kohlenforschung.[6]

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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 meanwhile 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, in partial fulfillment of the requirements for the Ph.D. degree. The entire latter 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 the entire translation.

In order to integrate the information in the thesis with existing data that were either unpublished or inaccessible to Pichler and Merkel in writing their paper, a foreword entitled, "Introduction to the Carbides of Iron and Their Physical and Chemical Properties," by L. J. E. Hofer, follows. (Immediately after the foreword is inserted an appendix 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

FOREWORD

By L. J. E. Hofer[7]

INTRODUCTION TO CARBIDES OF IRON AND THEIR PHYSICAL AND CHEMICAL PROPERTIES

Almost simultaneously with the first announcement of the so-called "Fischer-Tropsch reaction," the carbides were suggested as intermediates 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 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 the Fischer-Tropsch synthesis, compared the rate of the synthesis,

$$2xCO + x\,H_2 \longrightarrow (CH_2)_x + xCO_2,$$
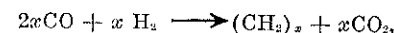
with the rate of carbide formation,

$$2CO + 2Fe \longrightarrow Fe_2C + CO_2,$$
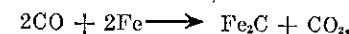
and showed that the rate of formation of the carbide and hydrogenation of the carbide for certain iron catalysts was more

[7] See footnote 5 (p. 1).

[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 1690, 1898.

[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]: Compt. rend., vol. 203, 1936, pp. 1378–1380. [Synthesis with Hydrogen and Carbon Monoxide Over Iron Catalysts]: Congres chim. ind., Compt. rend. 18th Congres, Nancy, September–October 1938, pp. 725–730.
LeClerc, G. [Catalytic Activity of Cubic Iron Sesquioxide in Synthesis with Hydrogen and Carbon Monoxide at Atmospheric Pressure]: Compt. rend., 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 Tech. Paper 709, 1948, 213 pp.

[14] Eidus, Ya. T., and others [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-Thorin-Potassium Carbonate-Kieselguhr]: Bull. Acad. Sci. U.R.S.S., Classe Sci. Chim., 1945, pp. 62–70. Universal

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. The experimental techniques by which this evidence was obtained can give information only about carbide in bulk[16] and not about surface carbide.[17] But it is quite unlikely that bulk carbide is an intermediate, since it is well-known that most heterogeneous gas reactions proceed on active 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 quantity of hydrocarbon formed from bulk carbide during Fischer-Tropsch synthesis was small compared with that 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, this "hexagonal nickel"

Oil Products Co. 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 Co. Surv. For. Petrol. Lit., Transl. 656.

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 Co. 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 Co. 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 Co. Surv. For. Petrol. Lit., Transl. 441.

[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 Co. 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 Rept. 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.

[18] Kummer, J. T., De Witt, T. W., and Emmett, P. H., Some Mechanism Studies of the Fischer-Tropsch Synthesis Using C[14]: Abs. of Papers, 111th Meeting, Am. Chem. Soc., April 14–18, 1947, Div. of Physical and Inorganic Chemistry, 29 pp.

[19] Weller, S., Hofer, L. J. E., and Anderson, R. B., The Role of Carbide in the Fischer-Tropsch Synthesis: Jour. Am. Chem. Soc., vol. 70, 1948, pp. 799–801.

[20] LeClerc, G., and Michel, A. [Preparation and Properties of Hexagonal Nickel]: Compt. rend., vol. 208, 1939, pp. 1583–1585.

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

is really nickel carbide. This was originally pointed out by Craxford and Rideal.[22] The crystal structure of these two materials seems to be the same[23]; the conditions of formation and decomposition are similar—both are either strongly paramagnetic or weakly ferromagnetic. In short, they are identical.

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

[22] Craxford, 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. B26, 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.
[24] Manchot, W., and Manchot, W. J. [Preparation of Ruthenium Carbonyls and Nitrosyls]: Ztschr. anorg. Chem., vol. 226, 1936, p. 385.
Pichler, H., correspondence with author.

CEMENTITE

The best-known iron carbide is cementite; its physical and chemical characteristics are well-known. It occurs in carbon steels as a component of pearlite (0.9 percent carbon), the eutectoid mixture of α-iron (ferrite) and cementite; as a component of ledeburite (4.2 percent carbon), the eutectic mixture of γ-iron (austenite) and cementite; 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 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]

Cementite may also be formed by carburizing iron with carbon monoxide or methane at temperatures in the region of the α to γ transition ($910° \pm 3°C$. for pure iron) and cooling the product to room temperature. This process consists of two stages: First, during the actual carburization, and second, the formation of a solid solution of carbon in γ-iron (austentite) and 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 mediums 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 carbonrich 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 that is most likely related to cementite formation in the Fischer-Tropsch reaction. Samples of nearly pure microcrystalline cementite can be prepared in this

[25] Epstein, S., The Alloys of Iron and Carbon; vol. 1, Constitution: McGraw-Hill Book Co., New York, 1936, 476 pp.
[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.
[28] Hägg, G. [Powder X-ray Patterns of a New Iron Carbide]: Ztschr. Krist., vol. 89, 1934, pp. 92–94.

