[CONTRIBUTION FROM THE CENTRAL EXPERIMENT STATION, U. S. BUREAU OF MINES]

X-Ray Diffraction and Magnetic Studies of Unreduced Ferric Oxide Fischer–Tropsch Catalysts[1]

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Catalysts prepared by precipitation with potassium carbonate or hydroxide of a ferric salt are inactive in the Fischer–Tropsch synthesis if the original solution contains chloride anion and active if the original solution contains nitrate anion only. This difference in activity is an extremely marked one; the catalysts precipitated in the presence of chloride ion in no case produced more than two or three grams of liquid hydrocarbons per cubic meter of synthesis gas, while catalysts precipitated in the presence of nitrate ion, in some cases, gave yields as high as seventy grams of liquid hydrocarbons per cubic meter of synthesis gas. This paper deals with the physical basis for this difference in catalytic activity.

Experimental

Preparation of the Catalysts.—The catalysts of one series (no. 10) were precipitated from 0.6 to 1.2 molar ferric nitrate solutions at 65–83° with 4 molar potassium carbonate. The time of precipitation varied from five to thirty minutes. Depending on the temperature and rate of precipitation, the precipitate varied in appearance and volume. Temperatures below 70° and rapid precipitation tended to produce a deep red-brown voluminous precipitate. Dense, light brown to tan precipitates were obtained at 80° and higher, and with slow addition of potassium carbonate. Catalysts 10-C, 10-D, 10-I and 10-J belonged to the latter category.

The 10 series of catalysts were washed sixteen to eighteen times by decantation with distilled water. At this stage, the wash water contained less than one part of nitrate ion in 16,000 parts of solution, as determined by the diphenylamine–sulfuric acid reagent. The temperature of the wash water was, in most cases, 65°. The catalysts were then filtered and dried.

All the catalysts with the exception of 10-A, parts b and c of 10-B, 10-D and part a of 10-F were air-dried about one hundred and twenty-five hours at room temperature and then dried about twenty hours at 150°. Parts b and c of 10-B were oven-dried directly with no prior air-drying. After the standard length of air-drying, 10-A was dried at 105° and part a of 10-F was dried at 85°. Catalyst 10-D was air-dried about forty-five hours at room temperature, and then dried at 150° for the same period. The crushed dry catalyst cake was mixed with 4% graphite and pelleted.

Catalyst 10-M behaved very differently from the rest of the 10 series, but this was due to the presence of an amount of potassium chloride equivalent to the amount of ferric nitrate in the original solution. The behavior during preparation of 10-M was similar to that of the 47 series of catalysts described below.

The 47 series of catalysts were prepared from ferric chloride solutions ranging from 0.5 to 0.8 molar at 75° by the addition of 3.5 molar potassium carbonate. The time of precipitation, in general, was thirty to forty-five minutes. In general, the precipitates of catalysts prepared from the chlorides were considerably more yellow than those prepared from ferric nitrate with potassium carbonate. The precipitates were washed by decantation about eighteen times. In each preparation, the supernatant liquid still gave a faint positive test for chloride. The temperature of wash water was 80°. Catalyst 47-F was precipitated in three minutes. Its color was brown immediately after precipitation but changed to reddish brown after several washings.

After filtration, the catalysts were air-dried for about ninety hours at room temperature, and then oven-dried at 150° for twenty hours. These catalysts also were crushed, mixed with 4% graphite and pelleted.

The 80-series catalysts were prepared in a way similar to the 10-series, but substituting 9 molar potassium hydroxide for potassium carbonate as the precipitant. The precipitation was carried out at 83° during a thirty-five minute period.

Synthetic $\alpha Fe_2O_3\cdot H_2O$ (goethite), $\beta Fe_2O_3\cdot H_2O$ and $\gamma Fe_2O_3\cdot H_2O$ (lepidocrocite) were prepared by the methods of Weiser and Milligan,[5] Weiser and Milligan,[6] Hahn and Hertrich,[7] and Albrecht,[8] respectively.

