TABLE 49.—*Bromine numbers of Fischer-Tropich products from cobalt–thoria–magnesia–kieselghur catalysts operated at atmospheric pressure*

Test No.	Catalyst	Form	Operating temp., °C.	Synthesis gas flow rates		Bromine No.
				Vols./vol. of catalyst/hour	cc./g. of catalyst/hour	
X-17b to k	89K	Granules	186	100	296	12.5
17p	89K	do	170	44	130	10.5
18b to k	89K	do	188	100	312	13.6
18p, q	89K	do	178	44	157	8.7
19b to k	89K	Pellets	176	100	129	6.2
19q	89K	do	184	164	211	10.4
19r	89K	do	189	228	294	12.3
19s	89K	do	194	308	397	12.7
19t	89K	do	199	391	504	25.5
19n	89K	do	209	599	772	33.0
19m	89K	do	218	690	889	28.6
20b to f	89N	do	193	98	112	10.5
21c to k	89J	do	185	112	184	11.7
22b to k	89O	do	181	96	168	7.3
22m	89O	do	192	157	275	16.1
22n	89O	do	198	208	365	14.9
22o	89O	do	202	271	476	14.6
22p	89O	do	206	351	616	28.5
22q	89O	do	207	296	520	20.2
22r	89O	do	192	159	279	11.7
23b to k	89I	do	190	97	125	9.2
24b to k	89H	do	194	95	135	9.0
26b to f	89I	Granules	194	100	455	15.0
27b to k	89Q	Pellets	182	100	146	8.8
27l	89Q	do	192	165	241	14.5
27m	89Q	do	192	145	212	21.2

In the tests at 100 pounds per square inch, about 90 percent of the product was a solid mixture of wax and oil whose bromine number was zero in all cases. The gaseous products formed at 100 p. s. i. were more saturated than those from tests at atmospheric pressure. This is illustrated in table 50 by the averages for the gaseous products recovered from the charcoal trap in test X21.

TABLE 50.—*Analysis of gaseous products recovered from charcoal trap in test X21*

Average of weeks	Pressure	C3		C4		C5	
		Saturates	Unsaturates	Saturates	Unsaturates	Saturates	Unsaturates
		Percent by volume					
c to n	1 atmos.	29.4	13.3	15.9	11.0	6.3	5.6
o to w	100 p. s. i.	35.6	8.2	20.0	5.2	8.8	1.7

CORRELATION OF PHYSICAL PROPERTIES OF CATALYSTS WITH THEIR ACTIVITY

X-RAY DIFFRACTION PATTERNS AND MAGNETIC PROPERTIES OF IRON CATALYSTS

INTRODUCTION

It is now generally recognized that such characteristics as crystal structure, surface area, particle size, crystallite size, crystal habit and orientation, lattice parameter of crystallites, impurities, intermediate compounds, etc., may profoundly influence the course and rate of a catalytic reaction occurring on a solid catalyst.[7] [8] [9] Physical and chemical procedures which can give information about characteristics such as these may be expected to yield important information about the mechanism of catalysis and may give important clues for the preparation of superior catalysts. Such characteristics may be studied with a large number of available tools. For example, surface area may be measured by the Brunauer-Emmett-Teller method[9]; crystal habit, orientation, and lattice parameter may be attacked by well known X-ray and electron diffraction methods; particle size and shape may be studied by the small angle scattering of X-rays[10]; crystallite size and shape may be studied by the X-ray diffraction method of Scherrer, Laue, and Brill.[11] The crystalline phases of catalysts may be identified by the X-ray diffraction analysis method of Hanawalt.[12] The catalyst characteristics described above are not the only important ones nor are the methods described for their determination exclusive.

For catalysts that contain either ferromagnetic or potentially ferromagnetic constituents, various magnetic studies constitute powerful tools, although such studies in the past have not been nearly as exhaustive as possible. A very instructive example of what can be done is illustrated by the paper of Morris and Selwood.[13] By means of the magnetic balance, it is possible by determination of Curie points to identify crystalline ferromagnetic phases. When the ferromagnetic phases are well-crystallized it is possible to make a quantitative as well as qualitative determination of the ferromagnetic phase. Even when such clear-cut determinations are not possible, the presence or absence of ferromagnetism as indicated by field dependence of the magnetic susceptibility may be of great significance. For example, in the paper of Morris and Selwood, which dealt with copper catalysts containing traces of nickel, it was shown that the active catalysts were ferromagnetic, whereas the inactive catalysts were paramagnetic.

[7] Beek, O., Catalysis, A Challenge to the Physicist: Review of Modern Physics, vol. 17, 1945, pp. 61–71.
[8] Brunauer, S., The Adsorption of Gases and Vapors, Physical Adsorption: Princeton University Press, 1943, 511 pp.
[9] Morris, H., and Selwood, P. W., Magnetic Measurements on Some Catalytically Active Substances: Jour. Am. Chem. Soc., vol. 65, 1943, pp. 2245–2252.
[10] Guinier, A., Determination de la taille des particules submicroscopiques par les rayons X: Jour. Chim. Phys., vol. 40, 1943, pp. 133–150.
[11] Brill, R. T., Teilchem Grössenbestimmungen mit Hilfe von Röntgenstrahlen: Ztschr. Krist, vol. 68, 1928, pp. 387–403.
[12] American Society for Testing Materials, Data Cards for the Identification of Crystalline Materials by the Hanawalt X-Ray Diffraction Method: Philadelphia, Pa.
[13] Work cited in footnote 9, p. 131.

The natural conclusion, therefore, is that in the inactive catalysts the nickel was in solid solution, whereas in the active catalysts it formed a separate phase. An effect such as this could not have been demonstrated by X-ray diffraction, since the smallest amount of a phase that can be identified by X-ray diffraction is about 2 to 5 percent. The magnetic balance is thus well-suited to demonstrating and identifying extremely small amounts of a ferromagnetic phase.

The experiments here described were made to survey the field of physical measurements as they related to Fischer-Tropsch catalysts. They are intended to be used as the basis for further experiments.

EXPERIMENTAL METHODS

X-RAY DIFFRACTION STUDIES

The X-ray diffraction studies were made by the powder method. A Debye-Scherrer-type cylindrical camera of 71.6-mm. diameter was used. The camera was equipped with collimating lead pinholes 0.030 inch in diameter and 4 centimeters apart. A finely ground sample of the catalyst was partially extruded from a ¾-inch length of 19 gage stainless-steel tubing of 0.7 millimeter inside diameter by means of a stainless-steel wire fastened in a pin vise. This method of preparing samples is described by Barrett.[14] Tubes of the required characteristics may be obtained from the Superior Tube Co., Norristown, Pa. No binder of any sort was used in the extrusion. The samples, although brittle, were strong enough to withstand the handling required in loading the camera. A commercial sealed-off iron target tube of the Coolidge type equipped with 0.01-inch beryllium windows designed especially for diffraction work was used. The target was designed so that there would be a line focus. The radiation was filtered with commercial manganese dioxide filters so that no iron K β radiation could be detected photographically. The tube was generally run at 50,000 volts and about 8 milliamperes. Exposures ran from 1 to 2 hours, using Eastman Kodak No-Screen Film.

Identification of the various crystalline phases was accomplished both by comparison with the patterns of the synthetic samples described on pages 138, 141, and 143, and by reference to the Hanawalt[15] index cards of X-ray reflections and other X-ray diffraction data in the literature.

MAGNETIC STUDIES

Figures 28 and 29 are photographs of the instrument used in making the tests. This magnetic balance was modeled after one described by Buehl and Wulff.[16] The magnet cores, yoke, and pole pieces were made of cold-drawn Armco ingot iron. The micarta spools were wound with 5,400 turns of double-cotton-covered No. 16 copper wire. A total of 5,200 feet of wire was used. The inside diameter of the

[14] Barrett, C. S., Structure of Metals: McGraw-Hill Co., New York, 1943, p. 118.
[15] Work cited in footnote 12, p. 131.
[16] Buehl, R., and Wulff, J., A Simple Magnetic Apparatus for Phase Transformation Studies of Ferrous Alloys: Rev. Sci. Instruments, vol. 9, 1938, pp. 224-228.
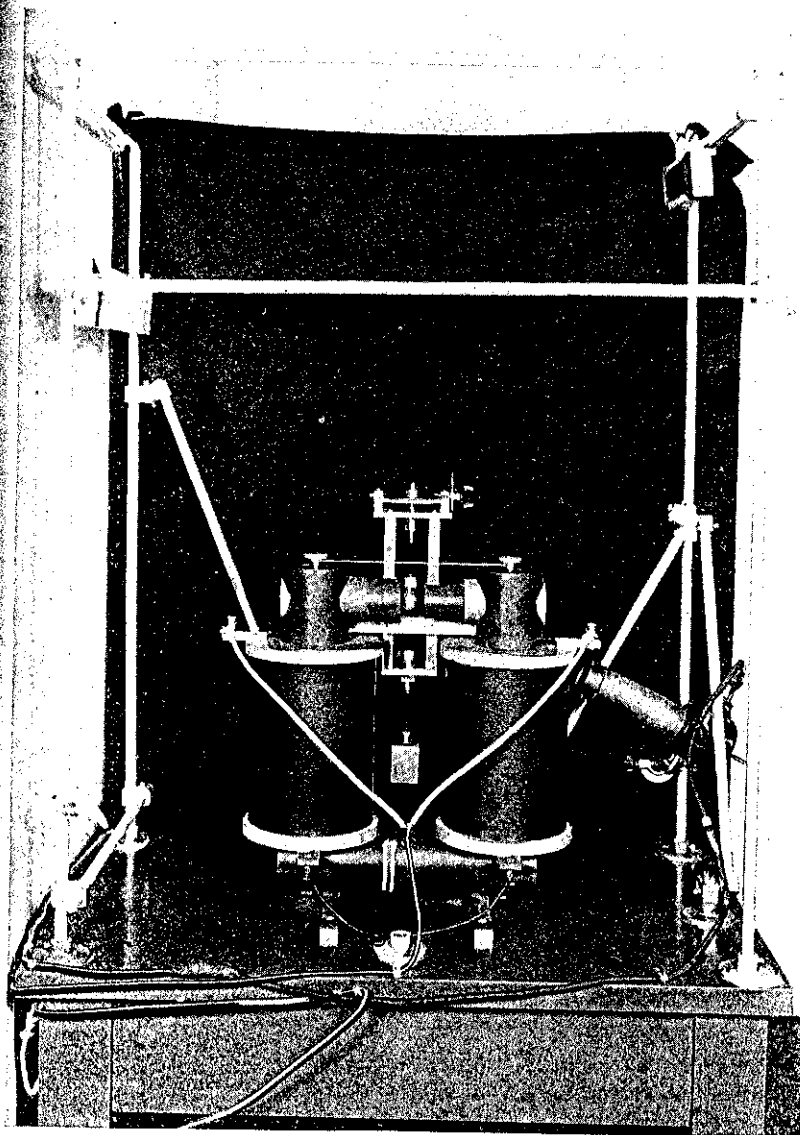
FIGURE 28.—Magnetic balance, front view.

