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PHYSICAL CHEMISTRY OF THE FISCHER-TROPSCH SYNTHESIS

By R. B. Anderson, J. F. Shultz, L. J. E. Hofer,
and H. H. Storch

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By

R. B. Anderson,[2] J. F. Shultz,[2] L. J. E. Hofer,[2] and H. H. Storch [3]

Summary

THIS PAPER summarizes the results of physicochemical studies of the Fischer-Tropsch synthesis (the catalytic hydrogenation of carbon monoxide) undertaken by the Federal Bureau of Mines as part of its program on improving processes for producing liquid fuels from coal.

Criteria for activity in the Fischer-Tropsch synthesis are considered. For example, ferromagnetism is a satisfactory criterion of activity in elements of the iron group and their compounds.

The effectiveness of iron catalysts after different pretreatments is examined. A precipitated ferric oxide containing copper oxide and potassium carbonate showed virtually the same activity after a variety of pretreatments; its selectivity, however, varied widely. Catalysts treated directly with synthesis gas or carbon monoxide were reduced to magnetite and yielded a high-molecular-weight product, whereas catalysts reduced in hydrogen, as well as those reduced in hydrogen and subsequently converted to carbide, yielded products of lower molecular weight. Those reduced in hydrogen and nitrided yielded products having the lowest molecular weight and high concentrations of oxygenated chemicals.

The same general trends in selectivity were observed with fused iron oxide catalyst containing small amounts of magnesia and potassium oxide. However, catalysts converted to nitrides, carbonitrides, or carbides were more active than reduced catalysts. The reduced catalyst was more active than a re-oxidized catalyst. At pressures of 300 p.s.i.g. the activity of catalysts converted to carbides decreased rapidly, presumably because of the rapid oxidation rate of the carbide phases. On the other hand, nitrided catalysts oxidized slowly.

Detailed information is presented for changes in surface area, pore volume, and average pore radii of fused iron oxide catalyst during reduction, carburization, nitriding, and oxidation. The pore geometry of these catalysts can be varied over wide ranges by proper choice of reduction conditions.

With iron catalysts the synthesis rate increased linearly with operating pressure, and overall apparent activation energies of 18 to 21 kcal. per mole have been obtained. The variation of conversion with space velocity can be

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expressed by a simple first-order empirical equation. Apparently, the primary reaction produces water as its principal oxygenated product. This reaction is followed by the water-gas shift. Kinetic data on synthesis with cobalt and nickel catalysts are also summarized.

Information on the mechanism of chain growth was obtained from observed isomer and carbon-number distributions of the products from the Fischer-Tropsch synthesis. A simple growth scheme involving stepwise addition of carbon atoms to end or adjacent-to-end carbons at one end of the growing chain is described. This growth pattern led to the hypothesis of a more detailed mechanism for the synthesis involving oxygenated intermediates. For iron catalysts this hypothesis has been largely substantiated by experiments on incorporating alcohols tagged with carbon-14 into the synthesis products.

INTRODUCTION

The Fischer-Tropsch synthesis may be defined as a hydrogenation of carbon monoxide producing higher hydrocarbons and oxygenated organic molecules that have predominantly straight carbon chains, at least in the range C_4 to C_7. This definition eliminates related processes, such as the higher alcohol and iso syntheses.

The Fischer-Tropsch synthesis is a composite of many reactions producing a variety of molecules of different types and carbon numbers. The catalyst and its environment during synthesis are no less complicated, for the pores are at least partly filled with high-molecular-weight hydrocarbons that are liquid at synthesis temperatures. In addition, carbides, oxides, elemental carbon, and carbonyls are formed to varying degrees, resulting not only in changes in the phases present but also in the physical structure of the catalyst.

This paper considers several physicochemical aspects of the synthesis. It is based in part on three recent reviews.[4-6] For more details on studies of the Fischer-Tropsch synthesis by the Bureau of Mines, the reader is referred to various references, [7-13] as well as to papers cited in the text.

[4] Anderson, R. B. [Contribution for Ullmann's Encyclopedia of Technical Chemistry]: Ullmann's Encyclopädie der technischen Chemie, Urban & Schwarzenberg, Berlin, vol. 9, 1957, pp. 684–748.

[5] Anderson, R. B., Hofer, L. J. E., and Storch, H. H., A Short Review of the Mechanism of the Fischer-Tropsch Synthesis: Chem.-Ing.-Tech., vol. 30, 1958 pp. 560–566.

[6] Anderson, R. B., Physical Chemistry of the Fischer-Tropsch Synthesis on Iron Catalysts: Ipatieff Prize Address presented at 123d Meeting, American Chemical Society, Mar. 15–19, 1953, Los Angeles, Calif.; preprinted in General Papers Presented Before the Division of Petroleum Chemistry of the American Chemical Society, No. 29, pp. 69–81.

[7] Storch, H. H., Anderson, R. B., Hofer, L. J. E., Hawk, C. O., Anderson, H. C., and Golumbic, N., Synthetic Liquid Fuels From Hydrogenation of Carbon Monoxide, Part 1: Bureau of Mines Tech. Paper 709, 1948, 213 pp.

[8] Storch, H. H., Golumbic, N., and Anderson, R. B., Fischer-Tropsch and Related Syntheses: John Wiley & Sons, Inc., New York, N.Y., 1951, 610 pp.

[9] Anderson, R. B., The Thermodynamics of the Hydrogenation of Carbon Monoxide and Related Reactions: Chap. 1 in Catalysis, vol. IV (P. H. Emmett, ed.), Reinhold Publishing Corp., New York, N.Y., 1956, pp. 1–27.

[10] Anderson, R. B., Catalysts for the Fischer-Tropsch Synthesis: Chap. 2 in Catalysis, vol. IV (P. H. Emmett, ed.), Reinhold Publishing Corp., New York, N.Y., 1956, pp. 29–255.

[11] Anderson, R. B., Kinetics and Reaction Mechanisms of the Fischer-Tropsch Synthesis: Chap. 3 in Catalysis, vol. IV (P. H. Emmett, ed.) Reinhold Publishing Corp., New York, N.Y., 1956, pp. 257–371.

[12] Hofer, L. J. E., Crystalline Phases and Their Relation to Fischer Tropsch Catalysts: Chap. 4 in Catalysis, vol. IV (P. H. Emmett, ed.), Reinhold Publishing Corp., New York, N.Y., 1956, pp. 373–441.

[13] Shultz, J. F., Hofer, L. J. E., Cohn, E. M., Stein, K. C., and Anderson, R. B., Synthetic Liquid Fuels From Hydrogenation of Carbon Monoxide, Part 2: Bureau of Mines Bull. 578, 1959, 139 pp.

ACTIVITY AND SELECTIVITY IN THE FISCHER-TROPSCH SYNTHESIS

All known active Fischer-Tropsch catalysts contain a major proportion of a metal from group VIII of the periodic table; those containing iron, cobalt, nickel, and ruthenium are efficient Fischer-Tropsch catalysts. Other metals of group VIII catalyze the hydrogenation of carbon monoxide to varying degrees; however, activity is low, and selectivity for producing higher hydrocarbons is poor. Available data are too incomplete to establish whether or not these elements should be classified as Fischer-Tropsch catalysts according to the definition given in the previous section.

The following generalizations may be made: (1) All active elements have partly filled *d* bands; (2) in the iron group active phases are ferromagnetic (this is probably a corollary of criterion 1); (3) for the iron group active phases, including metals, nitrides, carbonitrides, and oxides, can be converted to carbides by treatment with carbon monoxide at synthesis temperatures (150° to 300° C.); and (4) oxides of active elements are reducible in hydrogen at temperatures less than 500° C., and the ratio $p_{H2O}:p_{H2}$ required to produce bulk oxide from the metal is not lower than the value for iron, 0.013.

Criterion 1 includes elements such as chromium, manganese, and molybdenum; however, chromium and manganese can be eliminated on the basis of criteria 3 and 4. Although molybdenum meets requirements 1, 3, and 4, the only reports of its activity are found in patent literature.[14] Ruthenium, although active in the Fischer-Tropsch synthesis at high pressures, apparently does not form interstitial carbides.

For catalysts of the iron group, ferromagnetism is a satisfactory criterion for activity, as shown in table 1. Ferromagnetism *per se* probably does not contribute significantly to catalytic activity; however, it may be taken as an index of the necessary type of vacancy in the *d* bands. The catalytic activity and other properties of phases found in these catalysts have been described in detail by Hofer.[15]

In the last 10 years nitrides and carbonitrides of iron have been found to be effective Fischer-Tropsch catalysts.[16–18] Nitrides can be prepared by treating reduced iron catalysts with ammonia at 300° to 350° C. Although these nitrides are hydrogenated very rapidly in pure hydrogen, in synthesis gas at 5 to 30 atmospheres and at temperatures lower than 270° C. a large fraction of the nitrogen remains for long periods; most of the nitrogen eliminated is replaced by carbon to form carbonitrides.

The activity of nitrided catalysts usually equals or exceeds that of catalysts pretreated in other ways, and nitrided catalysts are oxidized at a slower rate. Nitrides and carbonitrides yield a product with lower molecular weight and large quantities of oxygenated molecules, especially alcohols; however, the relative usage of hydrogen and carbon monoxide is about the same as that for reduced or carburized catalysts.

TABLE 1.—*Catalytic activity and ferromagnetism of various phases of iron-group metals*

Phase	Formula [1]	Activity	Ferromagnetic
Metallic iron	α-Fe	High	Yes.
Magnetite	Fe_3O_4	Probably high	Yes.
Ferric oxide	α-Fe_2O_3	Unknown [2]	No.
	γ-Fe_2O_3	do [2]	Yes.
Ferrous oxide	FeO	do [3]	No.
Iron carbides:			
Hexagonal	ϵ-Fe_2C	High	Yes.
Hägg	χ-Fe_2C	do	Yes.
Cementite	Fe_3C	do	Yes.
"FeC"	~"FeC" [3]	do	Yes.
Iron nitrides	γ'-Fe_4N	do	Yes.
	ϵ-Fe_3N-Fe_2N	do	Yes.
Iron carbonitrides	γ'-$Fe_4(N,C)$	do	Yes.
	ϵ-$Fe_2(N,C)$	do	Yes.
Metallic cobalt	α-Co	do	Yes.
	β-Co	do	Yes.
Cobalt oxide	Co_3O_4	Low [4]	No.
Cobalt carbide	Co_2C	do	No.
Metallic nickel	Ni	High	Yes.
Nickel oxide	NiO	Low [4]	No.
Nickel carbide	Ni_3C	do	No.
Sulfides, chlorides, sulfates of iron, cobalt, and nickel.		do	No.

[1] Formulas shown are only approximate. In some instances composition may vary over a range.
[2] These phases are probably not stable in the synthesis and revert to magnetite, iron, or iron carbide.
[3] Uncertainties in the composition of the so-called "FeC" carbide are very large.
[4] May reduce at synthesis conditions; however, initial activity is low.

[14] For example, Balthis, J. H., Hydrocarbon Polymers From Carbon Monoxide: U.S. Patent 2,795,561, June 11, 1957.
[15] See footnote 12, p. 3.
[16] Anderson, R. B., Shultz, J. F., Seligman, B., Hall, W. K., and Storch, H. H., Studies of the Fischer-Tropsch Synthesis. VII. Nitrides of Iron as Catalysts: Jour. Am. Chem. Soc., vol. 72, 1950, pp. 3502-3508.
[17] Anderson, R. B., and Shultz, J. F., Iron Nitride Catalyst in Carbon Oxide Hydrogenation: U.S. Patent 2,629,728, Feb. 24, 1953.
[18] Anderson, R. B., Iron Nitrides as Fischer-Tropsch Catalysts: Advances in Catalysis, vol. V, Academic Press, Inc., New York, N.Y., 1953, pp. 355-384.

Carburization of reduced catalysts with carbon monoxide seldom changes the selectivity.

Figure 1 shows changes in selectivity produced by various pretreatments for a precipitated Fe_2O_3–CuO–K_2CO_3 catalyst used in synthesis with $1H_2+1CO$ gas at 7.8 atmospheres.[19] The distribution of hydrocarbons plus oxygenated organic molecules is shown as gaseous hydrocarbons and distillation cuts of condensed fractions. The symbols and numbers have the following meaning: (=) Volume-percent olefins in gaseous fractions; (Br) bromine number of liquid fractions; and (OH) and (CO), the weight-percent of hydroxyl and carbonyl groups, respectively.