way. Carbon monoxide and hematite form cementite at about $500°C$.[29] Other methods for preparing cementite have been reported, such as decomposition of potassium ferrocyanide.[30]

Mittasch, Kuss, and Emert[31] decomposed $Fe(CN)_2$ with hydrogen 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 believe that the reverse occurs.[33] The carbide of Halle and Herbst (see below) decomposes into the Hägg carbide. Martensite and retained austenite (carbonrich) 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 $a_o = 4.514–4.507$ A., $b_o = 5.079–5.073$ A., and $c_o = 6.730–6.734$ A.[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 of cementite occurs at about $205°$ to $220°C$.[36]

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

$$Fe_3C + 6H+ \longrightarrow 3Fe^{++} + (CH_2)_x + 2H_2,$$
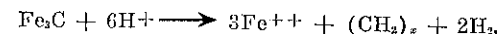
is not quantitative under all conditions. High hydrogen and low ferrous ion concentrations favor complete conversion to hydrocarbons. This is not simply an example of the mass action law because high ferrous ion concentration favors carbon deposition. The reaction is not well-adapted to quantitative 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.

[29] Lipson, H., and Petch, N. J., The Crystal Structure of Cementite, Fe₃C: 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.
[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 in 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 Physicochemical Study of Carburized Steel]: Dissertation, Upsala, 1904, p. 215.
[36] Honda, K., and Murakami, T. [On the Thermomagnetic Properties of the Carbides Found in Steels]: Sci. Rept., Sendai, ser. 1, vol. 6, 1917, pp. 23–29.
[37] Schenck, R., and Stenkhoff, R., work cited in footnote 26.

MARTENSITE

Martensite may be regarded as a deformed supersaturated solid solution of carbon in α-iron,[38] formed by very rapid quenching of a solid 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 ± 0.3 percent carbon at 1,150°C.[39] The lattice parameter varies with carbon content from 3.564 X.u. for pure γ-Fe to 3.62 X.u. 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 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 ± 0.02 percent at the eutectoid temperature (723°C.). At room temperature, the maximum carbon content is 0.006 ± 0.003 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.

[38] Lipson, H., and Parker, A. M. B., The Structure of Martensite: Jour. Iron Steel Inst., vol. 149, 1944, pp. 123–141.
[39] Petch, N. J., The Positions of the Carbon Atoms in Austenite: Jour. Iron Steel Inst., vol. 145, 1942, pp. 111P–128P.
[40] Koster, W. [The Effect of Heat Treatment Below the A₁ Point on the Properties of Technical Iron]: Archiv, Eisenhüttenwesen, vol. 2, 1929, pp. 503–522.

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. 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 unable to identify, in the diffraction patterns, the spacings of Brill and Mark or 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 the appendix. 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.

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

[41] Brill, R. and Mark, H., work cited in footnote 30.
[42] Hofmann, U., and Groll, E. [Carbon Deposition from Carbon Monoxide on Iron III. Formation of Iron Oxides and Carbides]: Ztschr. anorg. allgem. Chem., vol. 191, 1930, pp. 414–428.
[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 Catalyst]: Bull. Inst. Phys. Chem. Research, Tokyo, vol. 8, 1929, pp. 609–613.
[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 in footnote 28.

TABLE 1.—*Comparative X-ray diffraction data of the carbides of Tutiya, Hofmann and Groll, and Brill and Mark*

Tutiya, d/n	Hofmann and Groll		Brill and Mark, d/n
	d/n	I[1]	
2.32	2.263	m.	2.28
2.20	2.172	m.	—
2.065	2.050	st.	2.12
1.815	1.862	v.w.	1.826
1.706			1.716
—	1.543	m.	—
—	1.465	w.	1.491
1.377	1.372	w.	1.367
1.251	1.244	v.w.	—
1.212	1.212	m.	1.206
1.165	1.167	m.	1.148

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

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 before 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 has an hexagonal close-packed structure as far as the iron atoms are concerned. The results of this study are being published.[46] This Pichler and Merkel carbide may be the same as the hexagonal carbide of Herbst and Halle.

CARBIDE OF BAHR AND JESSEN

Bahr and Jessen[47] 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 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.

[46] Hofer, L. J. E., Cohn, E. M., and Peebles, W. C., The Modifications of the Carbide Fe₂C: Their Properties and Identification: Jour. Am. Chem. Soc. In press.
[47] 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.

CARBIDE OF HÄGG

Hägg,[48] 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[49] whose reflecting interplanar spacings are the same as those of the carbide of Hägg. Jack considered the crystalites 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[50] 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 stabilized 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.[51] In a later paper, in which considerably more data were presented, Michel stated that the lowest possible Curie point of a saturated solid solution of K_2O in γ-Fe_2O_3 is 630°C.[52] In view of this contradiction in the literature, other explanations for the 250°C. Curie point observed by Lefebvre and LeClerc may be advanced.[53] 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.

