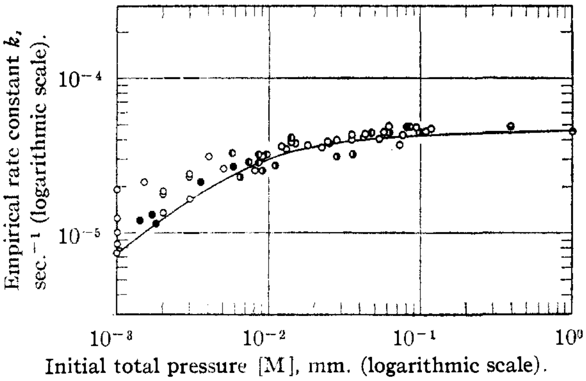

Fig. 6.—Comparison of experimental with computed rate constants; decomposition of pure $N_2O_5$, 27°, curve given by Equation 21: ○, Hodges and Linhorst; ●, Linhorst and Hodges; ◐, Ramsperger and Tolman; ◑, Schumaker and Sprenger; ◓, Daniels and Johnston; ◒, Mills and Johnston.

of nitrogen pentoxide at any concentration of gases can be written

$$k = \frac{(M)\sum\limits_i a_i}{2 + (M)\left[\sum\limits_i d_i/e\right]\left[\sum\limits_i a_i/\left(\sum\limits_i c_i a_i/b_i\right)\right]} \qquad (20)$$

As has been previously shown in the text, $\sum\limits_i a_i = 2.3 \times 10^5$, $\sum\limits_i d_i/e = 6.5 \times 10^3$ and $\sum\limits_i c_i a_i/b_i = 0.29$ sec.⁻¹ When $(M)$ is expressed in units of moles per cc., Equation 20 becomes

$$k = \frac{(M)\ 2.3 \times 10^5}{2 + (M)\ 5.2 \times 10^9}\ \text{sec.}^{-1} \text{ at } 27° \qquad (21)$$

The experimental points from all investigators who used large reaction vessels at low pressures are plotted in Fig. 6. The curve is that given by Equation 21. The experimental points show great scatter, and it has been shown by various authors[15] that heterogeneous reactions are important at very low pressures. The indicated curve was derived only from data for the reaction of nitric oxide with nitrogen pentoxide and from high-pressure data for the nitrogen pentoxide decomposition, yet it fits the low-pressure behavior of nitrogen pentoxide as well as could be desired. All of the individual rate constants that went into the complex expression, Equation 20, are of normal magnitudes. The low-pressure decomposition of nitrogen pentoxide is no longer an anomaly of chemical kinetics.

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[15] See for example A. G. Loomis and D. F. Smith, This Journal, **50**, 1864 (1928).

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# Studies of the Fischer–Tropsch Synthesis. IX. Phase Changes of Iron Catalysts in the Synthesis

By Robert B. Anderson, L. J. E. Hofer, Ernst M. Cohn and Bernard Seligman

Phase changes in a reduced fused-iron catalyst have been studied during the Fischer–Tropsch synthesis with $1H_2$-to-1CO gas at 7.8 atmospheres. In the first few days of the synthesis, α-iron was converted to Hägg carbide ($Fe_2C$). The iron as Hägg carbide increased to a maximum of 29% at 200 hours of synthesis, and then decreased slowly throughout the remainder of the test. Magnetite was formed at a slower rate than Hägg carbide, apparently chiefly at the expense of the α-iron phase. The magnetite phase increased through the experiment.

The study of phase changes in iron catalysts during the Fischer–Tropsch synthesis is difficult because there are no satisfactory chemical methods for differentiating between carbon as carbide, free carbon or other carbonaceous material. In addition to cementite, $Fe_3C$, the existence of two low-temperature carbides of iron, h.c.p. and Hägg, with composition approximating $Fe_2C$, has recently been established by X-ray diffraction[1,2,3] and thermomagnetic studies.[3,4] The presence of one or both of these $Fe_2C$ carbides in used iron Fischer–Tropsch catalysts has been reported.[2,4,5] Recently, Hofer and Cohn[6] described a method of quantitative analysis of mixtures of Hägg carbide, α-iron and magnetite by a combination of thermomagnetic, X-ray diffraction and gravimetric analyses. The present paper gives the results of such analyses of samples of a fused-iron catalyst removed at convenient intervals during a 100-day period of testing. Changes in catalyst composition are compared with observed changes in activity.