Despite different pretreatments, the average activity was essentially constant. In test X149 the catalyst was pretreated with synthesis gas at atmospheric pressure and 230° C. In tests X245, X220, and X273A the catalyst was almost completely reduced in hydrogen at 300° C. and subsequently nitrided in ammonia at 300° C. in tests X220 and X273A. After 6 weeks of synthesis in test X273A, the catalyst was treated with hydrogen at 300° C. for test X273B. Products from nitrided catalysts in tests X220 and X273A had a relatively low molecular weight and high concentrations of oxygenated molecules. Removal of nitrogen by hydrogenation in test X273B caused marked increases in molecular weight and unsaturation (bromine number) and a decrease in alcohol content.

In test X341 the raw catalyst was treated with carbon monoxide at 200° to 250° C. for 16.6 hours. This treatment did not greatly change the selectivity as compared with test X149 in which the raw catalyst was pretreated with synthesis gas. Detailed magnetic, gravimetric, and X-ray diffraction studies of the carburization of similar catalysts under similar

[19] Shultz, J. F., Seligman, B., Shaw, L., and Anderson, R. B., Studies of the Fischer-Tropsch Synthesis. XI. Effect of Nitriding on Three Types of Iron Catalysts: Ind. Eng. Chem., vol. 44, 1952, pp. 397–401.

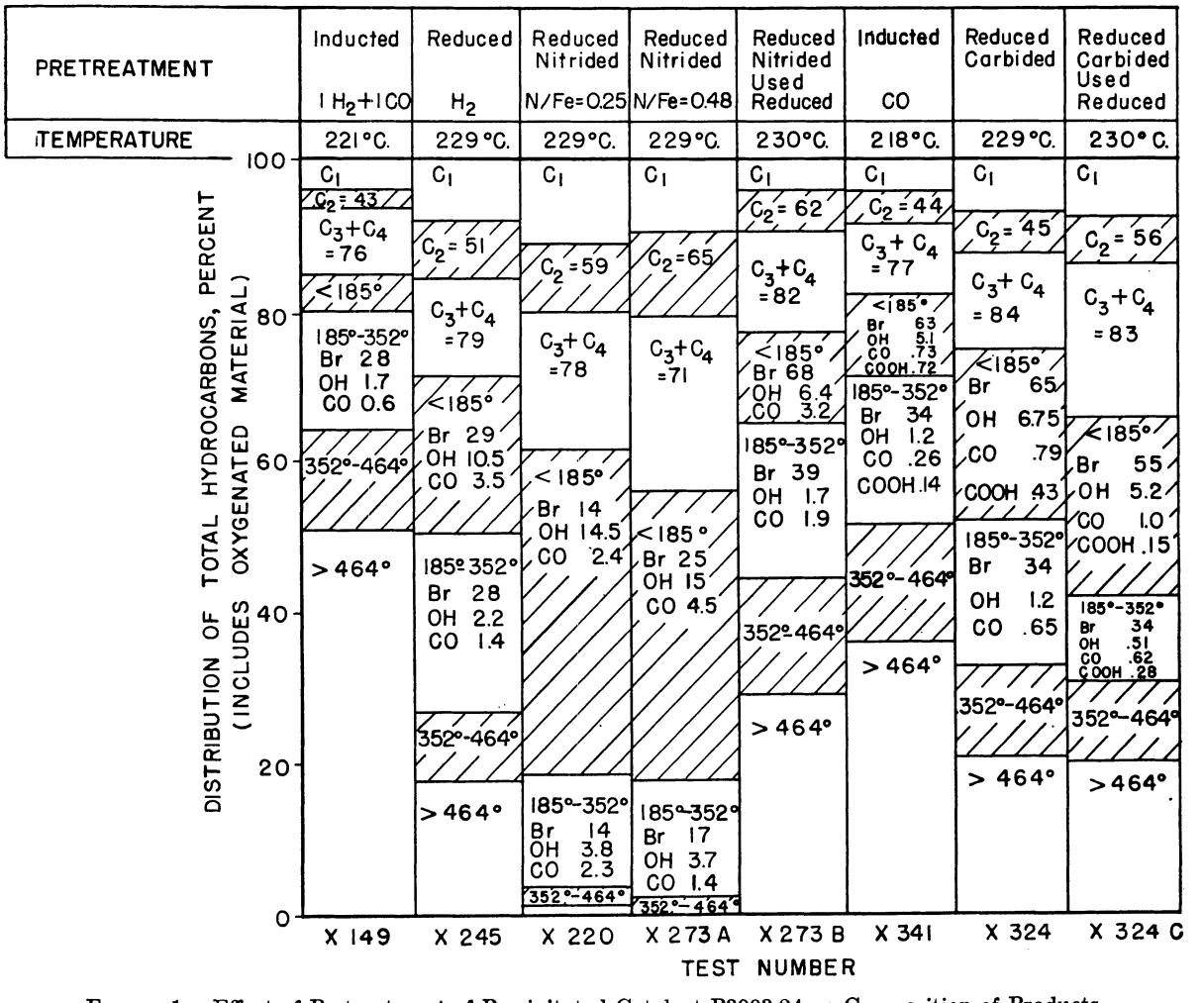

FIGURE 1.—Effect of Pretreatment of Precipitated Catalyst P3003.24 on Composition of Products.

conditions [20] indicate that this catalyst could contain magnetite, possibly a poorly defined form of Hägg iron carbide, and free carbon. This poorly defined Hägg iron carbide can sometimes be detected only by magnetic analysis. The diffraction analysis of the catalyst in test X341 both before and after operation is consistent with the above observation, except that reflections of metallic copper can also be detected.

In test X324 the catalyst was reduced in hydrogen at 296° C. and then converted to Hägg carbide by treatment with carbon monoxide at 185° to 300° C. The selectivity in this test was similar to that of test X245, in which the catalyst was reduced in hydrogen. The selectivity was not greatly changed by rereducing the catalyst of test X324 in hydrogen at 298° C. after 8 weeks of synthesis (test X324C).

With fused iron oxide catalysts similar changes in selectivity can be produced by varying the pretreatment; in addition, the activity of these catalysts may be varied over a wide range by the pretreatment. The standard fused catalyst, D3001, has the following composition in the raw state: Fe 67.4, MgO 4.6, K_2O 0.6, SiO_2 0.7, and Cr_2O_3 0.7 weight-percent, the remainder being oxygen in this state. The catalyst has the structure of a mineral magnetite in which the nonferrous constituents are dissolved in solid solution. The surface area is also well below 0.1 m.²/g. Samples of 6- to 8-mesh catalyst D3001 were given the pretreatments shown in table 2 before being used in the synthesis with $1H_2+1CO$ gas at 300 p.s.i.g. pressure and an hourly space velocity of 300. Although the conditions of reduction varied somewhat, these differences produced only small changes in activity and selectivity.

Activity per gram of iron in the catalyst, corrected to 240° C., and product distribution are pictured in figures 2 and 3, respectively. Oxidation (X397) greatly decreased the catalytic activity; however, the selectivity was about the same as that of the reduced catalyst despite the higher temperature of operation. The selectivities of cementite (X343) [21] and Hägg iron carbide (X342) [22] are similar to that of the reduced catalyst. The initial activity of Hägg carbide was very high; but its activity, as well as that of cementite, decreased rapidly.

Iron nitride (X225A) had a high activity compared with the reduced and carburized samples.[23] Carbonitride prepared by carbiding iron nitride (X279) was as active as the nitride (X225A), but carbonitride prepared by nitriding iron carbide was less active. Despite the somewhat lower operating temperature, both nitride and carbonitride yielded products with a relatively low average molecular weight and large fraction of alcohols and other oxygenated molecules.[23] Iron carbonitrides prepared by carburizing iron nitrides were expected to have the same activity and selectivity as the nitrides, since the latter are converted to carbonitrides in the synthesis.[24] Removal of nitrogen from nitrides and carbonitrides by hydrogenation changed their selectivity to that of reduced or carbided catalysts.

The results of these and other experiments indicate that the initial activities of fused

[20] Cohn, E. M., Bean, E. H., Mentser, M., Hofer, L. J. E., Pontello, A., Peebles, W. C., and Jack, K. H., The Carburization of Iron Oxide With Carbon Monoxide; Modifications of Hägg Iron Carbide: Jour. Appl. Chem., vol. 5, 1955, pp. 418–425.

[21] Shultz, J. F., Hall, W. K., Dubs, T. A., and Anderson, R. B., Studies of the Fischer-Tropsch, Synthesis. XV. Cementite as Catalysts: Jour. Am. Chem. Soc., vol. 78, 1956, pp. 282–285.

[22] Shultz, J. F., Hall, W. K., Seligman, B., and Anderson, R. B., Studies of the Fischer-Tropsch Synthesis. XIV. Hägg Iron Carbide as Catalysts: Jour. Am. Chem. Soc., vol. 77, 1955, pp. 213–221.

[23] See footnote 16, p. 4.

[24] Shultz, J. F., Seligman, B., Lecky, J., and Anderson, R. B., Studies of the Fischer-Tropsch Synthesis. XII. Composition Changes of Nitrided Iron Catalysts During the Synthesis: Jour. Am. Chem. Soc., vol. 74, 1952, pp. 637–640.

TABLE 2.—*Pretreatment of catalyst D3001*

Test	Reduction temperature, ° C.	Subsequent treatment		Initial catalyst composition, atom ratios			Phases present
		Gas	Temperature, ° C.	C:Fe	N:Fe	O:Fe	
X282	400–525	None	None	0	0	0	α–Fe.
X397	450	H_2O in N_2	325	0	0	.73	α–Fe, Fe_3O_4.
X343	500	CO	250	.37	0		Fe_3C, α–Fe.
		He	475				
X342	500	CO	150–350	.44	0		Fe_2C(Hägg), α–Fe.
X407	550	CO	150–250	.32	.20		ϵ–Fe_2(N,C).
		NH_3	350				
X279	550	NH_3	400	.30	.23		ϵ–Fe_2(N,C).
		CO	350				
X225A	550	NH_3	350	0	.44		ϵ–Fe_2N.

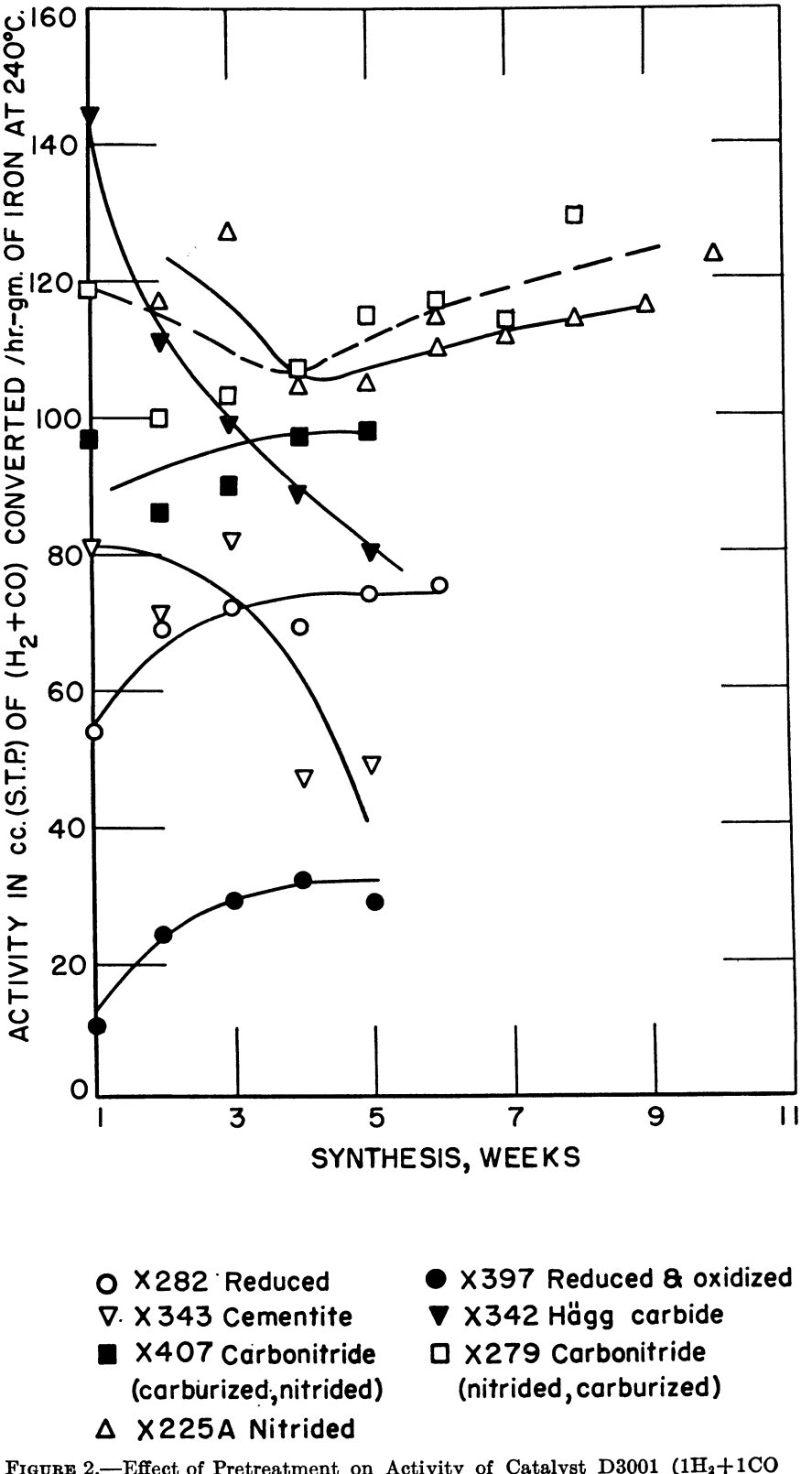

FIGURE 2.—Effect of Pretreatment on Activity of Catalyst D3001 ($1H_2$+1CO Gas at 300 p.s.i.g.)