spool was 2¼ inches, and its wall thickness was ¼ inch. The spool was 8½ inches tall and could be covered to 7½ inches of this height. The coil was about 1½ inches deep. The coils could be operated at 2½ amperes for extended periods without overheating. For short periods 3½ amperes have been used without detectable damage.
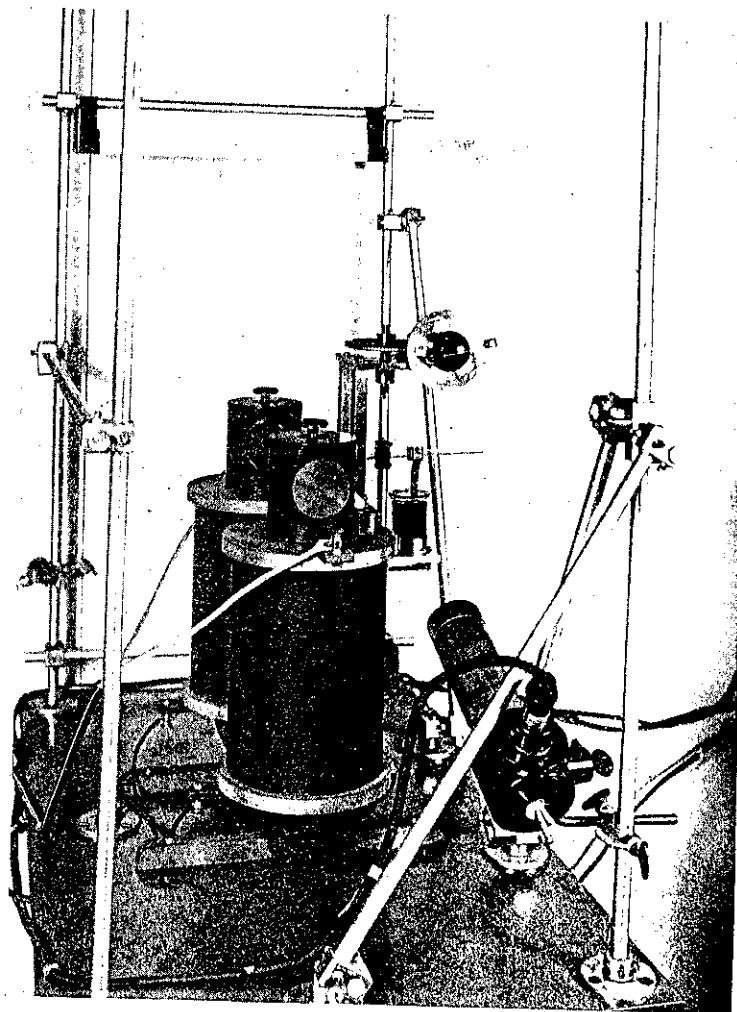
In this equation F is the force exerted in dynes, m is the mass of the sample in grams, H is the field strength in gauss, $\frac{dH}{ds}$ is the field gradient in gauss per centimeter, and X is the specific magnetic susceptibility in electromagnetic C. G. S. units. It is unnecessary, therefore, to locate the sample accurately along the polar axis. Because the pole faces are quite large compared with the usual sample (about 1 gram), the field gradient radial to the polar axis is less than 2 percent within 1 centimeter of the polar axis, and hence accurate radial location is unnecessary. This eliminates much of the very tedious field mapping necessary with other instruments and also the precision positioning of sample essential with other methods. The constancy of $H\frac{dH}{ds}$ along the polar axis also leads to another desirable result, stability of the

FIGURE 29.—Magnetic balance, side view.

According to the suggestion of Foreday,[17] and Buehl and Wulff,[17a] the two-pole faces were made unequal in diameter, and the larger pole piece was hollowed out on a radius of 3 inches. The purpose of this was to produce a magnetic field whose gradient along the polar axis is such that the product $H\frac{dH}{ds}$ anywhere along the polar axis is constant. The advantage of this condition is obvious when one considers that the equation for the magnetic force exerted on a paramagnetic body in a magnetic field; namely, $F=Xm\,H\frac{dH}{ds}$ contains the product $H\frac{dH}{ds}$.

[17] Foreday, R. A., A Method of Comparing Small Magnetic Susceptibilities: Proc. Phys. Soc., vol. 42, 1930, pp. 251–262.
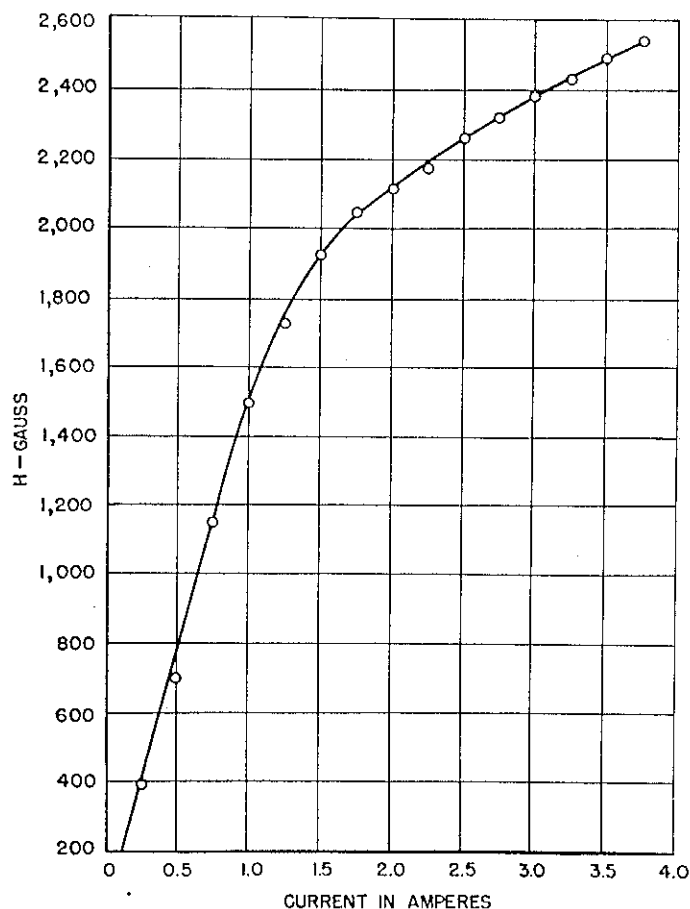[17a] Work cited in footnote 16, p. 132.

FIGURE 30.—Relationship between field strength and magnetizing current, for magnetic balance.

sample in the field. This factor will be discussed in the paragraph on the torsion balance.

For most of the work, a distance of 27 millimeters between the pole faces was used. In figure 30 the relationship between field strength and magnetizing current is given, using this interpolar distance. The field was measured with a Cenco fluxmeter. All the measurements were made at 2,120 gauss.

The sample was supported in the field by means of a glass tube attached to a vertical wire acting as the torsion filament of the balance. The upper end of the torsion wire was rotated by means of a worm-and-pinion arrangement and the amount of rotation determined on a dial. The lower end of the torsion wire did not rotate. The torsion wire was kept taut by means of a suspended weight. A small mirror was attached to the specimen support, and a beam of light was reflected from this mirror to a scale about 8 feet away. Any movement of the specimen was indicated by a corresponding movement of the beam on the scale. The position of the beam on the scale, and hence the position of the specimen in the field, was kept constant by applying a compensatory twist to the worm and pinion of the torsion head. The amount of this twist, read on the dial, was proportional to the magnetic force on the specimen.

The procedure used in making the measurements was as follows: The sample was placed in the holder between the poles, and an initial dial reading was taken with no field. Then the field was switched on, and another reading was taken. The field was again switched off, and a third reading was taken. Then the field was turned on, but in the reverse direction, for a fourth reading. Finally, for a fifth reading, the field was turned off. The difference between any two successive readings should be the same and was proportional to the magnetic force exerted by the specimen. In some cases the first two or three readings were not constant. In such instances another cycle of readings was run off. It was found that, even when the initial cycle was erratic, subsequent cycles of readings gave very satisfying checks. Those samples that gave these erratic results on the first cycle of readings seemed to be slightly ferromagnetic rather than paramagnetic.

The stability of sample in the field mentioned previously is a very important consideration. Stability is defined as the possibility of reaching stable equilibrium in any portion of the field between the poles without the danger of having the sample drawn to either pole. The condition for stability, as has been stated by Buehl and Wulff, is that the rate of increase of restoring force produced by the torsion balance must exceed the rate of increase of magnetic force. In a properly designed magnet of this type $H \frac{dH}{ds}$ is constant and hence F, the force on the sample, is constant throughout the field. Therefore, $\frac{dF}{ds}$ equals zero. However, due to fringing effects, ferromagnetic character of some samples, and other factors, $\frac{dF}{ds}$ is not quite zero. This puts a limit to the fineness of the suspension if both upper and lower suspensions are taken to be the same size.

The conditions for stability may be expressed mathematically:

$$\frac{d}{ds}(F_1+F_2) > \frac{dF}{ds},$$

or

$$\frac{T_1+T_2}{L^2} > \frac{dF}{ds},$$

where

F_1 = restoring force due to the upper part of the suspension,
F_2 = restoring force due to the lower suspension,
T_1 = torsion constant of upper suspension,
T_2 = torsion constant of lower suspension,
L = distance from specimen to the axis of rotation,
$\frac{dF}{ds}$ = rate of change of magnetic force with distance along the polar axis at the position of the sample.

Because the sum of the two torsion constants is involved in stability and only the upper torsion constant need be involved in sensitivity, requirements of stability and sensitivity can both be met by choosing the upper suspension to give the desired degree of sensitivity, while the lower suspension can be chosen stiff enough to insure stability. In most of the work, the upper suspension was a 0.01-inch-diameter phosphor-bronze wire, 2 inches long, while the lower suspension was a 0.02-inch-diameter phosphor-bronze wire also 2 inches long.