[48] Hägg, G., work cited in footnote 28.
[49] Jack, K. H., work cited in footnote 32.
[50] Lefebvre, H., and LeClerc, G., work cited in footnote 12, p. 3.
[51] Michel, A., and Chaudron, G. [Study of Stabilized Cubic Iron Sesquioxide]: Compt. rend., vol. 201, 1935, pp. 1191-1193.
[52] Michel, A. [Magnetic Properties of Some Solid Solutions]: Ann. Chim., 11th ser., vol. 8, 1937, pp. 317-423.
[53] Storch, H. H., Anderson, R. B., Hofer, L. J. E., Hawk, C. O., Anderson, H. C., and Golumbic, N., work cited in footnote 13, p. 3.

By treating a precipitated-iron catalyst (1 percent Cu and 1.5 percent K_2CO_3) with carbon monoxide (0.1 atmosphere pressure and 325°C.), Fe_3O_4 (magnetite) was obtained first, then the Curie-point 265°C. carbide. In 12 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[54] (reduction with hydrogen 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 X-ray technique alone. However, as they pointed out, this 265°C. Curie point is beyond question due to the same phase that Lefebvre and LeClerc[55] considered cubic iron oxide (γ-Fe_2O_3).

Recent X-ray diffraction and thermomagnetic work by 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 published.[56]

CARBIDE OF DURAND

Calcium carbide reacts with an aqueous solution of ferrous chloride to yield the corresponding acetylide and a solution of calcium chloride.[57] 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 instances and not at all adequate 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, and Tutiya are similar in their X-ray diffraction patterns. Tutiya 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 does not fit in well with those of Hofmann and Groll and Tutiya. The Pichler and Merkel carbide II, with Curie point

[54] Bahr, H. A., and Jessen, V., work cited in footnote 47.
[55] Lefebvre, H., and LeClerc, G., work cited in footnote 12, p. 3.
[56] Hofer, L. J. E., Cohn, E. M., and Peebles, W. C., work cited in footnote 46.
[57] Durand, J. F. [Double Decomposition of Metallic Acetylides and Salts in Aqueous Solutions]: Compt. rend., vol. 177, 1923, pp. 693–695.

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}	$a_0 = 4.51$ $b_0 = 5.08$ $c_0 = 6.73$ kx	205–220	139	700–800	a. Rapid cooling of solution of carbon in Fe to room temperature. b. Carburization of γ-Fe with carbon-rich gas followed by cooling to room temperature. c. Decomposition of higher carbide.
	Martensite	do	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. Carbide appears as an impurity in a mixture of $Fe(CN)_2$ + Fe.
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_2C	Carbide of Tutiya.	Similar to Hofmann and Groll, and Brill and Mark's carbide							Action of CO on iron oxide.
	Carbide of Halle and Herbst.		Hexagonal						
Fe_2C	Carbide of Pichler and Merkel II					380	~140	Decomposes to Hägg carbide.	Develops in Fe Fischer-Tropsch catalysts during synthesis at comparatively low temperatures.
Fe_2C	Carbide of Bahr and Jessen.							About 800	Develops in reduced Cu-promoted Fe Fischer-Tropsch catalysts carburized at 205°C. obtained only in presence of Pichler and Merkel carbide I.
									Action of CO on reduced iron oxide at 225°C., product nearly free of free carbon.

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
	Carbide of Hägg.	Different from all above patterns.							Similar to Bahr and Jessen's carbide. Carburization of reduced Fe oxide at 225°C.
Fe₂C	Carbide of Jack.	Similar to Hägg carbide.	Ortho-rhombic		$a_0 = 9.04$ kx $b_0 = 15.66$ kx $c_0 = 7.92$ kx				Action of CO on iron nitride.
	"Cubic iron oxide" of Lefebvre and LeClerc.					250			Develops in Fe Fischer-Tropsch catalysts during synthesis.
Fe₂C	Carbide of Pichler and Merkel I.					265	~140	About 400	Develops in Fe Fischer-Tropsch catalysts during carburization at 325°C.
Fe₂	Carbide of Durand.								Action of CaC₂ on aqueous solution of FeCl₂.

380°C., has been tentatively identified with the Hofmann and Groll-Tutiya carbide by means of new Bureau of Mines data.

The carbide of Bahr and Jessen never was 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 116, frames 1673–1683) it appears that the Hägg carbide (Curie point found, ⁓250°C.) was also formed in Rheinpreussen (Moers, Ruhr Valley) catalysts during synthesis, although the distinctly different carbide was not recognized as such but was termed "unstable cementite."

APPENDIX

Two reports of the I. G. Farbenindustrie[58] 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 carbide was found by Dr. Herbst to be converted into the familiar Fe_2C carbide of Hägg. The addition of copper has a marked inhibitory effect on this change, and copper may therefore be considered to act as stabilizer for an intermediate state of the catalyst first arising during synthesis. The addition of 2 percent of copper, for instance, raises the conversion temperature by about 50°.

*   *   *

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.

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