Experimental Methods.—The X-ray diffraction patterns were made by the powder method. A finely ground sample of the catalyst was partly extruded from a $^3/_4$-inch length of 19-gage stainless steel tubing of 0.7 mm. inside diameter.[9] The tube with the extruded cylinder of powdered specimen was mounted in a Debye–Scherrer camera of 71.6 mm. diameter. FeKα radiation filtered with a manganese dioxide filter was used. Identification of the crystalline phases was accomplished both by comparison with the diffraction patterns of the synthetic samples of the ferric oxides and ferric oxide hydrates and by reference to the Hanawalt index cards of X-ray reflections.[10]

The magnetic susceptibility of the catalysts was determined with an apparatus similar to that of Buehl and Wulf.[11] The apparatus was calibrated at several field strengths with Mohr salt the susceptibility of which at 27° was taken as 31.6×10^{-6}.[12] The probable error of the measurements is in all cases about $\pm 0.5 \times 10^{-6}$. All the measurements here reported were made at a field strength of 2120 gausses. The sample holder was of Pyrex glass. No attempt was made to correct the results for the magnetic susceptibility of the holder since it is of the same magnitude as the probable experimental error.

All catalyst testing is at present arbitrary. It is impossible to predict the optimum conditions for operating any given catalyst prepared under any given set of conditions. In this study, however, the difference in activity between unpromoted ferric oxide precipitated in the presence of chloride ion and those prepared in the presence of nitrate ion only was so striking as to overshadow any differences due to varying methods of reduction, induction, and operation.

The apparatus used for testing activity consisted essentially of a converter containing the catalyst, meters for measuring the feed and exit gases, and traps for collecting the products. The converter itself consisted of 0.5-inch

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(5) Weiser and Milligan, *J. Phys. Chem.*, **39**, 25 (1935).

(6) Weiser and Milligan, THIS JOURNAL, **57**, 238 (1935).

(7) Hahn and Hertrich, *Ber.*, **56**, 1729 (1923).

(8) Albrecht, *ibid.*, **62**, 1475 (1929).

(9) Barrett, "Structure of Metals," McGraw Hill Co., 1943, p. 118.

(10) Data Cards for the Identification of Crystalline Materials by the Hanawalt X-Ray Diffraction Method, Am. Soc. for Testing Materials, Philadelphia, Pa.

(11) Buehl and Wulf, *Rev. Sci. Instruments*, **9**, 224 (1938).

(12) Jackson, *Trans. Roy. Soc.* (London), **A224**, 1 (1923).

TABLE I

X-RAY DIFFRACTION, MAGNETIC SUSCEPTIBILITY AND ACTIVITY DATA ON UNREDUCED IRON CATALYSTS

Catalyst	X-Ray diffraction Phases	Diffuseness[a]	Magnetic susceptibility × 10^6	Activity Weeks tested	Optimum week	Yield[b]	Operating pressure gage, p.s.i.
10A + 10B	αFe_2O_3 (probably)	(X)	150	15	2nd	48.4	0
10B (pt. b)	αFe_2O_3	(B)	160	1	1st	16.7	0
10B (pt. c)	αFe_2O_3	(B)	150	2	1st	21.0	0
10C	αFe_2O_3; $\alpha Fe_2O_3 \cdot H_2O$	(B)	135	5	3rd	70.6	135
				1	1st	27.9	0
10D	αFe_2O_3; $\alpha Fe_2O_3 \cdot H_2O$	(B)	210	4	1st	62.8	100
10E	αFe_2O_3	(B)	220	..	...	..	...
10F (pt. a)	αFe_2O_3	(D)	130	1	1st	34.5	0
10F (pt. c)	αFe_2O_3	(D)	180	3	1st	52.6	100
10G	αFe_2O_3	(D)	170	..	...	..	...
10H	αFe_2O_3	(D)	170	..	...	..	...
10I	αFe_2O_3; $\alpha Fe_2O_3 \cdot H_2O$	(B)	140	..	...	..	...
10J	αFe_2O_3; $\alpha Fe_2O_3 \cdot H_2O$	(B)	180	..	...	..	...
10K	αFe_2O_3	(C)	170	..	...	..	...
10L	αFe_2O_3	(B)	170	..	...	..	...
10M	$\beta Fe_2O_3 \cdot H_2O$	(B)	43	1	1st	<2	100
10O	αFe_2O_3; $\alpha Fe_2O_3 \cdot H_2O$	(B)	130	..	...	..	...
47A	$\beta Fe_2O_3 \cdot H_2O$	(B)	44	1	1st	<2	0
47B	$\beta Fe_2O_3 \cdot H_2O$	(C)	56	1	1st	..	...
47C	$\beta Fe_2O_3 \cdot H_2O$	(C)	61	1	1st	<2	0
				1	1st	<2	100
47D	$\beta Fe_2O_3 \cdot H_2O$	(C)	61	1	1st	<2	0
47E	$\beta Fe_2O_3 \cdot H_2O$	(C)	40	1	1st	<2	0
47F	αFe_2O_3	(A)	130	1	1st	<2	0
47G	$\beta Fe_2O_3 \cdot H_2O$	(C)	56	..	...	..	...
80A	αFe_2O_3; $\alpha Fe_2O_3 \cdot H_2O$	(A)	140	3	1st	63.9	100
80B	αFe_2O_3; $\alpha Fe_2O_3 \cdot H_2O$	(A)	210	..	...	..	...