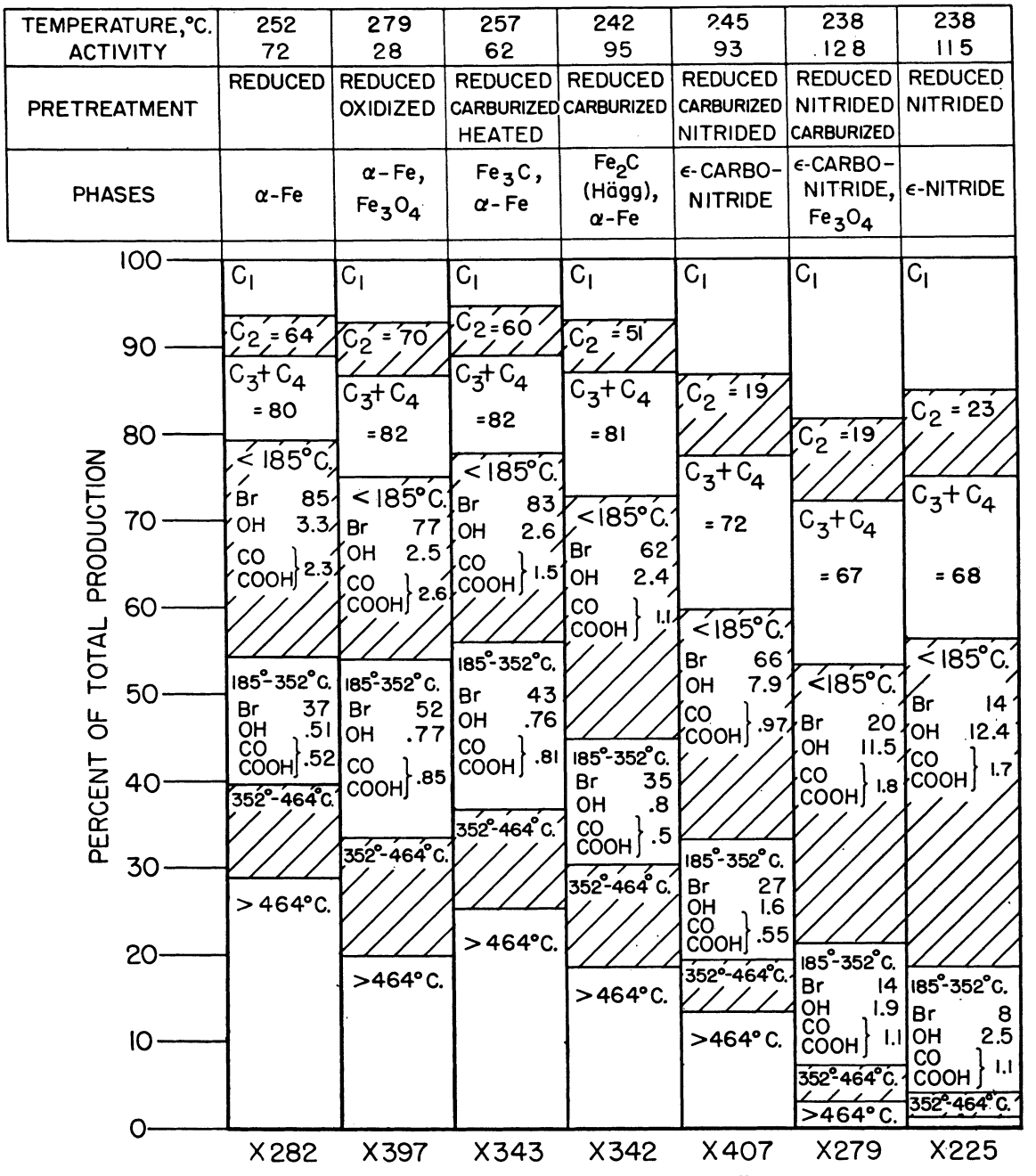

FIGURE 3.—Selectivity of Catalyst D3001 After Various Pretreatments.
Synthesis with $1H_2+1CO_2$ Gas at 300 p.s.i.g. Notations in blocks: Br, Bromine number of fraction; OH, CO, and COOH, weight-percentages of these groups.

iron catalysts converted to interstitial phases (carbides, nitrides, or carbonitrides) are higher than the initial activities of reduced catalysts; however, this advantage may be lost owing to chemical changes. Reduced catalysts oxidize rapidly at both 100 and 300 p.s.i.g. Carbides (Hägg and cementite) resist oxidation at 100 p.s.i.g. but oxidize as rapidly as reduced catalysts at 300 p.s.i.g.; this reaction may account for their rapidly decreasing activity at this pressure. Nitrides, however, resist oxidation at both pressures. Figure 4 shows the chemical changes occurring in a nitrided catalyst during synthesis at 100 p.s.i.g. pressure. In 75 days of synthesis with $1H_2+1CO$ gas at 100 p.s.i.g. the following percentages of the iron were converted to magnetite: Reduced catalyst, 38; Hägg carbide, 20; and ε-nitride, 9.

The unusual properties of nitrides and carbonitrides of iron suggest studies of other interstitial phases of iron-group metals, such as borides, borocarbides, boronitrides, etc. Unfortunately, these phases, as well as nitrides of cobalt and nickel, are very difficult to prepare in the finely divided state essential for catalysis.

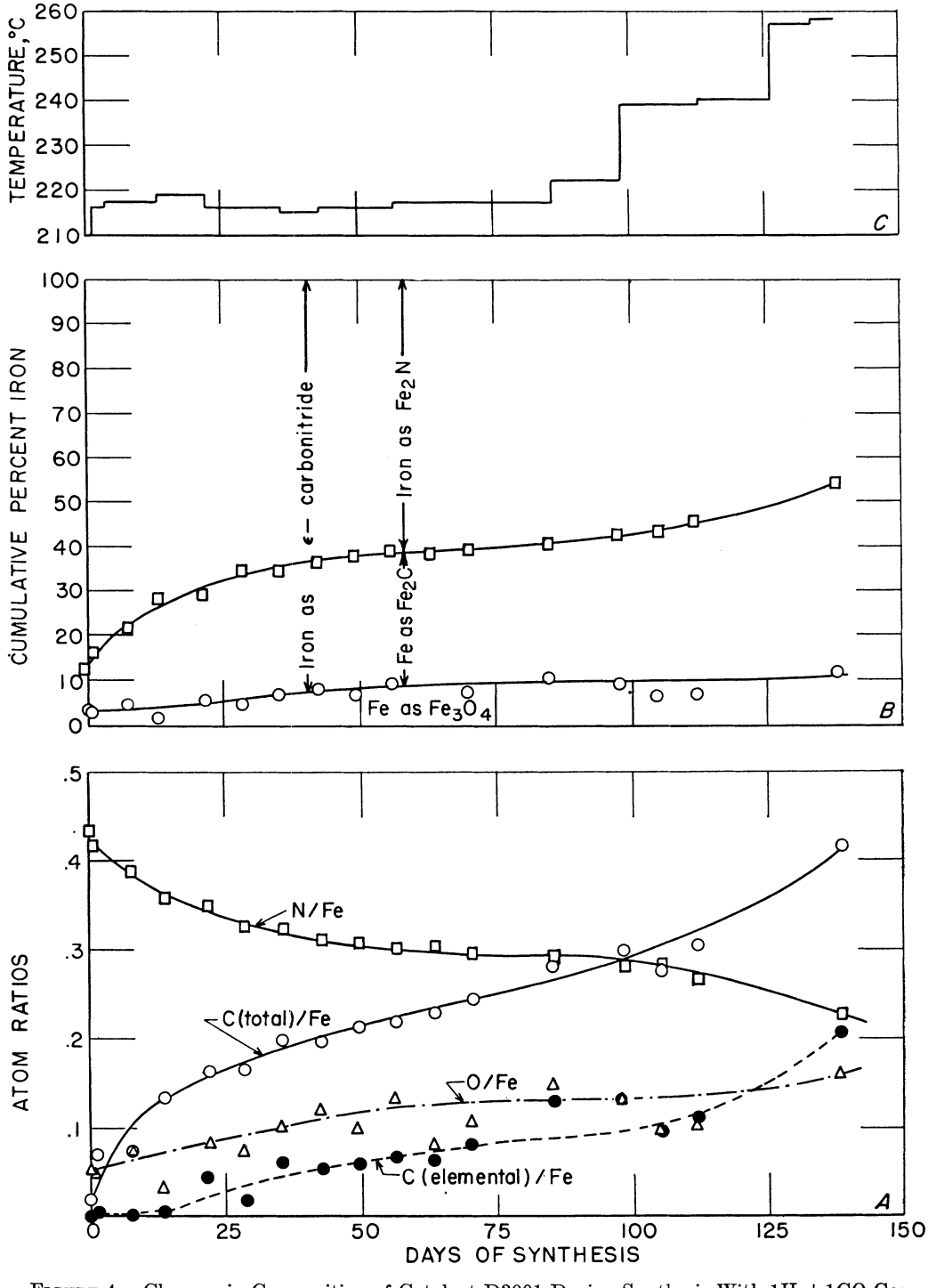

FIGURE 4.—Changes in Composition of Catalyst D3001 During Synthesis With $1H_2+1CO$ Gas at 100 p.s.i.g. in Test X218: *A*, Atom ratios of nitrogen, total carbon, elemental carbon, and oxygen to iron; *B*, distribution of iron as carbonitride and magnetite; *C*, temperature.