The specimen support was equipped with paddles dipping in oil in order to damp undesirable vibrations. The apparatus was so designed that a small furnace may be inserted between the pole faces about the specimen so that magnetic susceptibility may be studied as a function of temperature. This feature is necessary for use in the study of the Curie point of ferromagnetic phases, but so far only preliminary studies of this nature have been made. The instrument was calibrated with Mohr's salt, whose susceptibility was taken as 31.6×10^{-6}.[18]

FERRIC OXIDES AND FERRIC OXIDE HYDRATES

The only products which can be obtained by aging, hydrolysis, or precipitation from ferric salts, according to the literature, are hematite (αFe_2O_3), goethite ($\alpha Fe_2O_3 \cdot H_2O$), $\beta Fe_2O_3 \cdot H_2O$, or amorphous hydrous ferric oxide [19] [20] [21] [22] [23]; however, two other ferric oxides or hydrates are known—lepidocrocite ($\gamma Fe_2O_3 \cdot H_2O$) and maghemite ($\gamma Fe_2O_3$). Lepidocrocite has hitherto always been prepared from ferrous ion under conditions that favor complex ion formation, and maghemite [24] [25] either by the dehydration of lepidocrocite at temperatures below 400° C. or by the careful oxidation of magnetite.[24] [25] It is rather unlikely, therefore, that either $\gamma Fe_2O_3 \cdot H_2O$ or γFe_2O_3 will be present

[18] Jackson, L. C., Investigations on Paramagnetism at Low Temperatures: Trans. Roy. Soc., London, vol. A224, 1922, pp. 1–48.
[19] Weiser, H. B., and Milligan, W. O., An Electron Diffraction Study of the Hydrous Oxides Amorphous to X-rays: Jour. Phys. Chem., vol. 44, 1940, pp. 1081–1094.
[20] Weiser, H. B., and Milligan, W. O., The Constitution of Colloidal Systems of the Hydrous Oxides: Chem. Rev., vol. 25, 1939, pp. 1–30.
[21] Milligan, W. O., and Weiser, H. B., The Direct Examination of Sols by X-ray Diffraction Methods: Jour. Phys. Chem., vol. 40, 1936, pp. 1095–1102.
[22] Weiser, H. B., and Milligan, W. O., X-ray Studies on the Hydrous Oxides. VII. Ferric Oxide: Jour. Phys. Chem., vol. 39, 1935, pp. 25–34.
[23] Baudisch, O., and Milligan, W. O., X-ray Studies on the Hydrous Oxides. V. Beta Ferric Oxide Monohydrate: Jour. Am. Chem. Soc., vol. 51, 1935, pp. 238–241.
[24] Baudisch, O., and Albrecht, W. H., Gamma-Ferric Oxide Hydrate: Jour. Am. Chem. Soc., vol. 54, 1932, pp. 943–952.
[25] Welo, L. A., and Baudisch, O., Active Iron II, Relationships Among the Oxide Hydrates and Oxides of Iron and Some of Their Properties: Chem. Rev., vol. 15, 1934, pp. 45–95.

in the unpromoted catalysts prepared from ferric salts. However, because both $\gamma Fe_2O_3 \cdot H_2O$ and γFe_2O_3 are ferric compounds, the possibility that they may be formed during precipitation should not be overlooked. The crystalline properties of the three crystalline ferric oxide hydrates and the two crystalline ferric oxides are tabulated in table 51. Figure 31 shows the diffraction patterns of the crystalline ferric oxides and their hydrates. Figure 32 contains electron micrographs of α, β, and $\gamma Fe_2O_3 \cdot H_2O$.

TABLE 51.—*Crystalline ferric oxide hydrates and ferric oxides*

Formula	Name	Crystal system	Space group	Lattice parameters	Color
$\alpha Fe_2O_3 \cdot H_2O$	Goethite Nadeleisenerz	Orthorhombic	P b n m	$a_0 = 4.64$ $b_0 = 10.0$ $c_0 = 3.03$	Yellow
$\beta Fe_2O_3 \cdot H_2O$		do		$a_0 = 5.28$ $b_0 = 10.24$ $c_0 = 3.34$	Do.
$\gamma Fe_2O_3 \cdot H_2O$	Lepidocrocite Rubinglimmer	do	A m a m	$a_0 = 3.87$ $b_0 = 12.51$ $c_0 = 3.06$	Do.
αFe_2O_3	Hematite	Rhombohedral	R$\bar{3}$c	$a_0 = 5.42$ $\alpha = 55°17'$	Red
γFe_2O_3	Maghemite	Cubic	Closely related to spinel.	$a_0 = 8.31$	Do.

The magnetic susceptibility of the various synthetic ferric oxides and ferric oxide hydrates was determined and the results tabulated in table 52. The results agree with the data of Albrecht which have been indicated for comparison. No prior magnetic data on $\beta Fe_2O_3 \cdot H_2O$ were found.

TABLE 52.—*Magnetic susceptibility of ferric oxides and ferric oxide hydrates*

Phase	Albrecht	Bureau of Mines
$\alpha Fe_2O_3 \cdot H_2O$	42×10^{-6}	49.2×10^{-6}.
$\beta Fe_2O_3 \cdot H_2O$		28.9×10^{-6}.
$\gamma Fe_2O_3 \cdot H_2O$		42.2×10^{-6}.
αFe_2O_3	42×10^{-6}	25×10^{-6}.
γFe_2O_3	20×10^{-6} Ferromagnetic	Ferromagnetic.

The yellow compound, $\alpha Fe_2O_3 \cdot H_2O$, formed when solutions of ferric salts other than the chloride are slowly hydrolyzed or permitted to stand for long periods of time,[26] is identical with the mineral goethite and Nadeleisenerz. It may also be formed by the oxidation of ferrous salts under certain conditions; but if conditions for complex ion formation exist, the product may be $\gamma Fe_2O_3 \cdot H_2O$. The water of hydration of the well-crystallized goethite is lost below 270° C., whereas that of the more amorphous limonite is lost below 180° C.[27] Böhm prepared $\alpha Fe_2O_3 \cdot H_2O$ by digesting precipitated ferric oxide with KOH in an autoclave at 150° C. for 2 hours.[28]

[26] Work cited in footnote 18, p. 137.
[27] Work cited in footnote 25, p. 137.
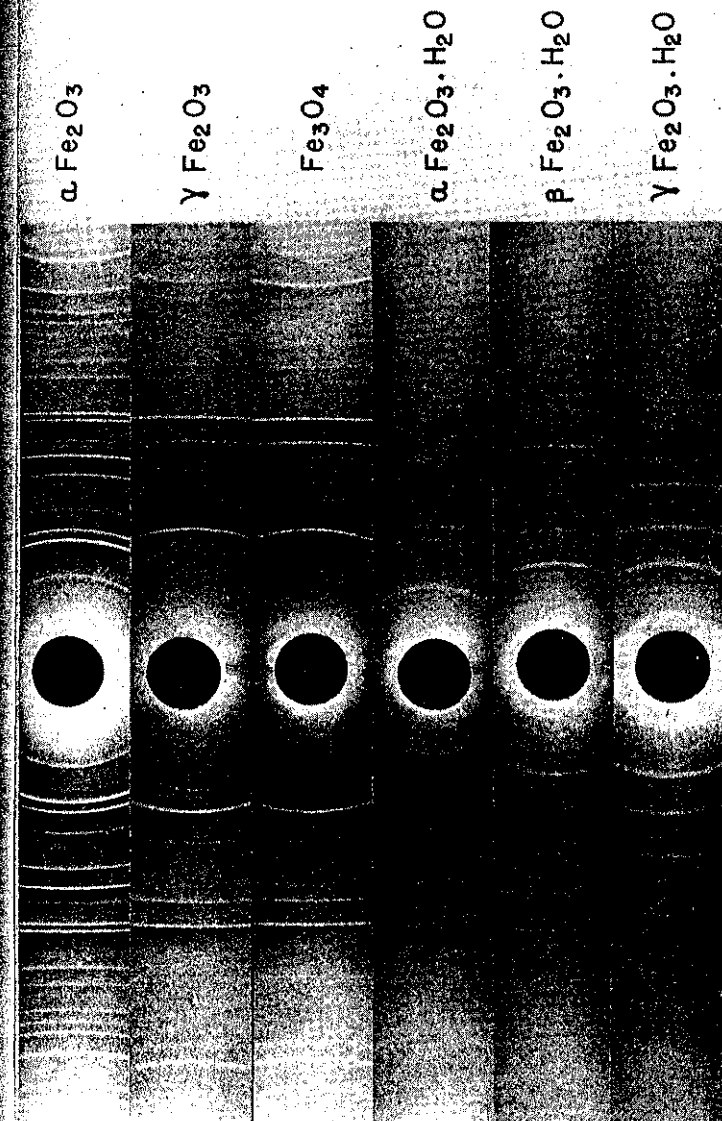[28] Böhm, J., Über Aluminum und Eisen Hydroxide I: Ztschr. anorg. allgem. Chem., vol. 149, 1925, pp. 203-216.

FIGURE 31.—X-ray diffraction patterns of some crystalline iron oxides and iron oxide hydrates.
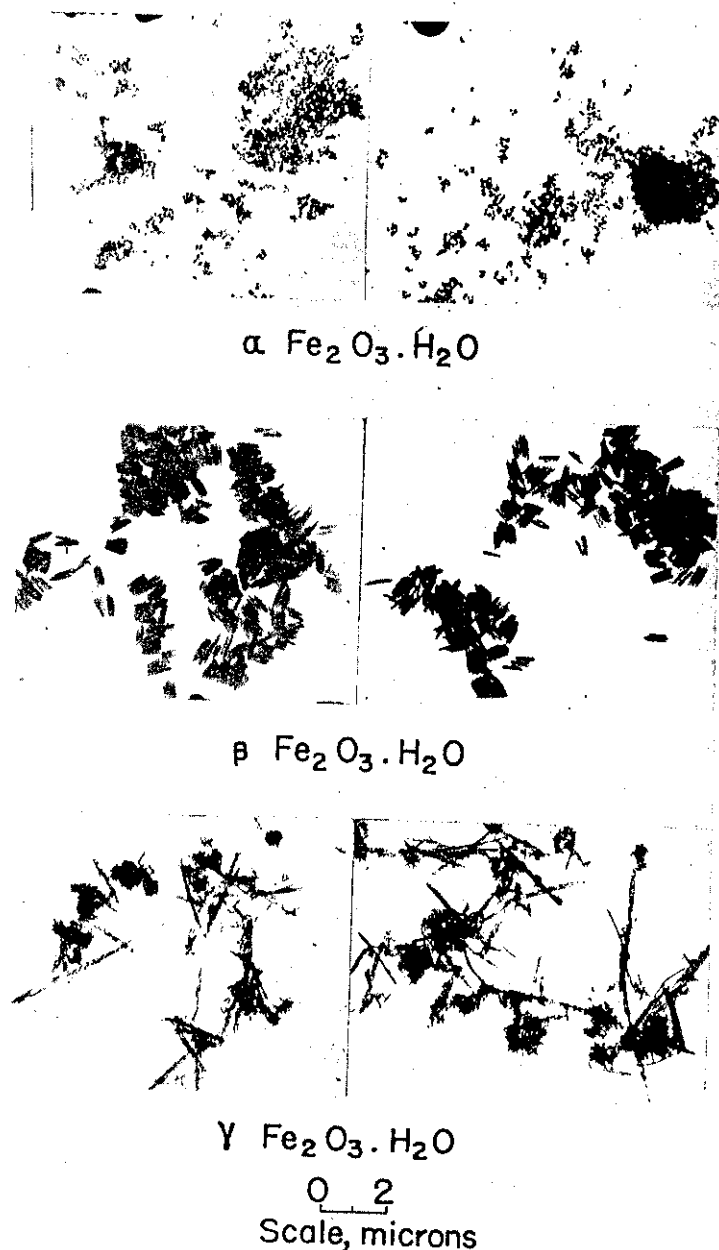
α Fe₂O₃.H₂O

β Fe₂O₃.H₂O

γ Fe₂O₃.H₂O

0 2
Scale, microns

FIGURE 32.—Electron micrographs of ferric oxide hydrates.