[a] (A) = sharp lines; (B) = diffuse; (C) = very diffuse; (D) = very very diffuse; (X) = undecipherable. [b] Grams of liquid hydrocarbons per cubic meter of synthesis gas.

standard black pipe filled to a depth of twelve inches with catalyst. The temperature of the tube was maintained by boiling dowtherm in an electrically-heated jacket surrounding the tube. The boiling temperature, and hence the temperature of the catalyst, could be regulated by varying the pressure on the dowtherm.

The catalysts were reduced *in situ* during a period of twenty-four hours with electrolytic hydrogen flowing at a space velocity of about 20 volumes per hour. During the first twenty hours, the temperature was gradually raised to 360°, and it was held at that point for four hours longer.

The induction was carried out by passing gas of composition CO + H_2 (synthesis gas) at such a temperature that a 30 per cent. contraction of the gas was observed. (Contraction may be defined as the ratio of the decrease in volume to the volume of the intake gas. No correction was made for the methane content of the exit gas which was not removed by the absorbers and traps used in this apparatus.) The induction periods lasted approximately thirty-six hours during which the contraction was gradually increased to 50–60% by gradually increasing the temperature. If the temperature reached 260° before such a contraction was produced, no further temperature increases were attempted. In this latter case, the catalysts were found to be quite useless for producing liquid hydrocarbons.

Catalysts 10-C, 47-C and 80A did not receive the above induction and reduction treatment. Gas of composition H_2 + CO was passed over the raw unreduced catalyst for fifteen hours at about 240° at a space velocity of 150 to 200 volumes per hour. The composition of the gas was then changed to $2H_2 + 1CO$. The new gas mixture was passed over 10-C for sixty-two and one-half hours and over 47-C and 80A for twenty-five hours.

The catalysts were all operated for unit periods of one week. At the end of each period, the solid and liquid hydrocarbons were collected and measured. The catalysts were then operated for another week if the previous week's performance warranted. To compensate for loss of activity, the temperature was gradually raised to, but not above, 260°.

TABLE II

MAGNETIC SUSCEPTIBILITY OF SYNTHETIC FERRIC OXIDES AND FERRIC OXIDE HYDRATES

Phase	Susceptibility (Albrecht)[8]	Susceptibility (present authors)
$\alpha Fe_2O_3 \cdot H_2O$	42×10^{-6}	49.2×10^{-6}
$\beta Fe_2O_3 \cdot H_2O$	....	29.0×10^{-6}
$\gamma Fe_2O_3 \cdot H_2O$	42×10^{-6}	42.2×10^{-6}
αFe_2O_3	25×10^{-6}	22×10^{-6}
γFe_2O_3	ferromagnetic	ferromagnetic

The gas mixture used in the synthesis was made of natural gas, steam, and carbon dioxide over a nickel catalyst at 1000° according to a previously described method.[13]

All the experimental data obtained are summarized in Tables I and II. Characteristic X-ray diffraction patterns are presented in Figure 1.