PORE GEOMETRY OF A FUSED IRON OXIDE CATALYST

Fused-iron catalysts in the raw state have virtually no porosity or internal surface area, the pore structure being developed during reduction as shown in table 3 for our standard

TABLE 3.—*Changes in pore geometry of fused Fe_3O_4–MgO–K_2O, catalyst D3001, during reduction in hydrogen at 450° C.*

Reduction, percent	Per gram of unreduced catalyst			Average pore diameter, A.
	Volume of mercury displaced, cc.	Pore volume, cc.	Surface area, $m.^2$	
0	0.203	0.002	0	
10	.203	.010	1.0	400
20	.203	.018	2.1	343
30	.203	.027	3.1	348
40	.202	.035	4.2	333
50	.204	.043	5.2	331
60	.201	.052	6.3	330
70	.200	.061	7.3	334
80	.200	.071	8.4	338
90	.199	.082	9.4	349
95	.199	.086	9.9	348
100	.198	.089	10.1	352

catalyst D3001.[25] The pore volume and total surface area of this catalyst increased linearly with extent of reduction, except in the interval from 95 to 100 percent, where the increase in area was less than linear. The average pore diameter, $\bar{d}$, calculated on the basis of long cylindrical pores ($\bar{d}=4V/A$, where V is pore volume and A surface area), remained essentially constant and finally increased slightly near 100-percent reduction. The external volume of the catalyst granules, measured by displacement of mercury at atmospheric pressure, remained virtually constant throughout the reduction. The external volume also remained constant during reduction at temperatures other than 450° C., and the pore volumes for these essentially completely reduced samples were about the same. (See table 4.) Microscopic examination of partly reduced catalysts shows a zone of reduced metal that increases in width with increase in reduction. Table 4 shows that varying the reduction temperature is a method

TABLE 4.—*Changes in pore geometry during reduction at different temperatures*

[Catalyst D3006 almost identical in composition to D3001]

Reduction temperature, ° C.	Per gram of unreduced catalyst			Average pore diameter, A.
	Volume of mercury displaced, cc.	Pore volume, cc.	Surface area, $m.^2$	
450	0.194	0.086	9.4	366
500	.198	.091	5.3	687
550	.195	.090	4.5	800
600	.193	.092	2.0	1,840
650	.199	.097	1.6	2,420
(1)	.201	.002	.0	

[1] Raw catalyst.

of "tailormaking" catalysts to a desired average pore size. The following statements characterize the reduction of fused iron catalysts:

(*a*) The external volume of the particles remains virtually unchanged, the pore volume being generated by removal of oxygen.

(*b*) Once initiated in a portion of the catalyst, reduction proceeds very rapidly, almost but not quite, to completion. Magnetite is reduced directly to iron.

(*c*) At a given temperature, the reduced portion of the catalyst is rapidly converted to a relatively stable structure of constant average pore diameter.

(*d*) On a macroscopic scale, reduction begins at the external surface and moves uniformly inward.

Oxidation of a reduced specimen using steam at 250° to 450° C. was initially fast (up to 30 to 40 percent oxidation) but then became very slow.[26] The reoxidized catalyst at 300° C. was reduced more quickly than the raw catalyst at 450° C.

During oxidation the total surface area decreased more rapidly than would be expected for a system of long cylindrical pores where oxidation might result in (*a*) a decrease in length of the pores, with the average diameter remaining constant, or (*b*) a decrease in the diameter of the pores, with the length remaining constant. An explanation consistent with these observations is that the walls of the larger pores have a sizable roughness factor and that oxidation, which proceeds all along the pore walls but to a greater extent near the external surface, tends to smooth the pore walls.

Changes in pore volume and surface area for fused catalyst D3001 after reduction with

[25] Hall, W. K., Tarn, W. H., and Anderson, R. B., Studies of the Fischer-Tropsch Synthesis. VIII. Surface Area and Pore Volume Studies of Iron Catalysts: Jour. Am. Chem. Soc., vol. 72, 1950, pp. 5436-5443.

[26] Hall, W. K., Tarn., W. H., and Anderson, R. B., Studies of the Fischer-Tropsch Synthesis. XIII. Structural Changes of a Reduced Iron Catalyst on Reoxidation and on Formation of Interstitial Phases: Jour. Phys. Chem., vol. 56, 1952, pp. 688-691.

hydrogen, oxidation with steam, carburization with carbon monoxide, and nitriding with ammonia are given in table 5.[26] During reoxidation the external volume of the particles was not changed, but their pore volume decreased. Conversion of metallic iron to carbide or nitride increased the external volume of the particles; the expansion was of the same magnitude as that occurring when massive iron is carbided or nitrided. This expansion also resulted in increasing the pore volume but had virtually no influence on the surface area or porosity.

Electron microscopic studies confirmed the pore structure suggested by the studies of surface area and pore volume.[27] Large pieces of raw catalyst were ground flat and polished by usual metallographic techniques. Replicas stripped from the flat surfaces of samples reduced in hydrogen at 450° or 550° C. showed a variety of ridges and peaks. The shortest dimensions of the structures that probably represent pores averaged 500 to 1,000 A. Replicas from polished surfaces of raw catalyst showed no fine structure.

[27] McCartney, J. T., and Anderson, R. B., Electron Microscopic Replica Studies of Porosity in Fused Iron Catalysts: Jour. Appl. Phys., vol. 22, 1951, pp. 1441–1443.

TABLE 5.—*Changes in pore geometry during oxidation, carbiding, or nitriding of catalyst D3001*

Treatment	Iron phases present, X-ray analysis	Composition	Per gram of unreduced catalyst			Average pore diameter, A.	Porosity, percent
			Volume of mercury displaced, cc.	Pore volume, cc.	Surface area, $m.^2$		
(1) None (raw)	Fe_3O_4		0. 203	0. 002	0		1
(2) Hydrogen at 550° C.	α–Fe	Almost completely reduced.	. 201	. 093	4. 7	785	46
(3) Treatment (2) plus steam at 250° C.	α–Fe, Fe_3O_4	68 percent reduced	. 200	. 061	2. 9	820	30
(4) Treatment (2) plus carbon monoxide at 150°–350° C.	Fe_2C(Hägg), α–Fe(?)	Atom ratio C:Fe =0.494.	. 225	. 096	4. 7	820	43
(5) Treatment (2) plus ammonia at 350° C.	ϵ–Fe_2N	Atom ratio N:Fe =0.482.	. 237	. 107	4. 8	898	45

KINETICS OF THE FISCHER-TROPSCH SYNTHESIS

To study the kinetics of a flowing system in which measurements are desired at moderate to high conversions, it is usually preferable to vary the flow of feed gas at constant temperature and pressure to obtain a wide range of conversions of $H_2 + CO$, x. The differential reaction rate, $r=dx/d(1/S)$, where S is the space velocity, can then be related to the exit-gas composition at the space velocity at which r is determined. Rate equations, either fundamental or empirical, may be tested by graphical differentiation of rate data or by integrating the rate equation. Integration is usually difficult for reactions as complex as the Fischer-Tropsch synthesis. Simple, reliable tests of the overall dependence of rate on temperature or pressure may be made by maintaining the conversion of $H_2 + CO$ constant and varying flow, as required, when temperature or pressure is changed. The space-time yield, xS, is then a reliable measure of rate that can be used to determine the effects of temperature or pressure.

IRON CATALYSTS

Hall [28] and workers of the Federal Bureau of Mines [29] have shown that the overall rate of synthesis increases linearly with pressure up to at least 45 atmospheres for experiments at approximately constant conversions, as figure 5

[28] Hall, C. C., Gall, D., and Smith, S. L., A Comparison of the Fixed-Bed, Liquid-Phase (Slurry), and Fluidized-Bed Techniques in the Fischer-Tropsch Synthesis: Jour. Inst. Petrol., vol. 38, 1952, pp. 845–876.

[29] Anderson, R. B., Seligman, B., Shultz, J. F., Kelly, R., and Elliott, M. A., Studies of the Fischer-Tropsch Synthesis. X. Some Important Variables in the Synthesis of Iron Catalysts: Ind. Eng. Chem., vol. 44, 1952, pp. 391–397.

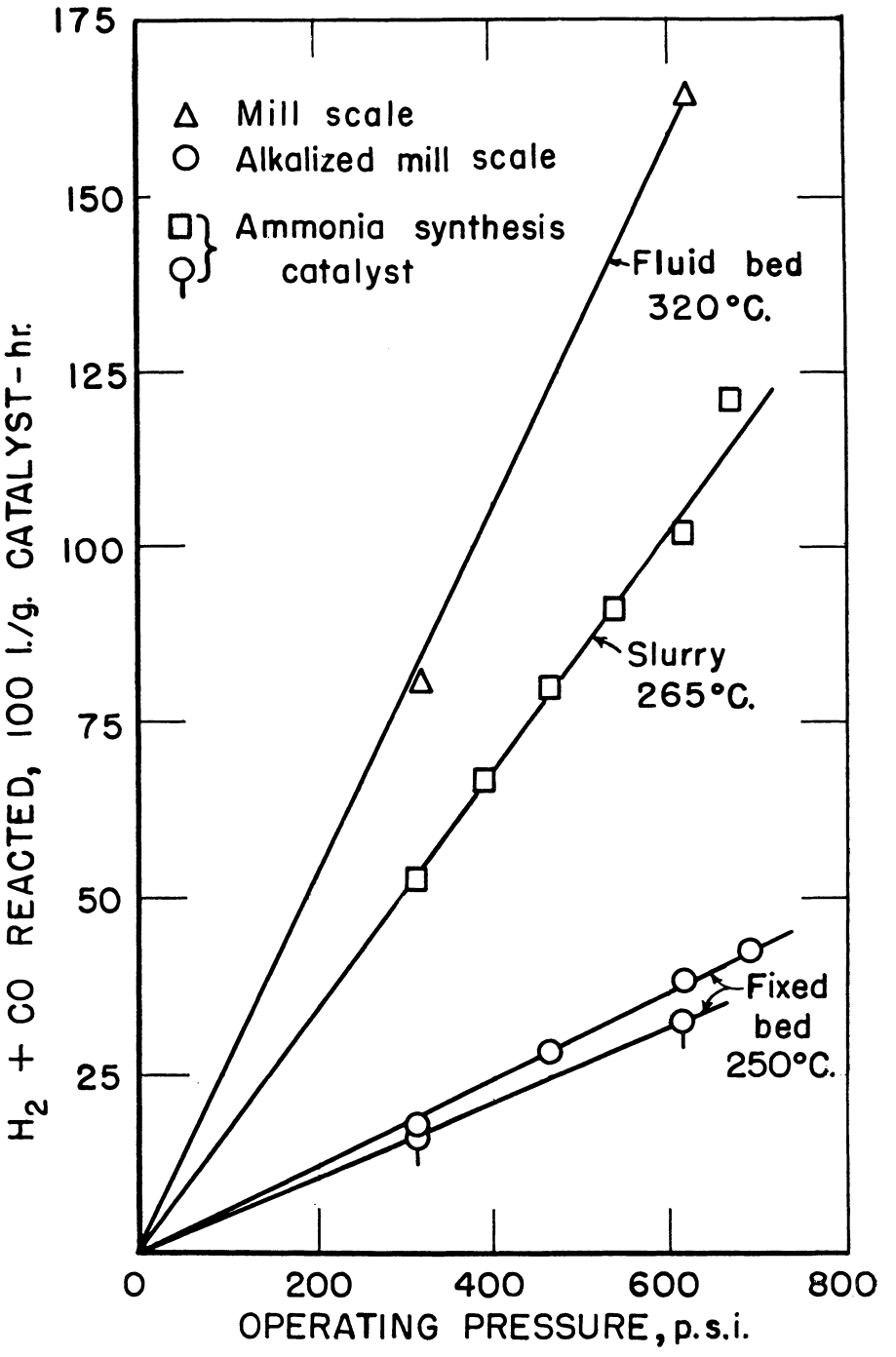

FIGURE 5.—Variation of Reaction Rate With Operating Pressure on Iron Catalysts for Three Types of Reactors Using $2H_2+1CO$ Gas.

shows. Data of Kölbel [30 31] indicate that this relationship is also valid for synthesis with H_2O+CO gas. In other experiments with $1H_2+1CO$ gas in which temperature was varied, overall apparent activation energies of 18 to 21 kcal. per mole have been obtained.

On iron catalysts the differential reaction rate decreases rapidly with increasing conversion (x), as figure 6 shows. The empirical equation,

$$-\log (1-x) = (AP/S) \exp (-E/RT), \qquad (1)$$

where P is the operating pressure and E overall activation energy, usually fits the rate data to within the experimental error between about 0- and 50-percent conversion. This equation has been useful in correlating activities of catalysts used in the Bureau of Mines testing program. For example, it was employed in computing activities reported in figure 2 (p. 7).

On fused iron catalysts at constant temperature, the rate of synthesis expressed as conversion of H_2+CO increased slowly with increasing H_2: CO ratio in the feed gas, passed through a relatively flat maximum for a volume ratio of H_2:CO near 1.5, and then decreased. The usage ratio, H_2:CO, increased with increasing H_2:CO ratio of the feed gas. For a given feed gas, the usage ratio varied widely with conversion but was usually independent of temperature, when compared at constant conversion.