## Experimental

The apparatus and procedure for reducing and testing the catalyst have been described previously[7,8,9]; 155 cc. of 6- to 8-mesh fused catalyst D3001[9] was used in this study. The catalyst composition was: Total iron, 67.4%; MgO, 4.61%; $K_2O$, 0.57%; $SiO_2$, 0.71%; and $Cr_2O_3$, 0.65%. The catalyst was reduced (97.7%) in dry hydrogen at a space velocity[10] of 2,500 at 450° for 40 hours and tested in the Fischer–Tropsch synthesis with $1H_2$ to 1CO gas at 7.8 atmospheres. Testing was continuous, except for brief interruptions when the products were removed or when the catalyst was sampled.

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[1] G. Hägg, *Z. Krist.*, **89**, 92 (1934).

[2] Herbst and Halle, F.I.A.T. Reel R-19, Frames 7136–7147; Group leader conferences, Ludwigshafen, T.O.M. Reel 26, Bag 2463; Report, Dr. Wenzel, T.O.M. Reel 134, ItemII/10.

[3] L. J. E. Hofer, E. M. Cohn and W. C. Peebles, This Journal, **71**, 189 (1949).

[4] H. Pichler and H. Merkel, *Bur. Mines Tech. Paper*, 718 (1949).

[5] M. H. Jellinek and I. Fankuchen, in "Advances in Catalysis," Vol. I, Academic Press, New York, N.Y., p. 279, 1948.

[6] L. J. E. Hofer and E. M. Cohn, *Anal. Chem.*, **22**, 907 (1950).

[7] R. B. Anderson, A. Krieg, B. Seligman and W. E. O'Neill, *Ind. Eng. Chem.*, **39**, 1548 (1947).

[8] H. H. Storch, *et al.*, *Bur. Mines. Tech. Paper* **709** (1948).

[9] R. B. Anderson, J. F. Schultz, B. Seligman, W. K. Hall and H. H. Storch, This Journal, **72**, 3502 (1950).

[10] Volumes of feed gas (S.T.P.) per volume of catalyst space per hour.

In a small tube-reactor, it is not possible to withdraw a representative catalyst sample with a simple mechanical "thief." In addition, preliminary analyses of used catalysts indicated that rather wide differences in composition were found if individual particles of a given sample were examined. These differences were presumably a function of the position of the particle in the catalyst bed and were of greater magnitude for particles of samples removed in the early part of an experiment. To minimize these sampling uncertainties, the entire catalyst charge was removed from the reactor, a representative sample taken and the catalyst recharged. To accomplish this, the pressure was released from the system, and the wax pot at the lower end of the catalyst tube removed. A jar of heptane was placed immediately under the catalyst tube and a rapid stream of pure nitrogen swept across the space between the heptane and the catalyst tube (usually 5 cm.). When the catalyst retention tube was removed, the catalyst did not drop until the reactor was tapped with a hammer, which caused the entire catalyst charge to fall into the heptane.

The catalyst in heptane was thoroughly mixed by stirring, and a 5-cc. sample was taken. The heptane was decanted from the jar; and the catalyst, wet with heptane, was recharged into the reassembled reactor. The pressure was increased to 7.8 atmospheres and the synthesis resumed. During the sampling procedure, the reactor was maintained at synthesis temperature with synthesis gas flowing. After the final operating period, in which the temperature had been increased to 300°, the entire catalyst charge was caked in the reactor and had to be drilled from the catalyst tube.

As a result of this sampling technique, the catalyst was recharged in a random condition compared with its previous orientation in the catalyst bed. Thus, the catalyst was "shuffled" at each sampling, increasing the probability of obtaining a representative sample with the number of sampling cycles. To minimize uncertainties in handling the individual samples, the entire sample in heptane was ground to a fine powder, and portions were taken for individual analyses. Thus, the analytical data should represent an average composition of the catalyst bed, and the consistency of the data appears to substantiate this contention.

One portion of the ground sample was used for thermomagnetic analysis and a second portion for X-ray diffraction analysis. A third portion was carefully extracted with boiling toluene, and, after removal of the toluene by evacuation at 100°, this portion was analyzed for total carbon and total iron by conventional methods. In handling the reduced or used catalysts (*i.e.*, transferring, sampling or analyzing the samples), special care was taken to preclude oxidation.

All analytical data are referred to the weight of iron in the sample. The results of the magnetic analyses are reported as the fraction of the total iron as α-iron, Hägg carbide, magnetite or non-magnetic iron.[11] Total carbon analyses are reported as the atom ratio of total carbon to total iron. Activities are reported as cubic centimeters of synthesis gas reacted per gram of iron per hour at 240°, when the flow is varied to maintain a 65% contraction; the method of computing the activity has been discussed previously.[12]

## Experimental Data and Discussion

The variation of catalyst composition and activity with hours of synthesis is shown in Fig. 1 and Table I for catalyst D3001 in Test X194.

