Studies of the Fischer-Tropsch Synthesis

Application of Wheeler Equation to Synthesis Data

ROBERT B. ANDERSON and LAWRENCE J. E. HOFER,
Central Experimental Station, U. S. Bureau of Mines, Pittsburgh, Pa.

THE PRECEDING article in this series (9) presented data for the variation of the reaction of the Fischer-Tropsch synthesis with catalyst geometry. At the temperatures and pressures used, the pores of the catalyst are filled with liquid hydrocarbons during synthesis, and mass transport involves dissolution and diffusion of reactants through liquid films and oil-filled pores. Calculations based on a simplified model indicate that average depth of effective catalyst extends only 0.01 to 0.04 cm. from the external surface. In the present paper equations based on a more realistic model, in which diffusion and reaction in catalyst pores are considered, are applied to the synthesis data.

A special solution of the differential equation of Wheeler (*11, 12*) was derived on the assumption that the particles are spheres and that the synthesis is a simple first-order reaction. The synthesis, to at least a first approximation (*1, 10*), is first-order with respect to the partial pressure of synthesis gas.

MODIFIED WHEELER EQUATION

Wheeler's differential equation (*11, 12*) for spherical particles is

$$\frac{d^2C}{dx^2} + \frac{2}{x}\frac{dC}{dx} = b^2C \qquad (1)$$

where c = concentration of reactants at distance x from center, $b = 2(k/\bar{r}\,D)^{1/2}$, k = first-order rate constant, $\bar{r}$ = average pore radius, and D = diffusivity. Equation 1 was solved for particles in which a layer of porous, active iron of depth $R - r$ (Figure 1) is formed on a core of inert magnetite by reduction. The following limiting conditions were used: $dC/dx = 0$ at $x = r$, where $0 < r < R$, and $C = C_0$ at $x = R$, where C_0 is concentration at pore mouth, to yield

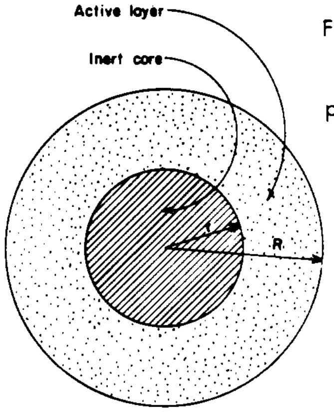

Figure 1. Idealized representation of partly reduced particle of catalyst

$$\left(\frac{dC}{dx}\right)_R = C_0b\left[\frac{\cosh(R-r)b + rb\sinh(R-r)b}{\sinh(R-r)b + rb\cosh(R-r)b} - \frac{1}{bR}\right] = C_0b\,X \qquad (2)$$

For porous catalysts in which the total surface area greatly exceeds the external area of the particles, the productivity per gram of iron, A, equal the product of the area of pore openings at the external surface times the rate of diffusion at this interface.

$$A = \frac{3\,V_gD}{2R}\left(\frac{dC}{dx}\right)_R = \frac{3\,V_GD\,C_0b\,X}{2R} = \frac{3\,V_GC_0}{R}\left(\frac{kD}{\bar{r}}\right)^{1/2}X \qquad (3)$$

Here V_G is the pore volume for the completely reduced catalyst per gram of iron. V_G is used only to define the ratio of the area of pore mouths to total external area which is equal to the porosity for a completely reduced catalyst (*11*). The porosity of the reduced portion of the catalyst is independent of the extent of reduction, f, for $f > 0$, and is most simply defined in terms of the completely reduced catalyst.