Integral and differential usage ratios (expressed as H_2 converted:(H_2+CO) converted) are shown as functions of conversion in figure 7. The integral curve decreases rapidly with increasing conversion, passing through a minimum and increasing. The differential curve has a similar shape,[32] but the minimum occurs at

[30] Kölbel, H., and Engelhardt, F., [Reaction Mechanism of the Fischer-Tropsch Synthesis. VI. The Function of Water Vapor in the Carbon Monoxide Hydrogenation]: Erdöl u. Kohle, vol. 3, 1950, pp. 529–533.

[31] Titles in brackets are translations from the language in which the item was originally published.

[32] Tramm, H. [Technology of Carbon Monoxide Hydrogenation]: Brennstoff-Chem., vol. 33, 1952, pp. 21–30.

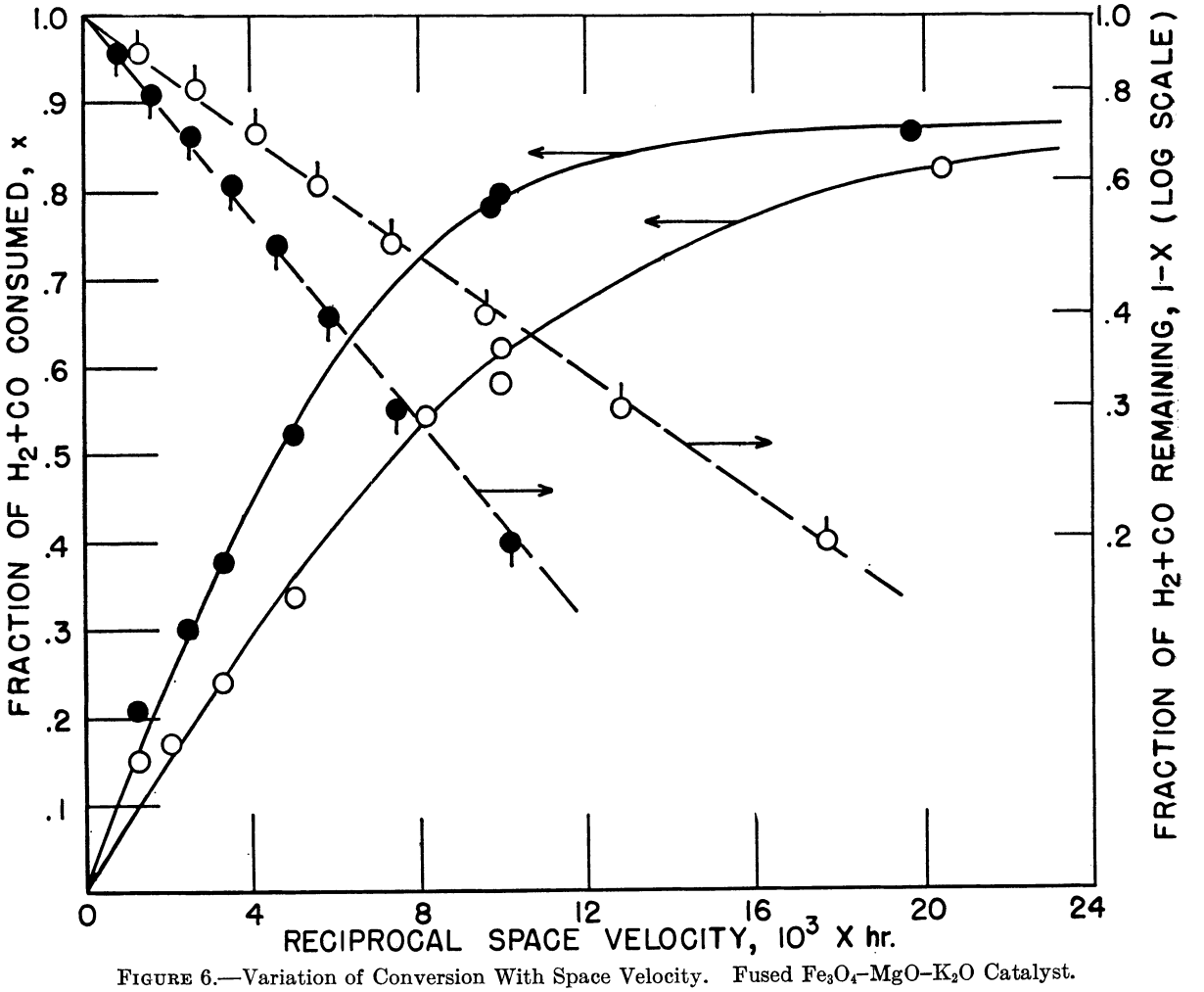

FIGURE 6.—Variation of Conversion With Space Velocity. Fused Fe_3O_4–MgO–K_2O Catalyst. $1H_2$:1CO, 7.8 Atm., ○○249°C., ●●261°C.

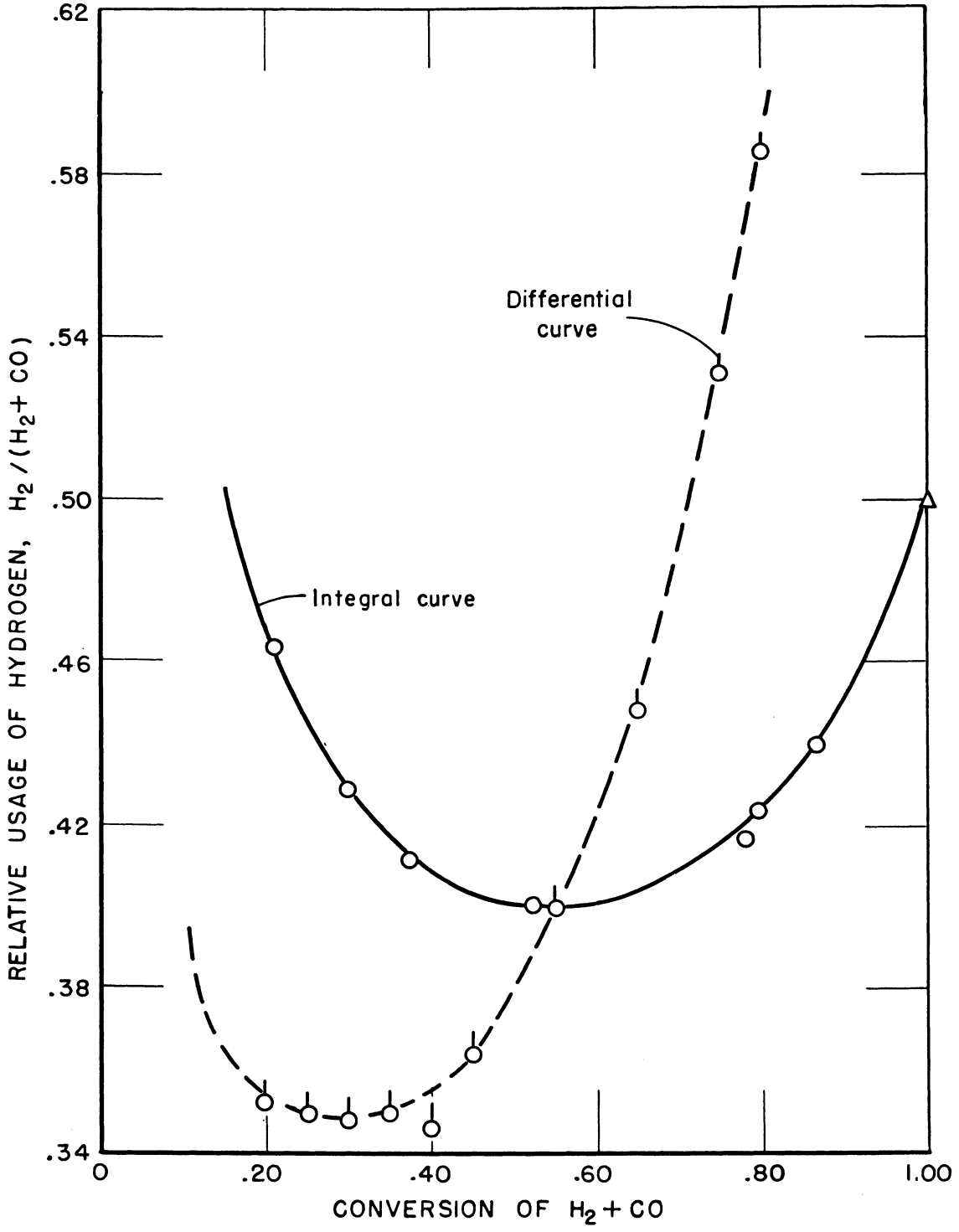

FIGURE 7.—Integral and Differential Usage of Hydrogen on Fused Iron Catalyst With $1H_2+1CO$ Gas at 7.8 Atm. and 249° C.

lower conversions. At low conversions the usage ratio is high, approaching $2H_2$:1CO.

With increasing conversion the partial pressure of water increases, and the water-gas shift sharply decreases the usage ratio.[32-35] As conversion increases, the H_2:CO ratio of the gas remaining increases sharply. This factor tends to increase the usage ratio and produces the minimum in the integral curve. Variations that decrease the partial pressure of water vapor in the gas stream, such as cold-gas recycle, increase the usage ratio. Apparently the relative rates of the primary synthesis reaction and the secondary water-gas reaction vary in the same manner as pressure and temperature are varied.

Studies of reduced fused catalysts having different particle size indicate that the activity increases with decreasing particle size to a high limiting value for small particles.[36] A simple approximate treatment of these data suggests that only a thin layer of catalyst (about 0.1 mm. in thickness from the external surface) is effective in the synthesis. These and other data lead to the qualitative picture of the mass transport in a catalyst pore, as shown in figure 8.

[33] See footnote 29, p. 11.
[34] See footnote 30, p. 13.
[35] Kölbel, H., Ackermann, P., Ruschenburg, E., Langheim, R., and Engelhardt, F. [The Fischer-Tropsch Synthesis With Iron Catalysts. I:] Chem.-Ing.-Tech., vol. 23, 1951, pp. 153-157.

[36] See footnote 29, p. 11.

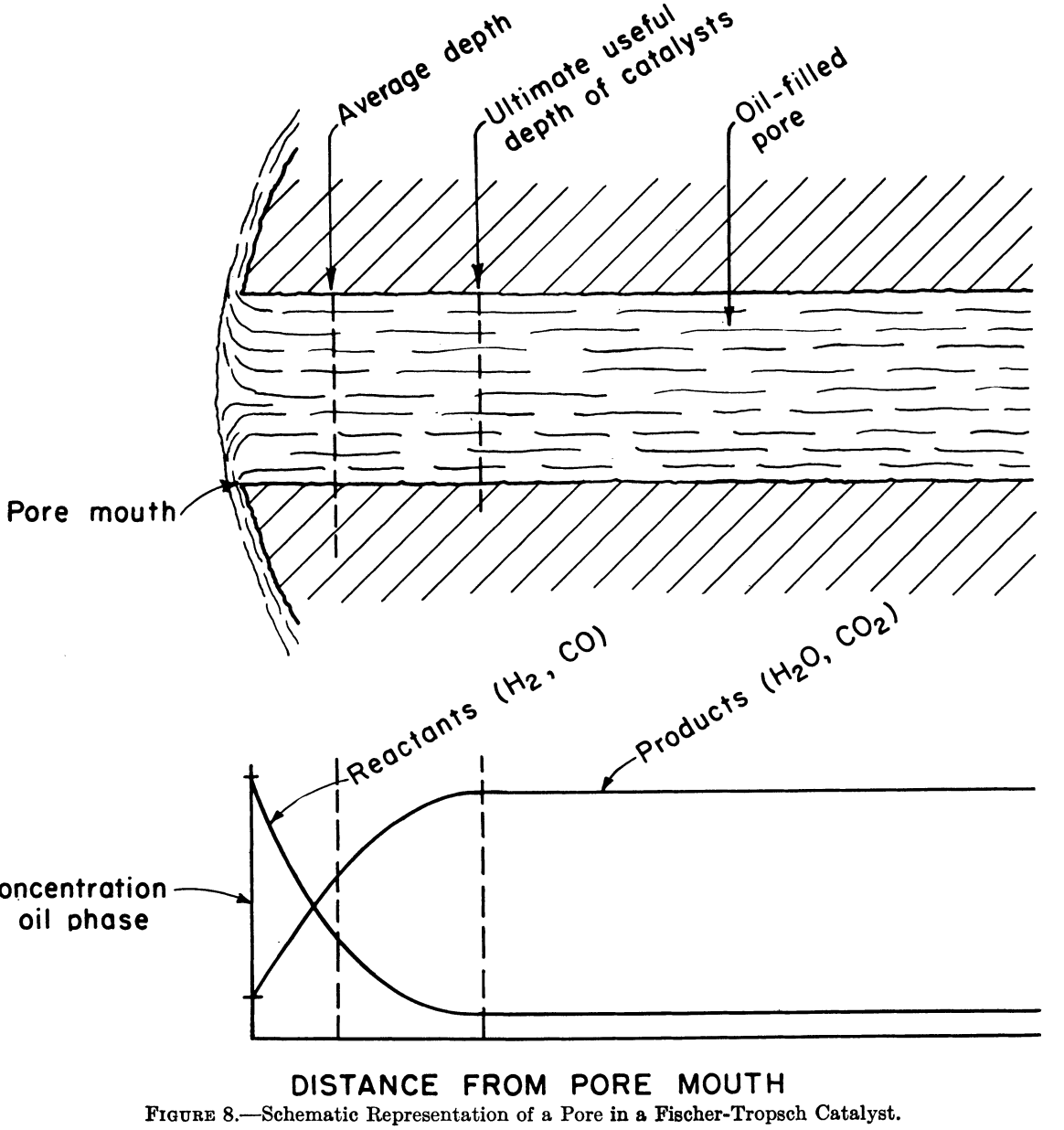

FIGURE 8.—Schematic Representation of a Pore in a Fischer-Tropsch Catalyst.