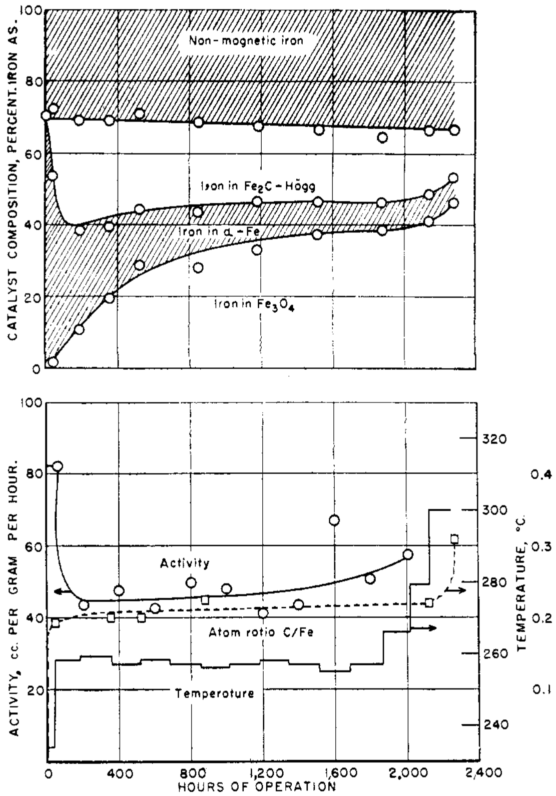

Fig. 1.—The variation of catalyst composition, activity and temperature with time: $Fe_3O_4$–MgO–$K_2O$ catalyst at 7.8 atmospheres of $1H_2$-to-1CO gas.

In the first 46 hours of testing, the temperature was held at 235°; from 46–1870 hours, the temperature was maintained at 257 ± 2°, and the flow of synthesis gas was varied to maintain the apparent contraction at about 62%; from 1870–2300 hours, the temperature was increased in several steps to 300°.

TABLE I

COMPOSITION AND ACTIVITY OF FUSED-IRON CATALYST D3001 ($1H_2$-TO-1CO GAS AT 7.8 ATMOSPHERES)

| Testing data | | | Total carbon | | Magnetic analysis, % Fe as | | | |
|---|---|---|---|---|---|---|---|---|
| Hours | Temp., °C. | Activity cc./g./hr.[a] | C:Fe[b] | Max. Fe as $Fe_2C$, %[c] | $Fe_2C$ Hägg | α-Fe | $Fe_3O_4$ | Non-magnetic |
| 0 | ... | .. | 0 | 0 | 0 | 69.2 | 0 | 30.8 |
| 46 | 235 | 82.0 | .193 | 38.6 | 17.8 | 50.0 | 1.9 | 30.3 |
| 200 | 259 | 43.2 | .200 | 40.0 | 29.2 | 28.0 | 12.0 | 30.8 |
| 400 | 257 | 47.5 | .200 | 40.0 | 26.8 | 20.2 | 21.9 | 31.1 |
| 600 | 258 | 42.6 | .205 | 41.0 | 25,0 | 15.9 | 27.9 | 31.2 |
| 800 | 257 | 49.7 | .210 | 42.0 | 23.8 | 13.2 | 31.5 | 31.5 |
| 1000 | 256 | 47.9 | .210 | 42.0 | 23.0 | 11.3 | 33.9 | 31.8 |
| 1200 | 257 | 41.2 | .212 | 42.4 | 22.3 | 10.1 | 35.6 | 32.0 |
| 1400 | 257 | 43.7 | .214 | 42.8 | 21.8 | 9.2 | 36.9 | 32.1 |
| 1600 | 255 | 67.0 | .215 | 43.0 | 21.7 | 8.8 | 37.2 | 32.3 |
| 1800 | 257 | 50.9 | .216 | 43.2 | 21.2 | 8.2 | 38.0 | 32.6 |
| 2000 | 266 | 57.3 | .218 | 43.6 | 20.3 | 7.8 | 39.1 | 32.8 |
| 2200 | 300 | 21.0[d] | .275 | 55.0 | 16.9 | 7.2 | 42.9 | 33.0 |
| 2300 | 300 | ..[d] | .313 | 62.6 | 12.8 | 6.8 | 47.4 | 33.0 |

[a] Volume (cc.) of $H_2$ + CO converted per gram of iron per hour at 240°. [b] Atom ratio. [c] This value assumes that all of the carbon is present as $Fe_2C$. [d] Very high percentage conversions of synthesis gas, for which the method of computing activities is not valid.