The synthetic sample of $\alpha Fe_2O_3 \cdot H_2O$ used in the present study was made by the method of Weiser and Milligan.[29] Twenty-nine grams of $Fe(NO_3)_3 \cdot 9H_2O$ were dissolved in 1 liter of water and heated slowly to boiling with constant stirring in a period of 16 hours. The filtered and air-dried product was a tan to chocolate brown powder.

The yellow precipitate formed by the slow hydrolysis of ferric chloride is not identical with either the hydrates $\alpha Fe_2O_3 \cdot H_2O$ and $\gamma Fe_2O_3 \cdot H_2O$ or with the oxides αFe_2O_3 or γFe_2O_3. Böhm showed that it had a unique X-ray diffraction pattern.[30] Schikorr[31] showed that the pattern was distinct from the basic chloride, FeOCl, of Stirnemann.[32] Böhm believed the yellow precipitate to be a basic chloride, but Schikorr, and Heller and Zocher[33] were uncertain as to whether it was a definite basic chloride. Schikorr, and Weiser and Milligan were able to show that this yellow precipitate contained 1 molecule of water per mole of Fe_2O_3. Weiser and Milligan have assembled a bibliography[34] dealing with the chloride content of ferric oxide hydrate precipitates prepared in such a way that the precipitate may be presumed to be $\beta Fe_2O_3 \cdot H_2O$. The chloride content expressed as Fe : Cl ratio varies from 2.33 to 8 in the papers of the bibliography. Weiser and Milligan[35] themselves experimentally found the content to vary from 4.79 to 45 in samples prepared in various ways. Weiser and Milligan take this evidence to mean that chloride ion is not an essential part of the structure. The function of the adsorbed chloride ion, they say, is to stabilize the $\beta Fe_2O_3 \cdot H_2O$ lattice. This is supported by their studies of the isobars; a sample with the Fe : Cl ratio of 4.79 lost its water of hydration at a temperature 50° higher than relatively pure samples (100° C.).

Kolthoff and Moskovitz[36] have made further studies on the yellow precipitate designated by Weiser and Milligan as $\beta Fe_2O_3 \cdot H_2O$. They have shown that the precipitate, when relatively chloride free, acts as an ion exchange agent when placed in dilute hydrochloric acid according to the reaction: $FeO(OH) + Cl^- \rightarrow FeOCl + OH^-$. No X-ray diffraction analysis was used in their work, and it has not been proved that the FeOCl of this reaction is identical with the FeOCl of Stirnemann.[37] Economy of hypotheses makes it desirable to assume that the FeOCl of the equation is $Fe_2O_3 \cdot H_2O$ with more Cl^- ion adsorbed than the original hydrate. Kolthoff and Moskovitz,[36] however, claim that a continuous series of solid solutions between the $\beta Fe_2O_3 \cdot H_2O$ of Milligan and Weiser[38] and the FeOCl of Stirnemann[37] is possible.

The synthetic sample of $\beta Fe_2O_3 \cdot H_2O$ used in the experiments described below was prepared by one of the methods of Weiser and

[29] Work cited in footnote 23, p. 137.
[30] Work cited in footnote 28, p. 138.
[31] Schikorr, G., Ueber das gelbe Eisen (III) Hydroxydsol: Kolloid Ztschr., vol. 52, 1930, pp. 25-31.
[32] Goldsztaub, S., Christallographie structure cristalline de l'oxy chlorure de fer: Compt. rend., vol. 198, 1934, pp. 667-669.
[33] Heller, W., and Zocher, H., Über die transversale magneto-optische Anisotropie einiger kolloider Lösungen: Ztschr. phys. Chem., vol. 166, 1933, p. 365.
[34] Work cited in footnote 23, p. 137.
[35] Work cited in footnote 23, p. 137.
[36] Kolthoff, I. M., and Moskovitz, B., The Constitution of Iron Oxide Monohydrate: Jour. Am. Chem. Soc., vol. 58, 1936, pp. 777-779.
[37] Stirnemann, E., Neues Jahrb. Mineral, vols. 52A and 53A, 1925, pp. 334 and 359, respectively.
[38] Work cited in footnote 21, p. 137.

Milligan.[39] Ninety grams of $FeCl_3 \cdot 6H_2O$ in 1 liter of water (1/3 M) was heated to 90° C. in 3 to 4 hours with stirring. The precipitate was allowed to settle overnight. It was then centrifuged with water once and five or six times with dilute (1–2) ammonium hydroxide wash and dried at 80° to 85° C. for 20 hours.

A definite crystalline form of ferric hydroxide, $Fe(OH)_3$, does not exist. The familiar voluminous, gellike precipitate obtained upon
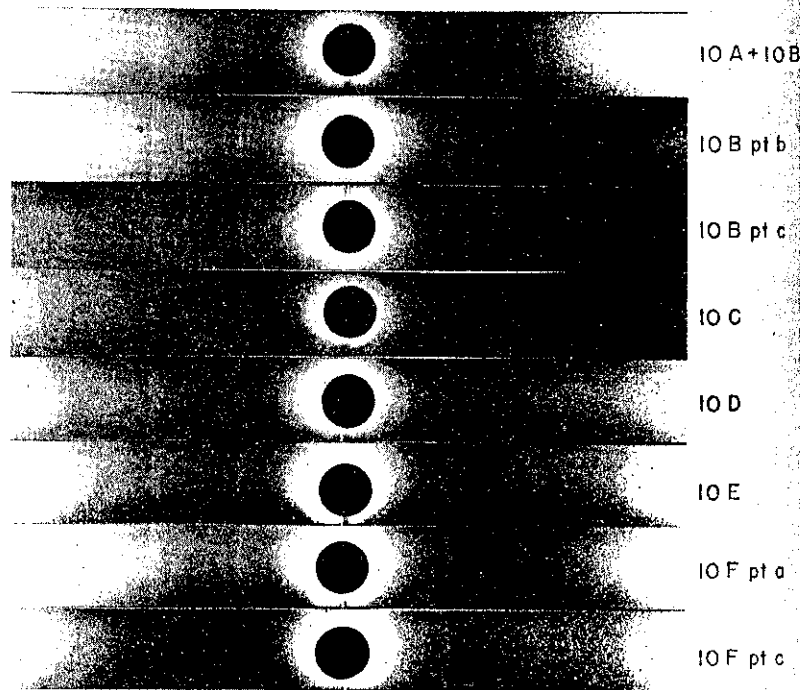

FIGURE 33. X-ray diffraction patterns of unpromoted iron catalysts.

treating ferric salt solutions at room temperature with a base is quite amorphous to X-rays. Weiser and Milligan's data [40] show that this amorphous precipitate is very finely divided hydrous αFe_2O_3. Krause,[41 42 43] on the other hand, considers this gel from the point of view of the organic chemist and explains its structure in terms of molecules bound together largely by covalent bonds. The processes occurring

[39] Work cited in footnote 23, p. 137.
[40] Work cited in footnote 20, p. 137.
[41] Krause, A., and Buczkowski, W., Über Silberferrite II, Die Struktur des durch Heisshydrolyse von FeCl₃-Lösung erhaltenen gelben Hydroxides: Ztschr. anorg. allgem. Chem., vol. 200, 1931, pp. 144–152.
[42] Krause, A., and Kowna, C. W., Über Silberferrite III, Struktur und Polymerisation des braunen Orthoferrihydroxyds: Ztschr. anorg. allgem. Chem., vol. 204, 1932, pp. 20–28.
[43] Krause, A., Lakoschukowna, H., and Achowak, J., Über Silberferrite VI, Der Reaktions-mechanismus der Bildung von Böhms Goethit und der Einfluss der H + Konzentration auf die Älterung des Orthoferrihydroxyds: Ztschr. anorg. allgem. Chem., vol. 208, 1932, pp. 282–292.

in the gel are described by him as similar to such classical organic reactions as polymerization, ring closure, oxygen bridging, etc. The theory of Krause is of limited application because it is applicable only to the amorphous hydrous oxide and is somewhat generous in its assumptions and hypotheses. Most of the catalysts described below contained at least 5 to 10 percent of definitely crystalline material, and in most cases the percentage probably was higher. In general, precipitates formed at temperatures between 50° and 100° C. are somewhat
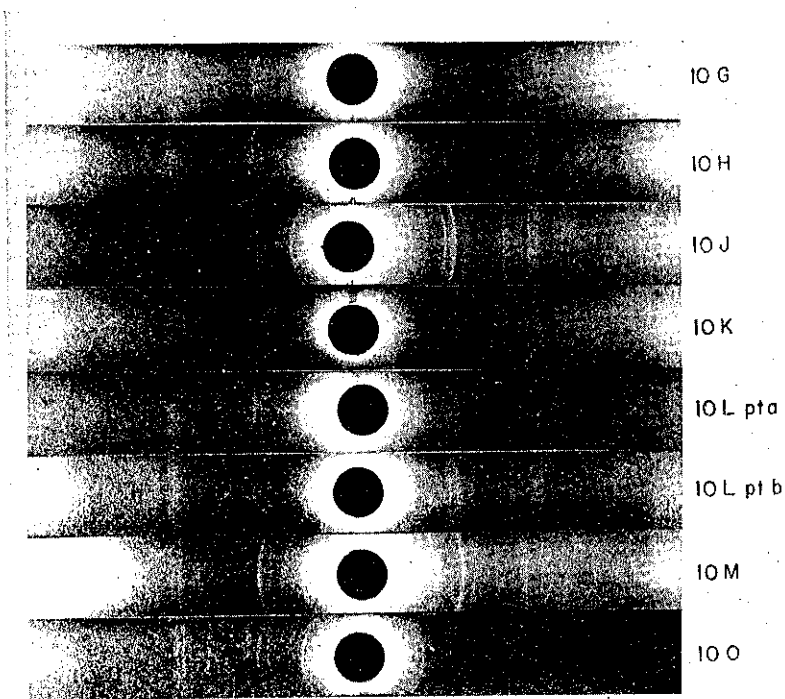

FIGURE 34. X-ray diffraction patterns of unpromoted iron catalysts.

crystalline, and even those precipitated at room temperature become crystalline if aged under water for several months at room temperature.