At synthesis temperatures less than 280° or 290° C. the pores of the catalyst are filled with liquid hydrocarbons, and H_2 and CO dissolve in the liquid and diffuse into the pores. As reaction at the catalyst surface produces the concentration gradients for the diffusion, the two processes are intimately connected. Figure 8 shows only one curve each for concentrations of reactants (H_2, CO) and products (H_2O, CO_2). The concentration of reactants falls sharply with distance from the pore mouth to a very low value at a short distance (of the order of 0.1 mm.). The concentrations of products vary in an inverse manner, increasing to a high constant value at approximately the effective depth. Thus, the interior of the particle affords ideal conditions for oxidation of iron (large H_2O:H_2 and CO_2:CO ratios) and the external portions ideal conditions for reduction of iron oxide and carbon deposition.

The following changes in depth of the active layer may be predicted: (1) As temperature is increased, the depth will decrease because the reaction rate at the surface increases more rapidly than the rate of diffusion; (2) the depth should be relatively independent of operating pressure as the solubility and diffusion of reactants and products in the oil-filled pores, as well as the reaction rate at the surface, are directly proportional to pressure. These hypotheses are consistent with virtually all information available about synthesis on iron catalysts. Diffusional difficulties of this magnitude complicate the kinetics, and no simple fundamental rate equation has been found.

COBALT AND NICKEL CATALYSTS

In synthesis with cobalt catalysts supported on kieselguhr, the rate is independent of pressure in the range from 0.2 to 15 atmospheres for tests in which the pressure is increased.[37] When pressure is decreased during the experiment, the rate decreases with decreasing pressure.[38] Atmospheric- and medium-pressure (5 to 25 atmospheres) syntheses appear to be basically different. At pressures near atmospheric most of the hydrocarbon product is vaporized, and high-molecular-weight wax is selectively adsorbed on the catalyst. The activity is largely independent of particle size and density, and the rate remains constant until the particle becomes filled with heavy wax.

In the medium-pressure synthesis most of the hydrocarbons are condensed and flow as liquid through the catalyst bed. Thus, the particle is quickly filled with hydrocarbons, and the composition of this material is the same as that of the synthesis product. As in the medium-pressure synthesis with iron, the activity remains essentially constant for long operating periods. In figure 9 the composition of wax on the catalyst is compared with the composition of wax in the product from data of Hall and Smith [39] for synthesis at 1 and 11 atmospheres.

In atmospheric synthesis plots of conversion as a function of reciprocal space velocity show long linear portions; [40] however, in the medium-pressure range, equation (1) may fit the data.[41] Apparent overall activation energies of about 25 kcal. per mole were observed in the atmospheric synthesis [42] [43] and 20 kcal. per mole in the medium-pressure range. At atmospheric pressure maximum synthesis rates are observed for $2H_2 + 1CO$ gas, and the catalyst appears to be poisoned by carbon monoxide-rich gas; however, in medium-pressure synthesis the activity is not adversely influenced by a carbon monoxide-rich gas such as $1.5H_2+1CO$. Broetz and Spengler [44] considered mass-transfer problems in cobalt catalysts and suggested that surface as well as bulk diffusion were important.

Rate data are available for nickel catalysts only at atmospheric pressure, and the data suggest that the kinetics of synthesis is similar to that on cobalt catalysts at this pressure.

Water appears to be the principal oxygenated product of synthesis on cobalt and nickel catalysts, and carbon dioxide is largely produced by subsequent water-gas shift. Kölbel and Engelhardt [45] demonstrated that the water-gas reaction at about 220° C. is equally rapid on cobalt and iron catalysts. The large production of carbon dioxide in synthesis with iron and small yields in synthesis with cobalt must result from the fact that the rate of the primary reaction on cobalt is much greater than that on iron; for example, cobalt catalysts usually convert synthesis gas to hydrocarbons as rapidly at 185° to 195° C. as iron catalysts do at 225° to 250° C.

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[37] See footnote 8, p. 3.

[38] Anderson, R. B., Hall, W. K., Krieg, A., and Seligman, B., Studies of the Fischer-Tropsch Synthesis. V. Activities and Surface Areas of Reduced and Carburized Cobalt Catalysts: Jour. Am. Chem. Soc., vol. 71, 1949, pp. 183–188.

[39] Hall, C. C., and Smith, S. L., Hydrocarbon Synthesis in the Presence of Cobalt Catalysts at Medium Pressures: Jour. Inst. Petrol., vol. 33, 1947, pp. 439–459.

[40] Anderson, R. B., Krieg, A., Friedel, R. A., and Mason, L. S., Fischer-Tropsch Synthesis. VI. Differential Reaction Rate Studies With Cobalt Catalysts: Ind. Eng. Chem., vol. 41, 1949, pp. 2189–2197.

[41] Gibson, E. J., and Hall, C. C., Fischer-Tropsch Synthesis with Cobalt Catalysts. II. The Effect of Nitrogen, Carbon Dioxide, and Methane in the Synthesis Gas: Jour. Appl. Chem., vol. 4, 1954, pp. 464–468.

[42] Anderson, R. B., Krieg, A., Seligman, B., and O'Neill, W. E., Fischer-Tropsch Synthesis. I. Tests of Cobalt Catalysts at Atmospheric Pressure: Ind. Eng. Chem., vol. 39, 1947, pp. 1548–1554.

[43] Weller, S., Kinetics of Carbiding and Hydrocarbon Synthesis With Cobalt Fischer-Tropsch Catalysts: Jour. Am. Chem. Soc., vol. 69, 1947, pp. 2432–2436.

[44] Broetz, W., and Spengler, H. [Physicochemical Behavior of Fischer-Tropsch Catalysts]: Brennstoff-Chem., vol. 31, 1950, pp. 97–102.

[45] Kölbel, H., and Engelhardt, F. [Reaction Mechanism of the Fischer-Tropsch Synthesis. I.]: Erdöl u. Kohle, vol. 2, 1949, pp. 52–59.

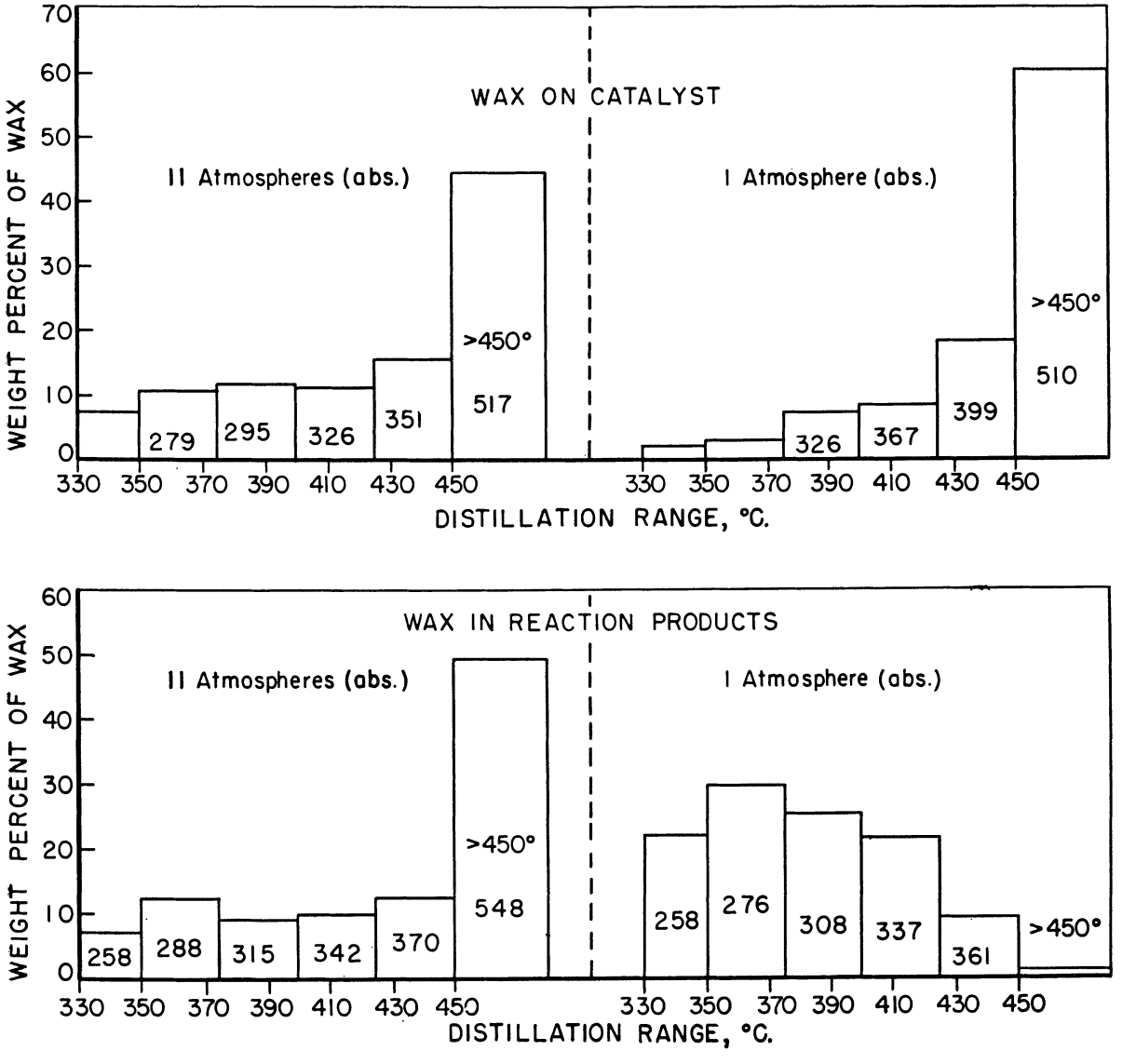


FIGURE 9.—Comparison of Catalyst Wax With Wax in Synthesis Products.
(Numbers in blocks are the average molecular weights.)

MECHANISM OF THE FISCHER-TROPSCH SYNTHESIS

The two principal hypotheses regarding the mechanism of the synthesis were proposed in 1926. Metal carbide was considered to be an intermediate product by Fischer and Tropsch,[46] and organic oxygenates were postulated to be intermediates by Elvins and Nash.[47] Detailed data on the composition of synthesis products later made possible formulation of mechanisms of chain growth, as the products are not in thermodynamic equilibrium with respect to isomers or ratios of alcohols to olefins and olefins to paraffins.

The carbide hypothesis, in its simplest form, postulates that adsorbed carbon monoxide is reduced to surface carbide according to

$$M\text{-}CO + H_2 \rightarrow M\text{-}C + H_2O, \text{ or} \quad (2)$$

$$M\text{-}CO + CO \rightarrow M\text{-}C + CO_2. \quad (3)$$

Equation (2) was believed to occur principally on cobalt and nickel surfaces and equation (3) on iron. The water-gas-shift reaction was incorrectly eliminated as a source of carbon dioxide on the basis of experimental evidence. The surface carbide is then hydrogenated according to

$$M\text{-}C + H_2 \longrightarrow M\text{-}CH_2 \quad (4)$$

and the adsorbed methylene groups polymerize and desorb as olefinic and paraffinic hydrocarbons. Craxford and Rideal[48] gave a more detailed version of the carbide hypothesis, especially with respect to chain growth, for which a polymerization-depolymerization mechanism was proposed.