Discussion

In the X-ray diffraction patterns of active catalysts produced by precipitation from a solution containing only nitrate ion in addition to the ferric ion, the diffraction lines of αFe_2O_3 (hematite), $\alpha Fe_2O_3 \cdot H_2O$ (goethite), or both, were iden-

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(13) Storch, Hirst, Fisher and Sprunk, "Bureau of Mines Tech. Paper," 622, part 1, pp. 18-23.

tified. On the other hand, 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 47-F.

The previous investigators, Weiser and Milligan,[14,15] Schikorr,[16] and Heller and Zocher,[17] prepared $\beta Fe_2O_3 \cdot H_2O$ by the slow hydrolysis of ferric chloride solutions. The formation of $\beta Fe_2O_3 \cdot H_2O$ by direct precipitation at temperatures near 75° has not been previously reported. Weiser and Milligan[18] studied a brown gel precipitated at room temperature from ferric chloride solution which was entirely amorphous to X-ray examination. That the gel is composed of minute particles of αFe_2O_3 too small to produce the characteristic hematite diffraction pattern is suggested by the fact that the chloride-free gel can be aged to crystalline hematite with no obvious break in the continuity of the process. Thus, depending on the temperature of the precipitation, one may obtain either $\beta Fe_2O_3 \cdot H_2O$ or a gel of αFe_2O_3 particles too small to produce a diffraction pattern.

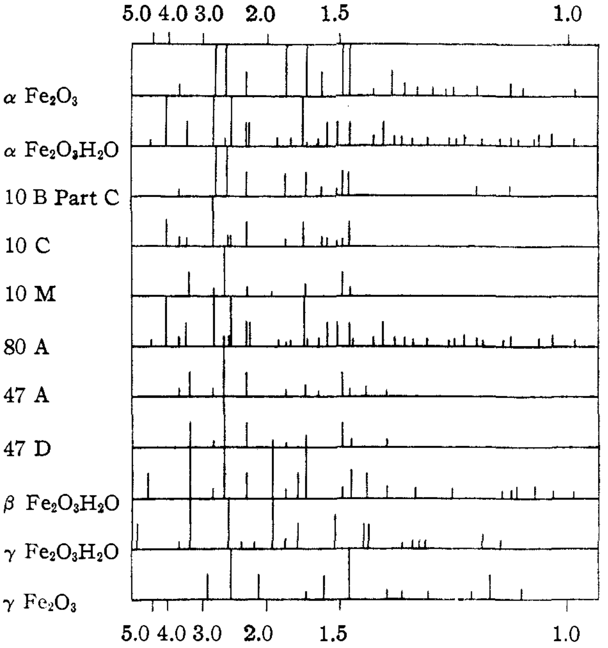

Fig. 1.—X-Ray diffraction powder patterns of various iron Fischer–Tropsch catalysts and the crystalline ferric oxides and ferric oxide hydrates.