The third ferric oxide hydrate, $\gamma Fe_2O_3 \cdot H_2O$, is known as lepidocrocite; it may be prepared from ferrous salt solutions under conditions that favor the formation of a complex ion. Hahn and Hertrich [44] showed that by oxidizing ferrous salt solutions containing sodium thiosulfate with potassium iodate, a yellow precipitate was formed which Albrecht [45] demonstrated was $\gamma Fe_2O_3 \cdot H_2O$. The sample used in our studies was prepared by the method of Hahn and Hertrich.

[44] Hahn, F. L., and Hertrich, M., Leicht Filtrierbares Eisenhydroxide durch Fällung mit Thiosulfat und Jodat: Ber. Deut. chem. Gesell., vol. 56, 1923, pp. 1729–1732.
[45] Albrecht, W. H., Magnetische und kystallographische Untersuchungen über Eisen-3-oxydhydrate: Ber. Deut. chem. Gesell., vol. 62, 1929, pp. 1475–1482.

The anhydrous oxides, αFe_2O_3 and γFe_2O_3, are obtained by dehydrating $\alpha Fe_2O_3 \cdot H_2O$, and $\gamma Fe_2O_3 \cdot H_2O$, respectively, at temperatures below 300° C. αFe_2O_3 is also obtained on dehydrating $\beta Fe_2O_3 \cdot H_2O$.[46] At temperatures above 300° C., $\gamma Fe_2O_3 \cdot H_2O$ will dehydrate to αFe_2O_3 directly if the γFe_2O_3 is not stabilized by alkali.[47] As mentioned above, the anhydrous αFe_2O_3 may be obtained also by aging amorphous ferric hydroxide under water. γFe_2O_3 may be made by oxidizing magnetite
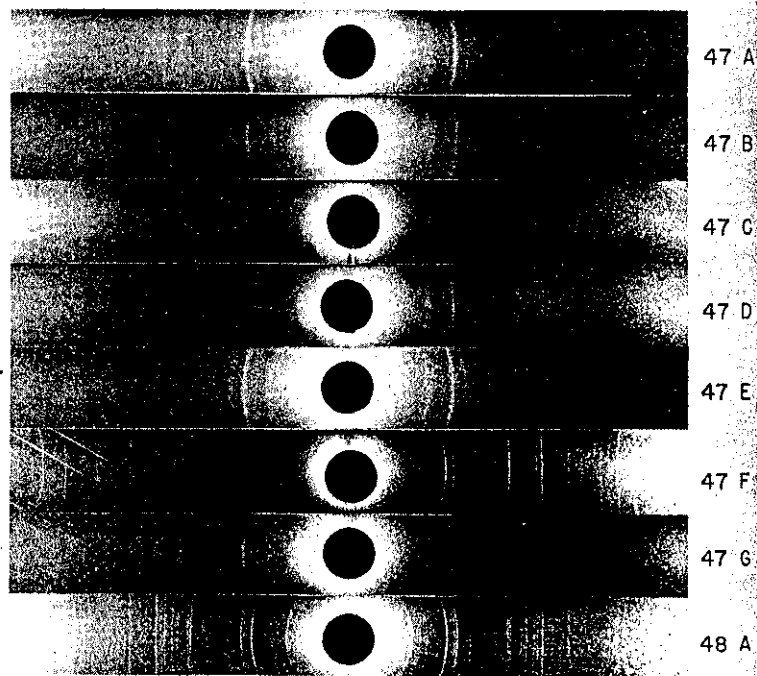

FIGURE 35.—X-ray diffraction patterns of unpromoted iron catalysts.

in a stream of air at 200° to 300° C. γFe_2O_3 is ferromagnetic, whereas all the other ferric oxide hydrates and ferric oxides are paramagnetic; its crystal structure is the same as magnetite, although the lattice parameter is slightly smaller. The oxygen necessary to convert magnetite to γFe_2O_3 may be removed from γFe_2O_3 merely by evacuating at about 200° C., indicating that the oxygen is quite loosely held. Baudisch and Welo [47] have written an exhaustive review of data on this interesting substance and closely related compounds.

X-RAY DIFFRACTION STUDIES OF UNPROMOTED-IRON CATALYSTS

All catalysts of the 10, 47, and 80 series were precipitated from ferric salt solutions with K_2CO_3 or KOH solutions (see table 16).

[46] Work cited in footnote 31, p. 141.
[47] Work cited in footnote 25, p. 137.

All the X-ray diffraction data on these catalysts are assembled in table 53, and the diffraction patterns themselves are shown in figures 33, 34, 35, and 36. Some of the diffraction patterns are shown in a schematic way in figure 38. Electron micrographs of unreduced catalysts 10D, 47D, and 80A are reproduced in figure 37; comparison of these with the electron micrographs of the pure ferric oxide hydrates
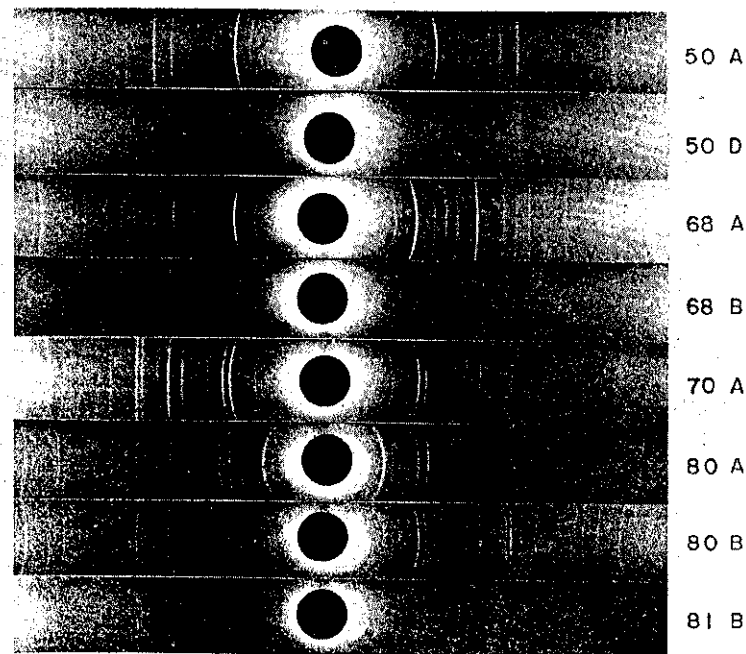
FIGURE 36.—X-ray diffraction patterns of unpromoted iron catalysts.

shown in figure 32 is insufficient for characterization of the phases present in the catalysts.

In the X-ray diffraction patterns of active catalysts produced by precipitation from a solution containing only nitrate ion in addition to ferric ion, the diffraction lines of αFe_2O_3 (hematite), of $\alpha Fe_2O_3 \cdot H_2O$ (goethite), or of both were identified. In the X-ray diffraction patterns of the inactive catalysts produced by precipitation from a solution containing chloride ion, $\beta Fe_2O_3 \cdot H_2O$ was identified in every case except 47F. The presence of $\beta Fe_2O_3 \cdot H_2O$ was somewhat surprising because the formation of $\beta Fe_2O_3 \cdot H_2O$ by direct precipitation

10 D

47 D

80 A

$\overset{0}{\underset{\text{Scale, microns}}{\rule{1cm}{0.4pt}}}\overset{2}{}$

FIGURE 37. Electron micrographs of unreduced iron catalysts.

at temperatures above 50° C. has not been previously reported. Other investigators, Weiser and Milligan,[48][49][50][51][52] Schikorr,[53] and Heller and Zocher,[54] prepared $\beta Fe_2O_3 \cdot H_2O$ by the slow hydrolysis of f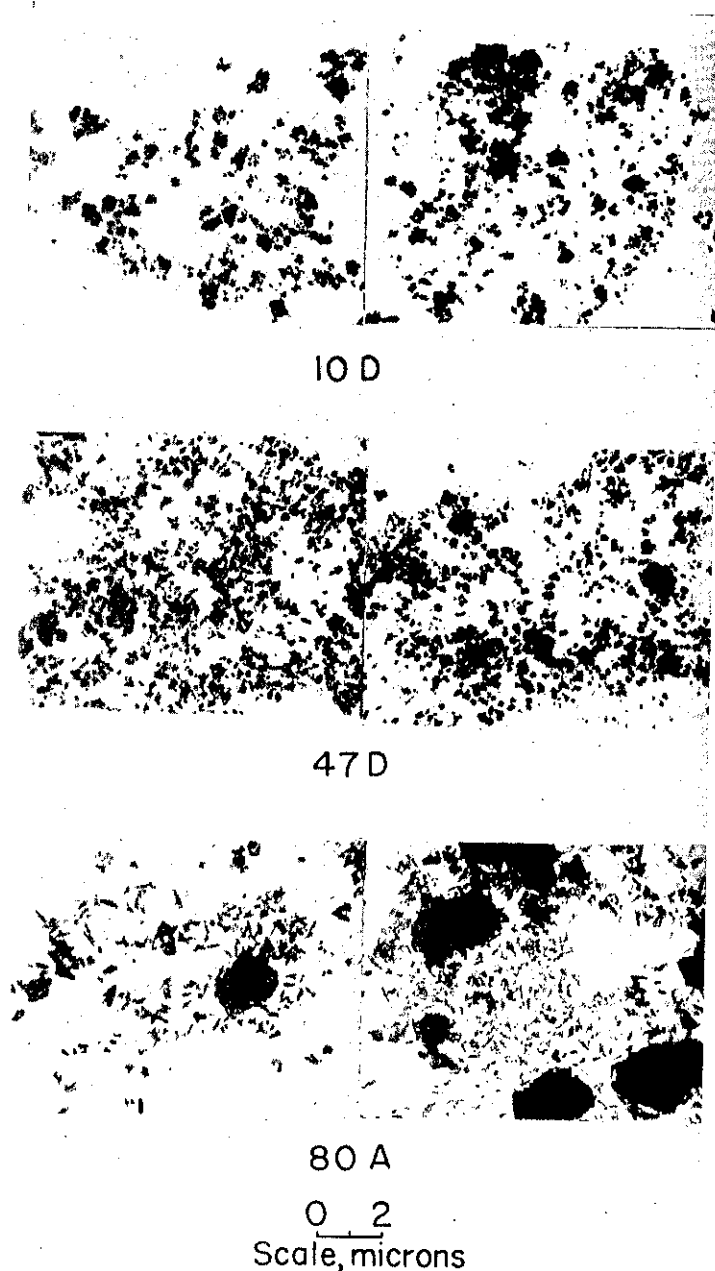erric chloride solutions. Weiser and Milligan, in studies of the brown gel precipitated at 20° C. from ferric chloride solution, found that it contained no $\beta Fe_2O_3 \cdot H_2O$. The gel was entirely amorphous to X-ray examination; but after being washed free of chloride ion, it aged over a period of months to αFe_2O_3 under water at room
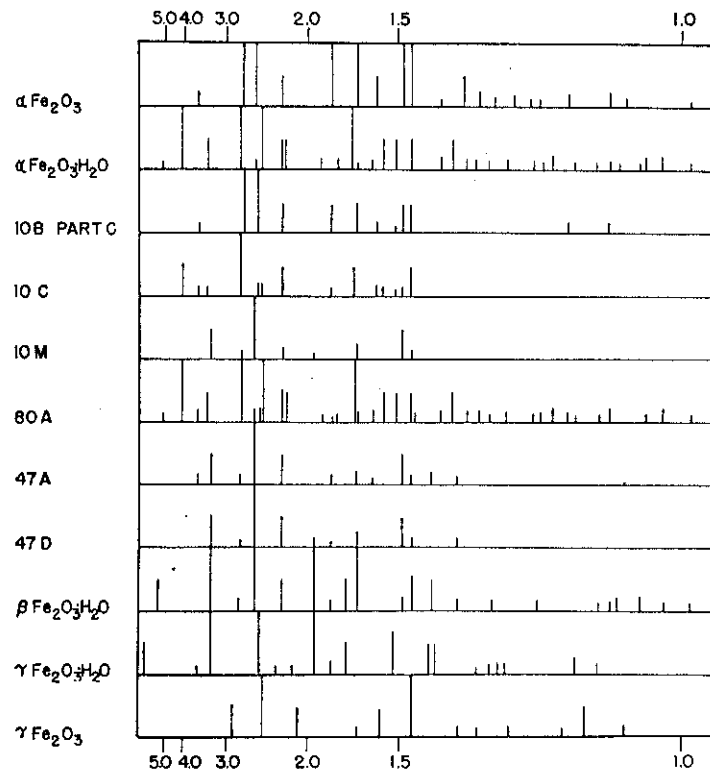
FIGURE 38.—X-ray diffraction powder patterns of various iron Fischer-Tropsch catalysts and crystalline ferric oxides and ferric oxide hydrates.