The carbide hypothesis was originally based on, and at many subsequent stages supported by, the observation that the chief Fischer-Tropsch catalysts—iron, cobalt, and nickel—react with carbon monoxide to form bulk carbides and that these carbides can react with hydrogen to form hydrocarbons. Little or no direct evidence exists to substantiate the existence of surface carbide, although the hypothesis of surface carbide is convenient in many ways. Subsequently, bulk carbides of cobalt and nickel were shown to be virtually inactive in synthesis.[49-51]

Kummer, DeWitt, and Emmett[52] studied the synthesis at atmospheric pressure on cobalt and iron catalysts that had been carburized with $C^{14}O$. Suitable preliminary studies were made to exclude exchange reactions as a source of carbon-14 in synthesis products. To avoid possible effects of surface heterogeneity, synthesis tests of short duration were made, so that only 1 percent of the surface carbide would be removed even if all products resulted from carbide hydrogenation. For experiments short enough to involve a maximum of 1 to 50 percent of surface carbide, only 10 to 15 percent of the product could possibly have been derived from carbide reduction at 260° to 300° C. These data do not preclude the possibility that carbon atoms may exist momentarily on the catalyst surface during some step in the synthesis.

Since 1947 evidence has accumulated indicating that several aspects of the carbide theory are incorrect: (*a*) The primary reaction produces chiefly water, and carbon dioxide is largely formed in a subsequent reaction; and (*b*) the observed distribution of hydrocarbon isomers is not consistent with postulates of Craxford and Rideal.

Eidus[53] proposed a more acceptable mechanism in which methylene radicals are intermediates in the synthesis. In his scheme two adjacent methylene radicals react to form adsorbed ethylene attached at two sites, and this group adds CH_2 radicals one unit at a time to form a long straight carbon chain. In this

[46] Fischer, F., and Tropsch, H. [Synthesis of Petroleum at Atmospheric Pressures from Gasification Products of Coal]: Brennstoff-Chem., vol. 7, 1926, pp. 97-104.

[47] Elvins, O. C., and Nash, A. W., Reduction of Carbon Monoxide: Nature, vol. 118, 1926, p. 154.

[48] Craxford, S. R., and Rideal, E. K., Mechanism of the Synthesis of Hydrocarbons From Water Gas: Jour. Chem. Soc., 1939, pp. 1604-1614.

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

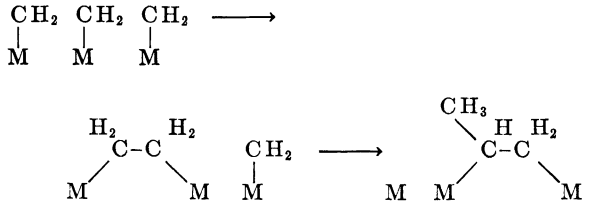
[50] See footnote 38, p. 16.

[51] Perrin, M. [The Synthesis of Aliphatic Hydrocarbons]: Doctoral dissertation, University of Lyon, Lyon, France, 1948, 85 pp.

[52] Kummer, J. T., DeWitt, T. W., and Emmett, P. H., Some Mechanism Studies on the Fischer-Tropsch Synthesis Using C^{14}: Jour. Am. Chem. Soc., vol. 70, 1948, pp. 3632-3643.

[53] Eidus, Y. T. [Mechanism of the Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen]: Uspekhi Khim., vol. 20, No. 1, 1951, pp. 54-70; trans. into English in Bureau of Mines Inf. Circ. 7821, 1958, pp. 7-10.

process the growing chain at the surface is an adsorbed α-olefin as equation (5) shows.



(5)

The mechanisms for chain termination and formation of branched hydrocarbons were not given; however, Bureau of Mines workers [54] [55] showed that observed isomer distribution could be explained with an α-olefinic intermediate, if one-carbon additions were permitted, but at different rates, on the two carbons of the olefinic bond, as will be described subsequently in this paper.

A serious shortcoming of this methylene polymerization hypothesis is its failure to explain the formation of alcohols—important primary products with iron and under some conditions cobalt catalysts. The Eidus hypothesis does explain the incorporation of ethylene and higher olefins into synthesis products when olefin is added to synthesis gas. Experiments involving the incorporation of tagged ethylene will be described later.

Herington [56] proposed that carbon chains grow one carbon atom at a time and assigned a probability that a given intermediate will grow at the surface rather than desorb. Friedel and Anderson [57] showed that, for any range of carbon numbers for which this probability is constant, the moles of product of carbon number n, ϕ_n may be related to moles in carbon number x, ϕ_x by

$$\phi_n = \phi_x \exp.\ [-\alpha(n-x)] \qquad (6)$$

where α is the probability that a chain will grow. Although equation (6) is seldom accurate over the entire range of carbon numbers, it is a useful approximation.

To explain isomer and carbon number distributions, Bureau of Mines workers [58] [59] considered schemes of stepwise growth of the carbon chain. In one scheme stepwise chain growth is assumed to occur at the first or second carbon from one end of a growing chain, with the restriction that growth does not occur at adjacent-to-end carbons already attached to three carbon atoms. First-order reactions of growing intermediates with respect to concentration at the catalyst surface were assumed. Rate constants, independent of chain length and structure, were assumed for addition to end and adjacent-to-end carbons for desorption from the catalyst surface.

The rate of appearance, in moles, of products formed by addition to an end carbon is then $R_{n+1}/R_n = a$ and for addition to adjacent-to-end carbons $R'_{n+1}/R_n = af$, where R_n is the rate of appearance of hydrocarbons of carbon number n in moles per unit time, a is a constant largely determining the carbon-number distribution, and f is a constant principally determining isomer distribution. Then, starting with C_2 and accounting for all possible reaction steps, the relative isomer and carbon-number distributions, in terms of a and f, may be developed to C_6, as shown in table 6. The carbon number distributions are in the form

$$\phi_n = 2\phi_2 F_n a^{n-2}, \qquad (7)$$

where F_n is the quantity in parentheses in the last column of table 6. This development assumes that both carbon atoms in the C_2 intermediate act as end carbons.

TABLE 6.—*Isomer and carbon-number distribution in terms of* a *and* f

Carbon chain	Relative isomer composition	Relative carbon-number distribution, moles
C_2	1	1
C_3	1	$2a$
C_4 n-C_4	1	$2a^2(1+f)$
C_4 2-methyl-C_3	f	
C_5 n-C_5	1	$2a^3(1+2f)$
C_5 2-methyl-C_4	$2f$	
C_6 n-C_6	1	$2a^4(1+3f+f^2)$
C_6 2-methyl-C_5	$2f$	
C_6 3-methyl-C_5	f	
C_6 2,3-dimethyl-C_4	f^2	

The best values of computed isomer distributions, obtained by assigning values to a and f by a trial-and-error method, are compared with observed values from iron and cobalt catalysts in table 7. Figures 10 and 11 show plots of equation (7) for data from iron catalysts in fluid-bed [60] and fixed-bed operation.[61]

[54] Storch, H. H., Golumbic, N., and Anderson, R. B., Fischer-Tropsch and Related Syntheses: John Wiley & Sons, Inc., New York, N.Y., 1951, 610 pp.

[55] Anderson, R. B., Friedel, R. A., and Storch, H. H., Fischer-Tropsch Reaction Mechanism Involving Stepwise Growth of Carbon Chain: Jour. Chem. Phys., vol. 19, 1951, pp. 313-319.

[56] Herington, E. F. G., The Fischer-Tropsch Synthesis Considered as a Polymerization Reaction: Chem. and Ind., vol. 65, 1946, pp. 346-347.

[57] Friedel, R. A., and Anderson, R. B., Composition of Synthetic Fuels. I. Product Distribution and Analysis of C_3-C_8 Paraffin Isomers From Cobalt Catalysts: Jour. Am. Chem. Soc., vol. 72, 1950, pp. 1212-1215, 2307.

[58] Weller, S., and Friedel, R. A., Isomer Distribution in Hydrocarbons from the Fischer-Tropsch Process: Jour. Chem. Phys., vol. 17, 1949, pp. 801-803.

[59] See footnote 55, p. 19.

[60] Weitkamp, A. W., Seelig, H. S., Bowman, N. J., and Cady, W. E., Products of the Hydrogenation of Carbon Monoxide Over an Iron Catalyst: Ind. Eng. Chem., vol. 45, 1953, pp. 343-349.

[61] Anderson, R. B., Catalysts for the Fischer-Tropsch Synthesis: Chap. 2 in Catalysis, vol. IV (P. H. Emmett, ed.), Reinhold Publishing Corp., New York, N.Y., 1956, pp. 29-255.

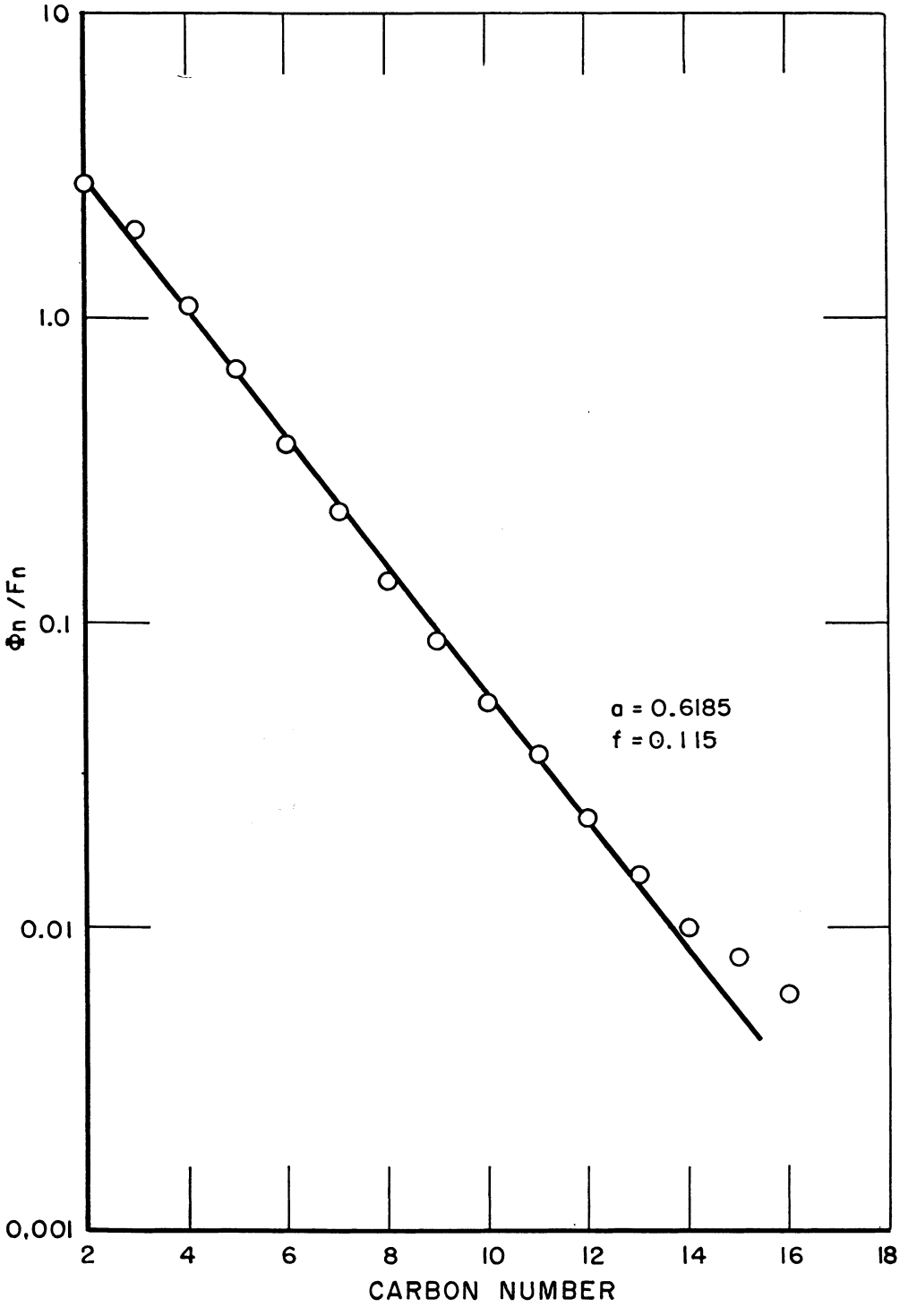


FIGURE 10.—Plot of Equation 17 for Data From Synthesis With Fluidized Iron Catalyst (Standard Oil).