For a graphical determination of the constants of Equation 3, the following transformations are made: A quantity, L, the "depth factor," is defined as $L = (R - r)b$; $r = ZR$, then $L = bR(1 - Z)$, $bR = L/1 - Z$, and $br = LZ/1 - Z$; Z is related to extent of reduction f by

$$z = r/R = (1 - f)^{1/3}$$

Then the expression for X in Equation 2 may be written as

$$X = \frac{\cosh L + \dfrac{LZ}{1-Z}\sinh L}{\sinh L + \dfrac{LZ}{1-Z}\cosh L} - \frac{1-Z}{L} \qquad (4)$$

Equation 3 then becomes:

$$Y = \frac{AR\,\bar{r}^{\,1/2}}{3\,V_GC_0} = (kD)^{1/2} \times X \qquad (5)$$

The value of L is given by

$$L = \frac{2R(1-Z)}{\bar{r}^{\,1/2}}\left(\frac{k}{D}\right)^{1/2} = L'\left(\frac{k}{D}\right)^{1/2} \qquad (6)$$

Double logarithmic plots of X (Equation 4) as functions of L and Z are presented in Figure 2. All of the terms in Y and

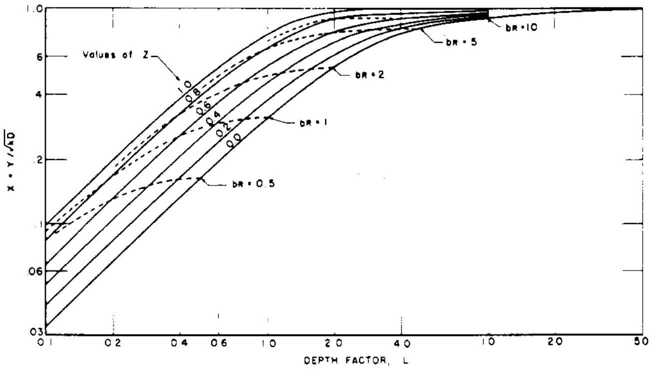

Figure 2. Double logarithmic plots of Equation 3

L can be evaluated in terms of measured quantities except k and D, and these quantities can be estimated from the values required to yield the best fit of experimental data in Figure 2. Also plotted on this graph as dotted lines are the variations of X, as $L = bR(1 - Z)$ is varied by changing the quantity of Z at constant values of bR of 0.5, 1, 2, 5, and 10. These lines indicate how the activity should vary with the extent of reduction.

APPLICATION OF THE MODIFIED EQUATION TO DATA OF FISCHER-TROPSCH SYNTHESIS

The previous paper (*9*) reported activity data for the three series of synthesis tests using fused iron catalyst D3001, both reduced and reduced-and-nitrided, with $1H_2 + 1CO$ at 21.4 atm.

A. Particle Size. Average particle radius varied from 0.0135 to 0.151 cm. Catalysts were essentially completely reduced.

B. Extent of Reduction. 6- to 8-mesh particles (average radius of 0.116 cm.) reduced in hydrogen to extents varying from 0.082 to 0.546 at 400° C.

C. Temperature of Reduction. 6- to 8-mesh particles (average radius of 0.116 cm.) essentially completely reduced in hydrogen at temperatures of 400°, 450°, 500°, 550°, and 600° C. The average pore radius, $\bar{r}$, increases from 113 to 1100 A. as the temperature varies from 400° to 600° C.

These experiments were made at different temperatures near 240° C., and the activity data were corrected to 240° C. using the Arrhenius equation with an activation energy of 19 kcal. per mole (*9*). Subsequent work showed that this activation energy was valid only for 6- to 8-mesh and larger particles; hence activation energies were determined as a function of particle size. Experiments were made on three samples of nitrided iron catalyst D3001, sieved after reduction (at 450° C.) and nitrided to yield particles with average hypothetical spherical radii of 0.116, 0.0508, and 0.0225 cm. Tests were made with $1H_2 + 1CO$ gas at 21.4 atm. after about 2 weeks of synthesis. The observed activation energies determined by least square evaluation of the data were 20.1, 27.0, and 27.6 kcal. per mole for catalysts with average particle radii of 0.116, 0.0508, and 0.0225 cm., respectively.