temperature and at 100° C. in a few hours. The fact that all the active catalysts precipitated from ferric solutions with potassium carbonate or potassium hydroxide contained αFe_2O_3, $\alpha Fe_2O_3 \cdot H_2O$, or both, whereas all the inactive catalysts contained $\beta Fe_2O_3 \cdot H_2O$, with the exception of 47F, suggested that $\beta Fe_2O_3 \cdot H_2O$ had some connection with the inactivity and that catalyst 47F was somewhat anomalous.

[48] Work cited in footnote 19, p. 137.
[49] Work cited in footnote 20, p. 137.
[50] Work cited in footnote 21, p. 137.
[51] Work cited in footnote 22, p. 137.
[52] Work cited in footnote 23, p. 137.
[53] Work cited in footnote 31, p. 141.
[54] Work cited in footnote 33, p. 141.

TABLE 53.—*Characterization of unpromoted Fischer-Tropsch iron catalysts*

	Catalyst dried at 120° C.				Catalyst heated 26 hours at 255°–260° C.												
Catalyst No.	X-ray diffraction		Magnetic susceptibility X 10⁻⁶		X-ray diffraction		Magnetic susceptibility X 10⁻⁶	Percent of acid insoluble fraction	Reduction	Induction	Induction press. p.s.i. gage	Operating press. p.s.i. gage	No. of weeks	Optimum run	Maximum yield g./m.³
	Phases	Diffuseness			Phases	Diffuseness									
10A+B pt. a	αFe₂O₃ (probably)	(X)	150		αFe₂O₃	(A)	62.1		Slow	Intermediate	0	0	2	b	48.4
10B, pt. b	αFe₂O₃	(B)	160		do	(A)	56.1		do	do	0	0	15	b	16.7
10B, pt. c	do	(B)	150		do	(A)	80.1		do	do	0	0	1	b	21.0
10C	αFe₂O₃; αFe₂O₃·H₂O	(B)	135		αFe₂O₃ only	(A)	66.8		Special conditioning	do	0	135	2	b	20.6
10D	do	(B)	210		do	(A)	126	28	Slow	Intermediate	100	0	5	b	27.9
10E	αFe₂O₃	(C)	220		do	(A)	143	0.0	do	do	0	100	1	b	62.8
10F, pt. a	do	(D)	130		do	(A)	74.2	.9	do	do	100	0	4	b	
10G	do	(D)	180					.9							
10H	do	(B)	170		αFe₂O₃	(A)	96	.7	do	do	0	100	1	a	34.5
10I	αFe₂O₃; αFe₂O₃·H₂O	(B)	140		αFe₂O₃ only	(A)	22.3	33.5	do	do	0	0	3	a	52.6
10J	αFe₂O₃	(B)	180		do	(A)	69.7	43	do	do					
10K	do	(B)	170		αFe₂O₃	(A)	127	6	do	do					
10L, pt. a	do	(B)	170		do	(A)	49.2	6.5	do	do					
10L, pt. b	do	(B)	170		do	(A)	33	1.4	do	do					
10M	βFe₂O₃·H₂O; αFe₂O₃·H₂O	(B)	43		αFe₂O₃	(A)	36.5	1.4	do	do					
10O	βFe₂O₃·H₂O	(C)	44		βFe₂O₃·H₂O; αFe₂O₃	(B)	39.7	32	Slow	Contraction	100	0	1	a	0
47A	do	(C)	56		do	(B)	43		do	Intermediate	0	0		a	0
47B	do	(C)	61		do	(B)	40.8	5	Slow, Special conditioning	do	0	0		a	0
47C	do	(C)	61		do	(B)	47.8		Slow	Intermediate	0	100		a	0
47D	do	(C)	40		do	(C)	45.5	76	do	do	100	0	1	a	0
47E	αFe₂O₃	(C)	130		αFe₂O₃; αFe₂O₃·H₂O	(C)	46.6	68	do	do	0	0	1	a	0
47F	βFe₂O₃·H₂O	(A)	56		do	(C)	94.7	75	do	do	0	0	1	a	0
47G	αFe₂O₃; αFe₂O₃·H₂O	(A)	230		αFe₂O₃ only	(C)	41.3	32	Special conditioning	do	0	0	1	a	0
48A	Fe₃O₄	(C)	9730		Fe₃O₄ (magnetite)	(A)	157		do	Rapid	0	0	1	a	0
58A	βFe₂O₃·H₂O	(C)	100		βFe₂O₃·H₂O	(C)	9590		do	Intermediate	0	0	1	a	0
58D	Definitely not limonite		165												
68A	αFe₂O₃	(X)	110		αFe₂O₃ only	(A)			do	do	0	0	1	a	45
70A	αFe₂O₃; αFe₂O₃·H₂O	(A)	72		do	(A)	64.9	58.5	Special conditioning	do	0	100	1	a	0
80A	do	(A)	140				111		do	do	100	0	3	a	63.9
81A	See 81B		210												
81B	αFe₂O₃	(C)	170		αFe₂O₃	(A)	117	11.5	do	Intermediate	0	0	1	a	0

¹ (A) Sharp, (B) Diffuse, (C) Very diffuse, (D) Very very diffuse, (X) So diffuse that identification of pattern is conjecture only.
² Reactivated by oxidation reduction.

Two possible causes for the presence of αFe_2O_3 in 47F suggested themselves. First, the presence of free base in the precipitant may have prevented the formation of $\beta Fe_2O_3 \cdot H_2O$, and second, the rapidity of precipitation may not have allowed sufficient time for the formation of $\beta Fe_2O_3 \cdot H_2O$. Neither of these hypotheses, however, accounts for the inactivity of the 47-type catalyst. In order to test these hypotheses, three catalysts, 47H, 47I, and 47J, were prepared exactly like 47F, except that 47I was precipitated with an alkali solution containing some KOH in addition to the K_2CO_3 and 47J was precipitated with a solution of KOH only. The reagents used in preparing the catalysts are listed in table 54. The following procedure was used: To the ferric chloride solution (2 liters) at 72° C. was added the alkaline solution (700 milliliters) in 3 minutes. After several washings, samples were removed, filtered, and air-dried for X-ray analysis. These catalysts contained αFe_2O_3 and $\alpha Fe_2O_3 \cdot H_2O$ but no $\beta Fe_2O_3 \cdot H_2O$, indicating that the absence of $\beta Fe_2O_3 \cdot H_2O$ in catalyst 47F was not fortuitous.

TABLE 54.—*X-ray diffraction study of catalysts precipitated in the presence of chloride ion*

Catalyst	Reagents	Weight, grams	Phases	Period of sampling
47H	FeCl₃·6H₂O	406	αFe₂O₃	7th wash.
	K₂CO₃	326		
47I	FeCl₃·6H₂O	406	αFe₂O₃·H₂O	6th wash.
	K₂CO₃	270		
	KOH	42		
47J	FeCl₃·6H₂O	406	αFe₂O₃	5th wash.
	KOH	300		
47HX	FeCl₃·6H₂O	406	βFe₂O₃·H₂O	Before first wash.
	K₂CO₃	326	αFe₂O₃	After first wash.

During the precipitation of catalysts 47H, 47I, and 47J, a dark chocolate-brown precipitate was formed, which became very much lighter and redder during the first washing. The record showed that similar observations were made in the case of 47F. In order to study the nature of this transformation, another catalyst (47HX, table 54) was prepared under the same conditions as 47F. Before the first washing two samples of the precipitate were removed and filtered. One was dried until dry to the touch; the other was dried until only slightly moist. Potassium chloride crystals formed on both samples. These were removed by washing. In the case of the dry sample, the washing was accompanied by no obvious peptization, but there was some peptization in the case of the moist sample. Both samples were again air-dried and examined by X-ray diffraction. Both contained $\beta Fe_2O_3 \cdot H_2O$. Similar samples removed after the first washing contained αFe_2O_3 or $\alpha Fe_2O_3 \cdot H_2O$ and possibly a trace of $\beta Fe_2O_3 \cdot H_2O$. After subsequent washes, no $\beta Fe_2O_3 \cdot H_2O$ could be detected. One may conclude that the αFe_2O_3 found in 47F was derived from $\beta Fe_2O_3 \cdot H_2O$ at least in part by aging. Such an aging of $\beta Fe_2O_3 \cdot H_2O$ to αFe_2O_3 in hot water was observed previously by Weiser and Milligan.[55] Presumably the $\beta Fe_2O_3 \cdot H_2O$ formed by rapid precipitation is more unstable toward aging than the $\beta Fe_2O_3 \cdot H_2O$ formed by slower precip-

[55] Work cited in footnote 23, p. 137.

itation. This would account for the absence of $\beta Fe_2O_3 \cdot H_2O$ in 47F and its presence in the other 47-type catalysts. It seems likely that all the 47-type catalysts at one time in their history contained $\beta Fe_2O_3 \cdot H_2O$.