The magnetic analyses indicated that the reduced catalyst contained 69.2% α-iron and 30.8% non-magnetic iron. The fraction of non-magnetic

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[11] As discussed in the paper of Hofer and Cohn,[6] a fraction of the iron is not detected by magnetic analysis, *i.e.*, the sum of the iron in magnetic phases does not equal the total iron as determined by chemical analysis. A large portion of this non-magnetic iron may be attributed to the relatively low field-strength (2160 gauss) used. Possibly a higher field-strength would saturate the magnetic phases more completely and eliminate much of the non-magnetic iron. The distribution of the non-magnetic iron among observed magnetic phases need not be proportional to the relative abundance of these magnetic phases, because the degree of unsaturation is probably not the same for all of the ferromagnetic phases present. As the non-magnetic iron is determined by difference, the uncertainties in its determination are a composite of the errors in the determination of the magnetic phases; however, as shown in Fig. 1, the values for the non-magnetic iron are quite consistent.

[12] R. B. Anderson, B. Seligman, J. F. Shultz, R. Kelly and M. A. Elliott, *Ind. Eng. Chem.*, to be published.

iron remained essentially constant throughout the test despite rather wide changes in catalyst composition. The thermomagnetic curves and X-ray diffraction patterns disclosed the presence of only three iron phases: α-iron, Hägg carbide and magnetite; other carbides or oxides, therefore, were not present in detectable amounts. In the initial 200 hours, the fraction of iron present as Hägg carbide increased to its maximum, 29.2%. In subsequent testing at 257° (200 to 1800 hours), the amount of iron present as Hägg carbide decreased to 21.2%. The α-iron phase decreased rapidly in the first 200 hours with the formation of both Hägg carbide and magnetite. Magnetite, which was formed at a slower initial rate than the carbide phase, increased throughout the experiment. The α-iron phase decreased more rapidly than Hägg carbide did, and it appears that the carbide phase may be more resistant to oxidation than α-iron.

The atom ratio of total carbon to total iron, as shown in Fig. 1 and Table I, increased very rapidly to C/Fe = 0.20, where it remained essentially constant throughout the period of testing at 257°. From the carbon:iron ratio, an upper limit of iron as Hägg carbide may be computed, the value from the magnetic analysis being a lower limit. In the period 1870–2300 hours, the temperature of operation was increased to 278° and then to 300°. The testing at 300° increased the C:Fe ratio from 0.216 to 0.313 and caused plugging of the catalyst tube. However, the thermomagnetic analysis showed that the iron as Hägg carbide decreased from 21.2 to 12.8% whereas the iron as magnetite increased from 38.0 to 47.4%. Thus, at 300° the Hägg carbide phase was quite rapidly transformed into magnetite, even though there was a net increase in total carbon. In these samples, the total carbon-to-iron ratio corresponds to more carbon than that in the Hägg carbide phase and in the non-magnetic phase, assuming as an upper limit that this phase is entirely Hägg carbide. The actual composition of the non-magnetic iron phase is not known. It may be attributed either to the presence of small or incomplete crystallites of ferromagnetic components, which are not magnetically saturated in the magnetic field used, or to the presence of non-ferromagnetic phases; however, the formation of non-ferromagnetic phases would not be expected under synthesis conditions.

Catalytic activity is a complex function of composition, extent, and accessibility of the surface; hence, a simple correlation between bulk phase composition and activity need not be expected and need not be meaningful, if found. In test X194, the activity was essentially constant from 200 to 1800 hours. In this period, the fraction of iron present as α-iron and magnetite varied considerably, while the iron as carbide decreased slowly and the amount of non-magnetic iron remained essentially constant. Thus, the best correlations exist between activity and the fraction of iron as Hägg carbide, non-magnetic iron, or the sum of these phases.

Analyses of numerous catalysts after use in the synthesis indicate that Fig. 1 represents the general behavior of a reduced catalyst in the Fischer–Tropsch synthesis. Although synthesis gas is a good reducing agent, the presence of carbon dioxide and especially water vapor formed in the synthesis causes the partly converted gas to become an oxidizing medium for both α-iron and $Fe_2C$ carbides. On this basis, the initial rapid formation of carbide must be attributed to the greater rate of carbide formation compared with the rate of oxidation. The carbides as well as the nitrides[9] of iron appear to resist oxidation in the synthesis, and this may be significant in producing the desirable effects attributed to the presence of interstitial phases. Although cementite is more stable than either h.c.p. or Hägg carbides, in our laboratory, cementite has never been formed in the course of synthesis in the range of temperatures, 200–300°.

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