Wheeler's simplified Equation 58 (*11*) was differentiated to obtain $E_{\text{obsd.}} = R\ d \ln A/d(1/T)$, where $E_{\text{obsd.}}$ is the observed activation energy. From the resultant equations, $E_{\text{obsd.}}/E_t$—where E_t is the activation energy at the surface —may be plotted as a function of R on double logarithmic scales to provide a curve for obtaining E_t and extrapolation. The activation energies are given in Table I; the value of E_t was 28.0 kcal. per mole.

Equation 3 requires that the productivity, A, be known at a constant value of reactant concentration, C_0. The productivity was calculated at zero conversion of reactants, where C_0 equal the concentration of reactant in the feed. For this purpose the well-tested empirical equation (*1, 4*), $-\ln(1-x) = k'/Q$, was used, where x is the fraction of hydrogen plus carbon monoxide reacted, Q is the feed rate in cubic centimeters (S.T.P.) of hydrogen plus carbon monoxide per second per gram of iron, and k' is a rate constant. At zero conversion the volume in cubic centimeters (S.T.P.) of gas converted per second per gram of iron equals k' (*4*). The value of k' was then corrected to 240° C. using the appropriate activation energy.

For series B and C using 6- to 8-mesh particles an activation energy of 19 kcal. per mole was used. For series A with both reduced and nitrided catalysts activation energies in Table I were used. Productivity, A, is defined here as cubic centimeters (S.T.P.) of hydrogen and carbon monoxide consumed per second per gram of iron at 240° C. and zero conversion, and concentration, C_0, is expressed as volumes (S.T.P.) of hydrogen plus carbon monoxide per unit volume.

An idealized model of catalyst geometry was used, and the average catalyst properties were obtained by gross measurements: equivalent spherical particle radii from particle density and the average weight of 100 particles, average cylindrical pore radii from surface area and pore volume, and depth of reduced layer from extent of reduction. Assumptions of the model and the methods of averaging may lead to moderately large discrepancies in some cases. In view of these factors, experimental uncertainties, and the method used in fitting data to theoretical curves (superposition of log-log plots), the reliability of values obtained for constants is not high.

Fair agreement of data from the particle size series and extent of reduction series with curves of Figure 2 was obtained, as shown in Figures 3 and 4. The values of Y in

Table I. Activation Energies as a Function of Particle Size for Nitrided Iron Catalysts

Mesh Size	Particle Radius, Cm.	Activation Energy, Kcal. per Mole
4-6	0.151	18.6[a]
6-8	0.116	20.1
12-16	0.0508	27.0
28-32	0.0225	27.6
42-60	0.0135	28.0[a]

[a] Obtained by extrapolation

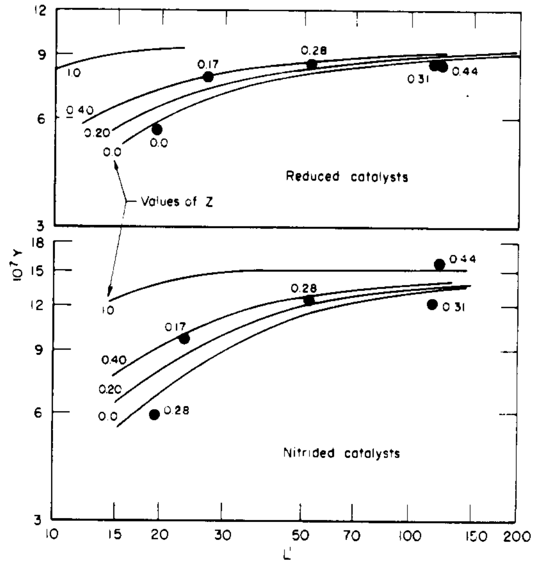

Figure 3. Data for particle size series superimposed on curves of Figure 2

Table II. Values of k and D

Series	Reduction Temp., ° C.	Average Pore Radius, A.	Reduced Catalysts: k, 10^8 cm./sec.	Reduced Catalysts: D, 10^6 sq. cm./sec.	Nitrided Catalysts: k, 10^8 cm./sec.	Nitrided Catalysts: D, 10^6 sq. cm./sec.
Extent of reduction	400	113	8.7	8.7	9.4	9.4
Particle size	450	194	12.4	7.0	12.0	18.8
	600	1112	. . .	. . .	19	75