It must be emphasized that neither of the above-mentioned oxide hydrates of iron, $\beta Fe_2O_3 \cdot H_2O$ and $\alpha Fe_2O_3 \cdot H_2O$, is stable at the temperature of the synthesis and αFe_2O_3 itself is not stable under the reducing conditions of the synthesis. This is illustrated by the effect of heating the catalysts containing $\alpha Fe_2O_3 \cdot H_2O$ and $\beta Fe_2O_3 \cdot H_2O$ shown in table 53. The deactivating effect of precipitation in the presence of chloride ion seems to be due, not to the presence of $\beta Fe_2O_3 \cdot H_2O$ itself, but to some characteristic that it imparts to the final catalyst. This idea is supported by the fact that catalyst 47F which, although it contained no $\beta Fe_2O_3 \cdot H_2O$ when examined, was formed in part from $\beta Fe_2O_3 \cdot H_2O$ and was inactive in the synthesis. Although chloride ion seems to have some deleterious effect on catalysts in its own right, the presence of $\beta Fe_2O_3 \cdot H_2O$ at some stage in catalyst preparation greatly accentuates this effect. Reasonably active catalysts can be produced by precipitation of solutions containing cupric nitrate and ferric chloride (catalyst 5A), cupric chloride and ferrous chloride (catalyst 85A), and ferrous chloride; in each of these cases, the precipitate would at no stage be composed of $\beta Fe_2O_3 \cdot H_2O$, because the presence of bivalent iron would favor the formation of other crystalline forms, possibly spinellike structures. Diffraction analysis revealed catalyst 85A to have the spinel structure of magnetite. Catalyst 5A was completely amorphous to X-rays; its subcrystalline structure will be discussed in the section on Magnetic Studies. In each of these cases there is no evidence that $\beta Fe_2O_3 \cdot H_2O$ exists at any stage of the precipitation.

As has previously been discussed in the section on the Ferric Oxides and Ferric Oxide Hydrates, $\beta Fe_2O_3 \cdot H_2O$ always contains some chloride ion in relatively large amounts, determinable by ordinary analytical procedures. Because this chloride ion is very difficult to remove by washing and is so intimately diffused through the $\beta Fe_2O_3 \cdot H_2O$ crystal structure, inclusions containing chloride will be dispersed through the ferric oxide and any other phase prepared from the $\beta Fe_2O_3 \cdot H_2O$. This fact alone can quite conceivably account for the difference in catalytic activity between those catalysts derived from $\beta Fe_2O_3 \cdot H_2O$ and those that are not.

The X-ray diffraction studies of the other unpromoted iron catalysts do not form a very complete series, and this makes it difficult to draw any definite conclusions. In general, all catalysts precipitated from ferric salts other than the chloride contained αFe_2O_3, $\alpha Fe_2O_3 \cdot H_2O$, or both. Catalysts 48A, 81A, and 81B, although they contained αFe_2O_3 and $\alpha Fe_2O_3 \cdot H_2O$ like the active 10-series and 80-series catalysts, were only slightly active. These catalysts, 48A, 81A, and 81B, were precipitated with sodium hydroxide and sodium carbonate; this may have something to do with their inactivity, although it has been shown by research at the Kaiser Wilhelm Institute [56] that iron catalysts prepared by precipitation with sodium carbonate and pretreated with pure carbon monoxide at 1/10 atmosphere and 325° C. are almost as

active as those containing some potassium. The catalysts, 48A, 81A, and 81B, will be discussed further under the section on Magnetic Studies of Unpromoted Iron Catalysts. Catalyst 50A is a commercially obtainable oxide. It is largely magnetite, and its inactivity may be due to the very large crystallite size or to the presence of some catalyst poison. Catalyst 50D is simply catalyst 50A after solution in acid and reprecipitation from a chloride solution. This latter process has already been shown to lead to inactive catalysts. The diffraction pattern shows $\beta Fe_2O_3 \cdot H_2O$. Catalyst 68A was claimed to be limonite ore; but limonite, according to Dana,[57] is a partly amorphous goethite. This material, however, consisted of well-developed crystallites of a phase that we were not able to identify; it is, however, definitely not limonite. Catalyst 68B is made from catalyst 68A by solution and reprecipitation. Owing to its amorphous nature no identification could be attempted. Catalyst 70A was prepared by the ignition of ferric nitrate and consists of hematite.

MAGNETIC STUDIES OF UNPROMOTED IRON CATALYSTS

The studies of the magnetic susceptibility of the ferric-oxide-type Fischer-Tropsch catalysts showed that all the 80-series catalysts and all the active 10-series catalysts, with the exception of 10M, had magnetic susceptibility equal to or higher than those catalysts of the inactive 47 series. In all cases the magnetic susceptibility of the active catalysts is very much higher than the normal magnetic susceptibility of any of the ferric oxides or ferric oxide hydrates whose presence could be confirmed by X-ray diffraction. By contrast, those catalysts of the 47 series containing $\beta Fe_2O_3 \cdot H_2O$ have a magnetic susceptibility not much greater than that of $\beta Fe_2O_3 \cdot H_2O$ itself. Catalyst 47F is somewhat exceptional in that it contains no $\beta Fe_2O_3 \cdot H_2O$, but only αFe_2O_3. This point has been previously discussed. Even the magnetic examination shows that this catalyst has a higher magnetic susceptibility than the rest of the 47 series, but no higher than the lowest susceptibility of active catalysts of the 10 or 80 series.

The enhanced magnetic susceptibility of most of the 10-series catalysts and 80 series has no completely satisfactory and tested explanation. The phenonomenon has attracted the attention of many students. Albrecht and Wedekind [58] observed that the magnetic susceptibility of precipitated oxides of ferric iron varied widely and that they were considerably larger than the susceptibility of goethite ($\alpha Fe_2O_3 \cdot H_2O$), lepidocrocite ($\gamma Fe_2O_3 \cdot H_2O$), or hematite ($\alpha Fe_2O_3$). Their observations, insofar as they do not relate to precipitated oxides prepared from ferric chloride, are identical with those presented in this paper. Albrecht and Wedekind ascribed the enhanced susceptibility to traces of highly magnetic hypothetical iron compounds, which they termed "ferrite." These "ferrite" compounds do not seem to be identical with such well-established ferrites as are described by Michel.[59] Albrecht and Wedekind suggested also that

[57] Palache, C., Berman, H., and Frondel, C., The System of Mineralogy of James Dwight Dana and Edward Salisbury Dana: John Wiley & Sons, vol. 1, 1944, 7th ed., 834 pp.
[58] Albrecht, W. H., and Wedekind, E., Kennzeichnung der verschiedenen Arten von Eisen-3-oxyden und Eisen-3-oxydhydraten durch ihre unterschiedlichen magnetischen Eigenschaften IV: Ztschr. anorg. allgem. Chem., vol. 202, 1931, pp. 209–226.
[59] Michel, A., Properties magnetiques de quelques solutions solids: Ann. chim., 11 ser., vol. 8, 1937, pp. 317–423.

in some cases the enhanced magnetic susceptibility is due to the presence of traces of γFe_2O_3. Hüttig and Kittel [60] suggested that the magnetic susceptibility is a function of the stoichiometric ratio of oxygen to iron in hematite, which these authors believe is not constant. Such deviations in stoichiometry in Bertholoid compounds reflect a stable, yet defective crystal structure. Herroun and Wilson [61] have attributed the high magnetic susceptibility to the presence of alkali ferrites. This idea is supported by the fact that most ferric oxide precipitates showing this enhanced susceptibility were prepared by precipitation by some alkali.

This excludes, of course, such ferric oxides as are either obviously or probably contaminated with magnetite or γFe_2O_3. This is also supported by the papers of Chevalier and Mathieu, [62 63 64 65] who showed that in precipitating ferric oxide from a solution of ferric sulfate with potassium hydroxide, the magnetic susceptibility of the precipitate is a strong function of the concentration and excess of base employed. The higher the concentration and excess of base, the higher the magnetic susceptibility of the precipitate.

Although Hüttig and Kittel [66] found the magnetic susceptibility of hematite prepared under carefully controlled conditions to be about 23×10^{-6} and to be independent of field strength and hence paramagnetic, nevertheless, Michel [67] has shown that hematite has a Curie point at 675° C. and very weakly ferromagnetic properties, particularly after it has been annealed at high temperatures. This point of view is supported by Hayes, [68] who claims that the magnetic susceptibility of pure hematite should range from 40 to 100×10^{-6} at room temperature, depending on the magnetic hardness, while magnetically contaminated hematites should have higher susceptibility. Unfortunately, Hayes [68] worked only with well-crystallized samples, hence his results do not compare well with samples of catalysts. His results were obtained on natural hematites exclusively, which raises the question of impurities. In any case, however, magnetic susceptibilities greater than 100×10^{-6} cannot be explained on the basis of the normal variability in the susceptibility of hematite. Susceptibilities greater than 100×10^{-6} have been attributed only to traces of ferromagnetic "ferrite" (Albrecht and Wedekind [69 70]), deviation of composition from stoichiometric ratio of iron to oxygen (Hüttig and Kittel [71]), and traces of alkali ferrites.