In order to investigate the reason for the nonexistence of β-$Fe_2O_3 \cdot H_2O$ in catalyst 47F, another catalyst was prepared as nearly like 47-F as possible and samples were withdrawn for X-ray diffraction analysis at various stages during the washing procedure. It was found that the samples removed from the slurry immediately after precipitation contained $\beta Fe_2O_3 \cdot H_2O$ but no trace of αFe_2O_3 or $\alpha Fe_2O_3 \cdot H_2O$. But samples removed after several washings did contain αFe_2O_3 and little or no $\beta Fe_2O \cdot {}_3H_2O$. This indicates that $\beta Fe_2O_3 \cdot H_2O$ is metastable and ages to αFe_2O_3. Such an aging of $\beta Fe_2O \cdot {}_3H_2O$ to αFe_2O_3 under similar conditions was observed by Weiser and Milligan.[15] Heller, Kratky and Nowotny,[19] and Kratky and Nowotny[20] have studied the kinetics of the aging of $\beta Fe_2O_3 \cdot H_2O$ in greater detail and they have shown that it is unstable even at room temperature although under their conditions aging lead to $\alpha Fe_2O_3 \cdot H_2O$. One may therefore conclude that catalyst 47-F in common with all the other 47-series catalysts contained $\beta Fe_2O_3 \cdot H_3O$ at one time in its history, but that all the $\beta Fe_2O_3 \cdot H_2O$ had aged to αFe_2O_3 prior to X-ray diffraction analysis. Presumably the $\beta Fe_2O_3 \cdot H_2O$ formed by rapid precipitation as in the case of the catalyst 47-F is more unstable toward aging than the $\beta Fe_2O_3 \cdot H_2O$ formed by slower precipitation as exemplified by the other 47-type catalysts.

It must be emphasized that neither $\alpha Fe_2O_3 \cdot H_2O$[21] nor $\beta Fe_2O_3 \cdot H_2O$[15] is stable at the temperature of the Fischer–Tropsch synthesis on iron catalysts (220–250°) and that αFe_2O_3 itself is not stable under the reducing conditions of the synthesis. The deactivating effect of precipitation in the presence of chloride ion is therefore not due to the presence of $\beta Fe_2O_3 \cdot H_2O$ itself, but to some characteristic which it imparts to the eventual catalyst. This is supported by the fact that 47-F, which contained no $\beta Fe_2O_3 \cdot H_2O$ when examined but which was formed in part at least from $\beta Fe_2O_3 \cdot H_2O$ as an intermediate, was inactive in the synthesis.

Although chloride ion seems to have some slightly deleterious effect,[22,23] the presence of $\beta Fe_2O_3 \cdot H_2O$ at any stage of catalyst preparation greatly accentuates this deactivating effect. Reasonably active catalysts can be produced by precipitation of solutions containing cupric nitrate and ferric chloride,[24] cupric chloride and ferrous chloride,[24] and ferrous chloride,[23] but in each of these cases, the precipitate should at no stage contain $\beta Fe_2O_3 \cdot H_2O$ since the presence of the bivalent ion would insure a crystalline form other than $\beta Fe_2O_3 \cdot H_2O$.

The data of Kolthoff and Moskowitz[25] indicate that the chloride ion does not simply adsorb on $\beta Fe_2O_3 \cdot H_2O$, but instead it exchanges slowly with the OH groups present both on the surface and in the interior of the crystallite according to the equation

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[14] Weiser and Milligan, *Chem. Rev.*, **25**, 1 (1939).

[15] Weiser and Milligan, THIS JOURNAL, **57**, 238 (1935).

[16] Schikorr, *Kolloid-Z.*, **52**, 25 (1930).

[17] Heller and Zocher, *Z. physik. Chem.*, **66**, 365 (1935).

[18] Weiser and Milligan, *J. Phys. Chem.*, **39**, 25 (1935).

[19] Heller, Kratky and Nowotny, *Compt. rend. Acad. Sci. Paris*, **202**, 1171–1173 (1936).

[20] Kratky and Nowotny, *Z. Krist.*, **100A**, 356–360 (1939).

[21] Fricke and Ackermann, *Z. Elektrochem.*, **40**, 630–640 (1934).

[22] Fischer and Tropsch, *Ges. Abhandl. Kenntnis Kohle*, **10**, 406 (1930).

[23] Captured German Documents, TOM Reel 101, PG 21581 NID, Kaiser Wilhelm Institute Researches on Synthetic Fuels, translated by Max Leva.

[24] Bureau of Mines data to be published.

[25] Kolthoff and Moskowitz, THIS JOURNAL, **58**, 777 (1936).

$$\beta\text{FeOOH} + \text{Cl}^- \longrightarrow \beta\text{FeOCl} + \text{OH}^-$$

and becomes a part of the crystal structure. A more descriptive formulation is thus βFeO[OH,Cl]. This observation readily accounts for the difficulty in washing $\beta Fe_2O_3 \cdot H_2O$ free of chloride as experienced by Weiser and Milligan.[15] In spite of their thorough washing, our 47 catalysts also contained considerable amounts of chloride ion. For example, catalyst 47-E contained 2% chlorine.