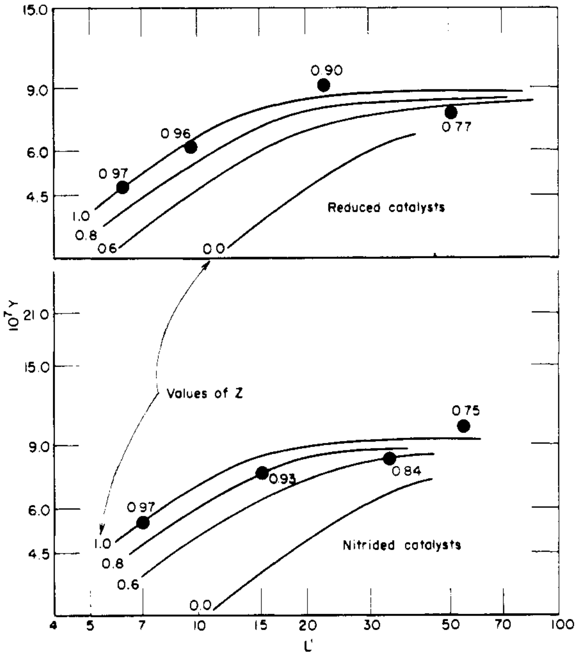

Figure 4. Data for extent of reduction series superimposed on curves of Figure 2

these plots usually deviated less than 10% from the theoretical curves. Sensible plots of data for the temperature of reduction series could not be made, as values of Y decreased with increasing values of L'.

The values of D for nitrided catalysts of the particle size and extent of reduction series (Table II) increase with increasing average pore radius; however, the reliability of these values is too low to permit a characterization of the relationship between D and $\bar{r}$. This variation of D with $\bar{r}$ may explain why the data from the temperature of reduction series do not fit the theoretical curves in Figure 2. For this series the assumption was made that $D = \gamma \bar{r}$, where γ is a constant. These data now fit the hypothetical curves in a satisfactory manner, and values of k of 27 × 10^{-8} were obtained for reduced and nitrided catalysts, respectively. The values of constant γ in Table III justify this relationship only as a rough approximation. It is difficult to decide whether the apparent increase in diffusivity with increasing pore diameter is real or merely a correction for deficiencies of the model. Electron micrographs of replicas stripped from this catalyst after reduction at 450° or 550° C. showed elongated pores with a shortest dimension of about 500 to 800 A. (*6*). These and other results suggest that the catalyst has a group of larger pores that are relatively independent of reduction temperature plus smaller pores or roughness that vary widely with reduction temperature.

DISCUSSION

Diffusivities of reactants in Fischer-Tropsch oils have not been determined; however, estimates were made with semi-empirical equations of Wilkes and Chang (*13*) for hydrogen and carbon monoxide in a normal C_{30} hydrocarbon at 250° C. using a viscosity extrapolated from the data of Rossini (*8*). These values, $D_H = 1.9 \times 10^{-4}$ sq. cm. per second and $D_{CO} = 1.2 \times 10^{-4}$, are of similar magnitude to to that estimated from data of Reamer, Duffy, and Sage (*7*) for methane in white oil (molecular weight = 340), $D_{CH_4} = 2.0 \times 10^{-4}$ sq. cm. per second.