[60] Hüttig, G. F., and Kittel, H., Aktive Oxyde XLIII, Die magnetische Suszeptibilität von Präparaten des Systems Eisenoxyd-Wasser: Ztschr. anorg. allgem. Chem., vol. 199, 1931, pp. 129-148.
[61] Herroun, E. F., and Wilson, S., On the Magnetic Susceptibility of Certain Natural and Artificial Oxides: Proc. Roy. Soc., London, vol. 33, 1920-1921, pp. 196-206.
[62] Chevalier, R., and Mathieu, S., Magnetisme—contribution magnetique des constituents de l'hydroxyde ferrique, evolué en milieu alcalin: Compt. rend., vol. 207, 1938, pp. 58-61.
[63] Chevalier, R., and Mathieu, S., Magnetisme—evolution spontanée des propriétés magnetiques de l'hydroxide ferrique: Compt. rend., vol. 206, 1938, pp. 1955-1958.
[64] Chevalier, R., and Mathieu, S., Magnetisme—sur les propriétés de l'hydroxide ferrique: Compt. rend., vol. 206, 1938, pp. 1469-1471.
[65] Chevalier, R., and Mathieu, S., Magnetisme—adsorption dans le precipitation de l'hydroxyde a partir du sulfate ferrique: Compt. rend., vol. 206, 1938, pp. 1249-1251.
[66] Work cited in footnote 60, p. 152.
[67] Work cited in footnote 59, p. 152.
[68] Hayes, E. T., Ferromagnetic Properties of Hematite: Bureau of Mines Rept. of Investigations 3570, 1941, 29 pp.
[69] Work cited in footnote 58, p. 151.
[70] Albrecht, W. H., and Wedekind, E., Kennzeichnung der verschiedenen Arten von Eisen-3-oxyden und Eisen-3-oxydhydraten III. Eisen-3-oxydhydraten aus Eisenpenta-carbonyl durch Zersetzung: Zschr. anorg. allgem. Chem., vol. 202, 1931, pp. 205-208.
[71] Work cited in footnote 60, p. 152.

In order to study the character of the enhanced magnetic susceptibility, it was measured at various field strengths. The results are tabulated in table 55. The susceptibility of $\alpha Fe_2O_3 \cdot H_2O$, $\beta Fe_2O_3 \cdot H_2O$, and $\gamma Fe_2O_3 \cdot H_2O$ does not vary greatly with field strength, and this may be taken as evidence for the paramagnetism. Catalyst 10A plus 10B seems to have a slightly field-dependent magnetic susceptibility. The susceptibility of 47D is almost field-independent. In contrast to these catalysts, the susceptibilities of 24C and 1E are strongly field-dependent. This is to be expected in the case of 24C, since the X-ray diffraction pattern reveals the presence of large amounts of magnetite. More will be said about the susceptibility of 1E in the section on promoted catalysts.

TABLE 55.—*Magnetic susceptibility as a function of field strength for ferric oxide hydrates and some characteristic catalysts*

Field (gauss)	$\alpha Fe_2O_3 \cdot H_2O$	$\beta Fe_2O_3 \cdot H_2O$	$\gamma Fe_2O_3 \cdot H_2O$	10A+B	47D	24C	1E
	($\times 10^6$)						
340						60,400	
1,150	49.0	30.4	43.2	159.6	61.4	27,100	1,146
1,500	49.8	28.7	41.0	153.6	61.9	21,800	1,010
1,730	50.9	29.4	44.3	155.4	62.3	20,000	987
2,120	48.1	28.4	41.4	148.8	59.3	16,100	877
2,530	48.4	28.0	41.4	149.7	58.7	14,000	824

Chevalier and Mathieu [72 73 74 75] have shown that the precipitate obtained from ferric sulfate and potassium hydroxide increases in magnetic susceptibility when aged in contact with the mother liquor, especially if the mother liquor contains an excess of base. In addition, the aging makes the precipitate less soluble in dilute acid. This seems to be due to the increase in goethite ($\alpha Fe_2O_3 \cdot H_2O$), which is difficultly soluble in dilute acid. Nevertheless, the enhanced magnetic susceptibility seems to be due to the acid-soluble fraction, as the insoluble residue has a magnetic susceptibility which never deviates appreciably from that of goethite.

Studies conducted by the Bureau of Mines have shown that precipitated oxides prepared from ferric nitrate behave very similarly to the oxides studied by Mathieu and Chevalier. A method was developed for separating goethite from the acid-soluble ferric oxide, which was based on the insolubility of goethite in $2\frac{1}{2}$ N HNO_3. The complex oxide was digested with $2\frac{1}{2}$ N HNO_3 at room temperature for 24 hours. The amount of the residue after it is filtered, ignited, and weighed as Fe_2O_3 was a measure of the yellow or goethite fraction. The iron in the filtrate was reprecipitated with ammonia, and the precipitate was filtered, ignited, and weighed as Fe_2O_3. The percentage of insoluble oxide reported in table 53 was the ratio of acid-insoluble oxide to the total amount of acid-soluble plus acid-insoluble oxide multiplied by 100. In every case in table 53 where X-ray diffraction analysis revealed the presence of goethite in the 10-series and 80-series catalysts, a much larger fraction of the catalyst was insoluble

[72] Work cited in footnote 62, p. 152.
[73] Work cited in footnote 63, p. 152.
[74] Work cited in footnote 64, p. 152.
[75] Work cited in footnote 65, p. 152.

in 2½N HNO_3 than in the cases where no goethite could be distinguished. In agreement with the results of Chevalier and Mathieu, precipitation over an extended period favored goethite formation. This is good evidence that the acid-insoluble fraction in these catalysts was goethite. In the case of 47-series catalysts this relationship broke down. The amount of acid-insoluble oxide seemed to bear no relationship to either the amount of $\beta Fe_2O_3 \cdot H_2O$ or the amount of αFe_2O_3. It is interesting to note that the αFe_2O_3 found by diffraction analysis in 47F seemed to be acid-insoluble. This may be related to the much greater crystallite size of the αFe_2O_3 in the 47F catalyst as compared with that of the hydrous αFe_2O_3 found in the 10- and 80-series catalysts.

To establish more clearly the similarity of behavior between the 10- and 80-series catalysts and the oxides of Chevalier and Mathieu, a check catalyst was prepared similar to the 10-series catalysts. It was precipitated over an extended period to insure formation of goethite. X-ray diffraction patterns of the complex oxide showed the presence of both goethite and hematite, and its magnetic susceptibility was 96 x 10^{-6}. Extraction of the complex oxide with 2½ N HNO_3 yielded a yellow residue of goethite only, whose susceptibility was 35 x 10^{-6}. The enhanced susceptibility, as in Chevalier and Mathieu's oxides, is due to the acid-soluble fraction of the complex oxide. The experiments conducted by the Bureau of Mines, therefore, indicate that the oxides precipitated from ferric nitrate with potassium hydroxide and potassium carbonate behave similarly, both magnetically and chemically, to the ferric sulfate oxides studied by Chevalier and Mathieu. This should not be interpreted to mean that Chevalier and Mathieu's oxides would necessarily make good Fischer-Tropsch catalysts, but it does mean that some of their experimental work can be used as a guide in preparing ferric oxide-type catalysts.

In discussion of the possibility that active Fischer-Tropsch catalysts contain alkali ferrites, the series of papers of LeClerc and Lefebvre [76 77 78] must be considered. These authors claim that after an iron catalyst has been properly conditioned it contains two phases—magnetite and a solid-solution limit of potassium oxide in γFe_2O_3 (saturated solution of K_2O in Fe_2O_3). The catalyst, after reduction with hydrogen, contains magnetite only, but during the conditioning period, which takes about 48 hours, the phase of the solid solution limit of potassium oxide in γFe_2O_3 appears and is accompanied by a great increase in catalytic activity. The identification of these phases in the catalyst was accomplished by thermomagnetic analysis, which consists in determining the Curie points of the various ferromagnetic phases in the unknown. Figure 39 is a reproduction of one of the thermomagnetic analysis curves of LeClerc and Lefebvre, showing the two Curie points. The Curie point of magnetite, 580° C., is well known. The Curie point of the solid solution limit of potassium oxide in γFe_2O_3 is 250° C.,

[76] LeClerc, G., [Catalyse—sur l'activité catalytique du sesquioxide de fer cubique dans la synthese d'hydrocarbures par hydrogenation de l'oxyde de carbone a la pression atmospherique]: Compt. rend., vol. 207, 1938, pp. 1099–1101.
[77] Lefebvre, H., and LeClerc, G., Les Catalyseurs au fer dans la synthese de l'essence par hydrogenation de l'oxyde de carbone: Congr. Chim. Ind. Compt. rend., 18th Congr. Nancy, September–October 1938, pp. 725–730.
[78] Lefebvre, H., and LeClerc, G., Chimie appliqué—étude thermo-magnetique des catalyseurs au fer utilisés dans la synthese des hydrocarbures par le procédé Fischer: Compt. rend., 1936, vol. 203, pp. 1378–1380.

according to Michel and Chaudron [79] (reference cited by Lefebvre and LeClerc). Unfortunately, Michel [80] himself subsequently states that this Curie point is 630° C. This latter value seems to be more reliable, and the interpretation of LeClerc and Lefebvre, which is based on the 250° C. value of the Curie point of the solid-solution limit of potassium oxide in γFe_2O_3, is therefore doubtful. Nevertheless, LeClerc and Lefebvre have shown that development of the second phase, corresponding to the Curie point at 250° C., during the conditioning period depends on the presence of potassium in the catalyst before
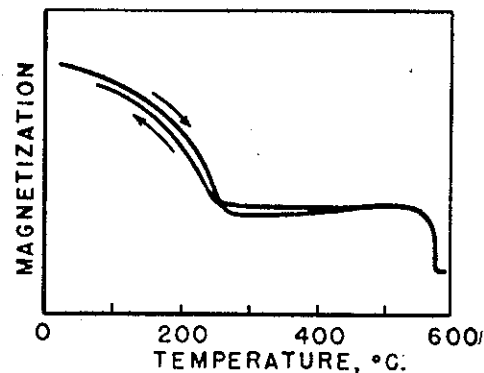

FIGURE 39.—Thermomagnetic curve for an iron Fischer-Tropsch catalyst.

drying, or it may be introduced by a special method of coprecipitation. The later method is superior. Whether the new phase corresponding to the Curie point of 250° C. is the solid-solution limit of potassium oxide in γFe_2O_3, or whether this new phase is something else in whose formation potassium played an important part, a physical-chemical basis for the action of potassium in the Fischer-Tropsch reaction has been demonstrated. This phase may well be cementite, Fe_3C, which has a Curie point at 220° C.

Although a magnetic susceptibility much greater than that of normal hematite, goethite, or $\beta Fe_2O_3 \cdot H_2O$ was found to be characteristic of the active catalysts precipitated from ferric nitrate solutions with potassium carbonate or potassium hydroxide, and although this enhanced magnetic susceptibility seems to be related to the presence of alkali ferrites in the oxide, these studies have not been advanced sufficiently to permit definite conclusions as to the relationship, either between magnetic susceptibility and catalytic activity or between magnetic susceptibility and alkali content. The data indicate only that highly active catalysts prepared from ferric nitrate have high magnetic susceptibility in the dry, unreduced state.

[79] Michel, A., and Chaudron, G., Chimie minerale, étude du sesquioxide de fer cubique stabilise: Compt. rend., vol. 201, 1935, pp. 1191–1193.
[80] Work cited in footnote 59, p. 152.