The studies of the magnetic susceptibilities of ferric oxide-type Fischer–Tropsch catalysts showed that all the active 10-series catalysts with the exception of 10-M and all the 80-series catalysts had higher magnetic susceptibilities than the inactive catalysts. For purposes of comparison, the magnetic susceptibilities of the various synthetic microcrystalline samples of ferric oxide and ferric oxide hydrates were determined and tabulated in Table II. The results agree rather well with the data of Albrecht,[8] which have been tabulated for comparison. No prior data on $\beta Fe_2O_3 \cdot H_2O$ could be found. In all cases, the magnetic susceptibility of the active catalysts is very much higher than that of any of the ferric oxides or ferric oxide hydrates whose presence could be confirmed by X-ray diffraction. By contrast, the suceptibility of the catalysts containing $\beta Fe_2O_3 \cdot H_2O$ does not greatly exceed the susceptibility of $\beta Fe_2O_3 \cdot H_2O$ itself. The enhanced magnetic susceptibility of precipitated oxides has been studied previously and has been variously attributed to the presence of traces of γFe_2O_3,[26] ferromagnetic ferrites,[26] alkali ferrites,[27,28] imperfect crystallization, and deviation of composition from the stoichiometric ratio of iron to oxygen.[29] Most of these factors might be expected to influence favorably the catalytic behavior of the catalyst. The catalytic activity of the catalysts of enhanced magnetic susceptibility may be due to the above characteristics.

Numerous mechanisms suggest themselves by which the deactivation of the catalyst proceeds. The following should be mentioned as chief possibilities:

1. The $\beta Fe_2O_3 \cdot H_2O$ phase may not adsorb sufficient alkali (sodium or potassium) for proper activation at the time of precipitation;
2. $\beta Fe_2O_3 \cdot H_2O$ in the form of βFeOCl may react with the adsorbed alkali by the reaction

$$2\beta\text{FeOCl} + K_2O \longrightarrow 2\text{KCl} + Fe_2O_3$$

3. Reduction of the βFeO[OH,Cl] may produce a reduced phase with some structural feature (crystal habit, crystal imperfection, low lattice energy, inclusions, etc.) which will deactivate the catalyst.
4. The chloride may deactivate the catalyst in a more strictly chemical sense.

These problems are being studied, and the results will be reported in future papers.

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Summary

1. Catalysts prepared by precipitation of hot ferric chloride with potassium carbonate contain $\beta Fe_2O_3 \cdot H_2O$ when freshly precipitated, and they are inactive as Fischer–Tropsch catalysts whether or not they contain $\beta Fe_2O_3 \cdot H_2O$ after washing and drying.
2. Catalysts prepared by precipitation of ferric nitrate solutions with potassium carbonate or potassium hydroxide contain αFe_2O_3 and in some cases $\alpha Fe_2O_3 \cdot H_2O$, and are active in the Fischer–Tropsch synthesis.
3. The magnetic susceptibility of active raw ferric oxide catalysts was considerably greater than that of any ferric oxide or ferric oxide hydrate which would be identified in the diffraction pattern of the catalysts.
4. The magnetic susceptibility of those catalysts containing $\beta Fe_2O_3 \cdot H_2O$ was very much lower than that of the active catalysts and did not greatly exceed that of $\beta Fe_2O_3 \cdot H_2O$ itself.

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[26] Albrecht and Wedekind, *Z. anorg. allgem. Chem.*, **202**, 205 (1931).

[27] Herroun and Wilson, *Proc. Phys. Soc. London*, **33**, 196 (1921).

[28] Chevalier and Mathieu, *Compt. rend.*, **207**, 58 (1938).

[29] Huttig and Kittel, *Z. anorg. allgem. Chem.*, **199**, 129 (1931).