Table III. Values of $\gamma = D/\bar{r}$

Series	Value of γ Reduced	Value of γ Nitrided
Particle size		
Reduced at 450°	3.6	9.7
Reduced at 600°	...	6.7
Extent of reduction	7.7	8.3
Reduction temperature	3.0	6.0

Eagle and Scott (*3*) found that the diffusivities of liquid hydrocarbons in silica and silica-alumina gels increased with increasing average pore radii and leveled out at the diffusivity of bulk liquid for radii of about 50 A. These data can be roughly approximated by $D = \gamma \bar{r}$ for values of $\bar{r} < 40$ A. However, the diffusivities estimated from present synthesis experiments had not leveled off at the highest pore radii studied: 1112 A. These values, 7 to 75 × 10^{-6} sq. cm. per second, are sufficiently smaller than the estimated bulk diffusivities 100 to 200 × 10^{-6}, so that the diffusivity-pore radius curve could flatten at the value of bulk diffusion. The observation that the diffusivity in pores is of the order of 5 to 50% of that in the bulk liquid explains why diffusion in pores, but not in bulk liquid (oil films on external surface of particles in dry-bed units and bulk liquid in oil-filled reactors) is the important slow step in the Fischer-Tropsch synthesis, at least at temperatures below about 290° C.

Kölbel (*5*) determined solubilities of gases in Fischer-Tropsch wax. At 233° C. the solubilities were: H_2 0.17; CO 0.20; CO_2 0.44; and H_2O 0.73 cc. (S.T.P.) per gram-atm. In unpublished Bureau of Mines work obtained by investigations of the oil circulation process (*2*), somewhat larger solubilities were observed in a 250° to 450° C. fraction of synthesis oil at 233° C.: H_2 0.26; CO 0.32; CO_2 0.83; and H_2O 0.78. In this process, synthesis plus recycle gas is passed upward through a fixed bed of catalyst submerged in synthesis oil, which is circulated upward through the bed. Apparently equilibrium was very nearly obtained at the outlet of the reactor, and solubilities during synthesis and in similar experiments with catalyst removed were essentially the same. Other unpublished studies demonstrated that about half of the normal rate of synthesis could be attained by passing synthesis gas through the cooling oil in an external absorber and circulating this oil through the catalyst bed. These results suggest that the transport of reactants through oil films external to the catalyst particles is not the rate-determining step.

LITERATURE CITED

(1) Anderson, R. B., Seligman, B., Shultz, J. F., Kelley, R. E., Elliott, M. A., *Ind. Eng. Chem.* **44**, 391 (1952).
(2) Benson, H. W., Field, J. F., Bienstock, D., Storch, H. H., *Ibid.*, **46**, 2278 (1954).
(3) Eagle, S.E., Scott, J.W., *Ibid.*, **42**, 1287 (1950).
(4) Karn, F.S., Seligman, B., Shultz, J.F., Anderson, R.B., *J. Phys. Chem.* **62**, 1039 (1958).
(5) Kölbel, H., Ackerman, P., Engelhardt, F., *Erdöl u. Kohle* **9**, 153 (1956).
(6) McCartney, J.T., Anderson, R.B., *J. Appl. Phys.* **22**, 1441 (1951).
(7) Reamer, H.H., Duffy, C.H., Sage, B.H., *Ind. Eng. Chem.* **48**, 285 (1956).
(8) Rossini, F.D., others, Natl. Bur. Standards (U. S.) Circ. **C461** (1947).
(9) Shultz, J. F., Abelson, M., Stein, K. C., Anderson, R. B., *J. Phys. Chem.* **63**, 496 (1959).
(10) Storch, H. H., Golumbic, N., Anderson, R. B., "Fischer-Tropsch and Related Syntheses," Chap. 6, Wiley, New York, 1951.
(11) Wheeler, A., in "Advances in Catalysis," W. G. Frankenburg, V. I. Komarewsky, E. K. Rideal, eds., Vol. **III**, p. 250, Academic Press, New York, 1951.
(12) Wheeler, A., in "Catalysis," P. H. Emmett, ed., Vol. **II**, p. 105, Reinhold, New York, 1955.
(13) Wilkes, C.R., Chang, P., *A.I.Ch.E. Journal* 1, 264 (1955).

RECEIVED for review October 5, 1959. Accepted March 11, 1960.