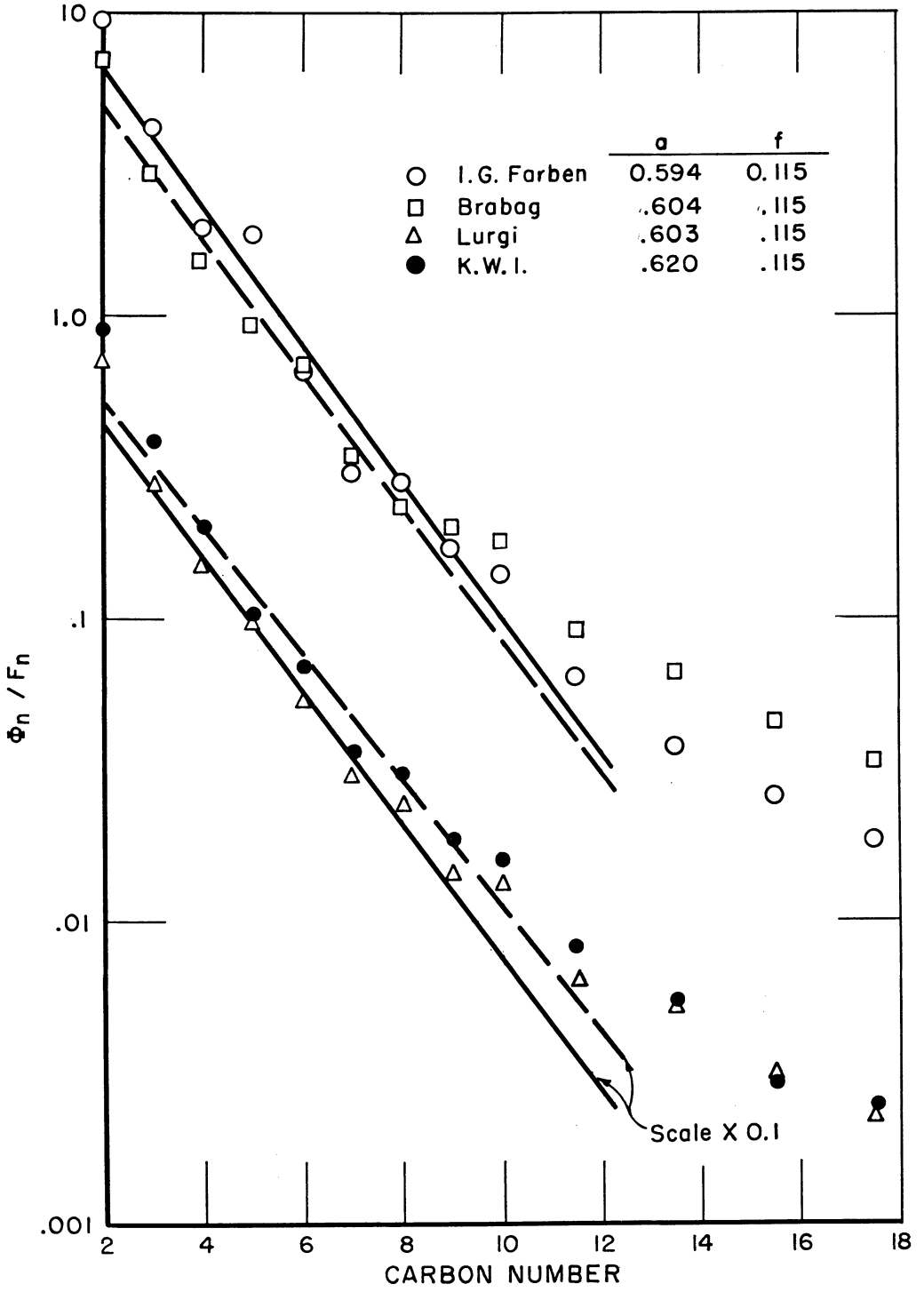


FIGURE 11.—Plots of Equation 7 for Data From Schwarzheide Tests of Iron Catalysts.

TABLE 7.—*Chain structures of hydrocarbons from cobalt and iron catalysts*

Carbon chain	Mole percent in fraction			
	Cobalt catalyst		Iron catalyst	
	Observed	Computed	Observed[1]	Computed
		f=0.035		f=0.115
C_4 n-C_4	97.0	96.6	89.4	89.7
C_4 2-methyl-C_3	3.0	3.4	10.6	10.3
C_5 n-C_5	95.0	93.4	81.2	81.3
C_5 2-methyl-C_4	5.0	6.6	18.8	18.7
C_6 n-C_6	89.6	90.2	78.8	73.5
C_6 2-methyl-C_5	5.7	6.4	11.2	16.9
C_6 3-methyl-C_5	4.7	3.2	9.5	8.5
C_6 2,3-dimethyl-C_4	0	.2	.4	.9
C_7 n-C_7	87.7	87.3	66.0	66.0
C_7 2-methyl-C_6	4.6	6.2	13.1	15.4
C_7 3-methyl-C_6	7.7	6.2	19.1	15.4
C_7 2,3-dimethyl-C_5	0	.2	1.6	1.7
C_7 2,4-dimethyl-C_5	0	.1	.3	.8
C_8 n-C_8	84.5	84.4	61.0	60.5
C_8 2-methyl-C_7	3.9	6.0	[2] 36.4	34.7
C_8 3-methyl-C_7	7.2	6.0		
C_8 4-methyl-C_7	4.4	3.0		
C_8 dimethyl-C_6's	0	.6	[2] 2.6	4.8

[1] Bruner, F. H., Quality of Synthetic Gasoline From Natural Gas: Ind. Eng. Chem., vol. 41, 1949, pp. 2511-2515.
[2] Data available for only these chain structure types.

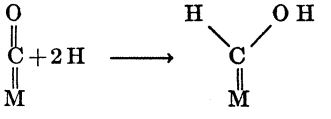
Deviations of the linear plots at high carbon numbers are large for products from fixed-bed tests.

Storch, Golumbic, and Anderson[62] proposed an oxygenated intermediate mechanism that was consistent with the chain-growth mechanism described above. The following assumptions were made: (*a*) Hydrogen is adsorbed as atoms on surface metal atoms; (*b*) chemisorption of carbon monoxide occurs on metal atoms with bonding similar to that in metal carbonyls; and (*c*) adsorbed carbon monoxide is partly hydrogenated according to equation (8).

Chain building may occur in two ways, at the end carbon (equations 9 and 10) and at the adjacent-to-end carbon (equations 11 and 12). In these steps the double bonds between carbon and metal atoms are assumed to be more resistant to hydrogenation if the carbon atom is also attached to a hydroxyl group. Growth processes leading eventually to chain branching involve partial hydrogenation of the carbon-metal bond, according to equations (11) and (12). Intermediate α is the same as in equation (10), but intermediate β may produce a chain with a methyl branch according to equation (12). Various equations, such as (13) and (14), can be proposed for terminating the growing chain to give aldehydes, alcohols, olefins, and paraffins. Acids and esters may result from Cannizarro reactions of aldehyde-like intermediates or from other side reactions.

[62] See footnote 54, p. 19.

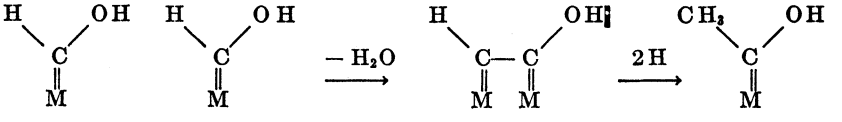
Initiation of chains:



(8)

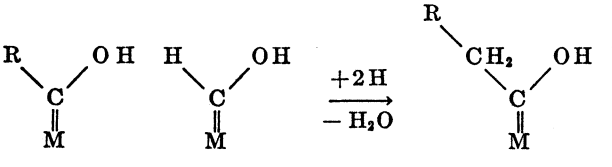
Growth of chains:

(a) At end carbon—



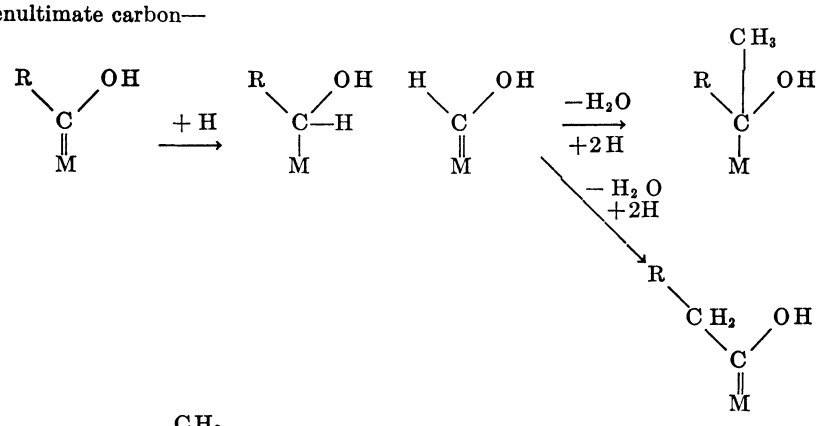
(9)

and

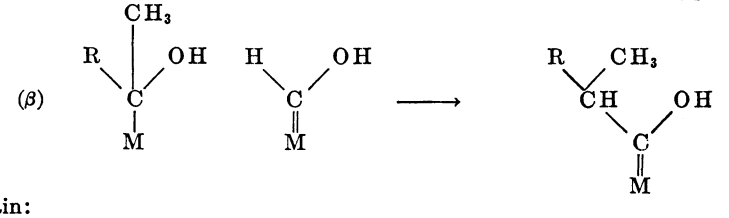


(10)

(b) At penultimate carbon—



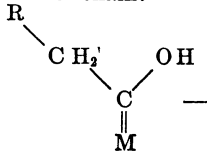
(11)



(12)

Termination of chain:

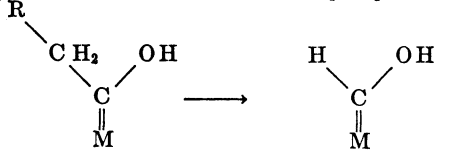
(a) R



$\longrightarrow$ RHC_2CHO $\longrightarrow$ acids, esters, and alcohols (13)

RCH_2CH_2OH $\longrightarrow$ hydrocarbons

(b) R



(14)

Emmett and coworkers [63-66] studied the incorporation of alcohols and other oxygenated molecules in the synthesis with iron catalysts at atmospheric pressure using alcohols tagged with C^{14}. When primary alcohols are introduced at low concentration (1.5 percent by volume), they are largely incorporated into synthesis products, presumably by having become intermediates in the synthesis. The important result is that the radioactivity of the hydrocarbon product per mole (for carbon numbers greater than that of the alcohols) is essentially constant, as figure 12 shows.

These data suggest that primary alcohols initiate chains that grow by a stepwise mechanism. For isopropanol the radioactivity per mole of hydrocarbon decreased with increasing carbon number. Analyses of the C_4 products from the incorporation of normal and isopropanol indicated that straight-chain butane and butenes were predominantly formed from propanol-1 and isobutane and isobutylene from propanol-2. Incorporation of radioactive methanol was smaller, and the radioactivity of hydrocarbon products per mole increased with increasing carbon number, suggesting that methanol acts as both a chain initiator and a chain-building unit. With ethanol and higher alcohols 40 to 60 percent of the hydrocarbon chains were initiated by the alcohol.

On cobalt catalysts with $2H_2+1CO$ plus 1.5 percent radioactive ethanol, the radioactivity of C_3^+ hydrocarbons per mole was relatively constant; however, the alcohol initiated only

[63] Kummer, J. T., Podgurski, H. H., Spencer, W. B., and Emmett, P. H., Mechanism Studies of the Fischer-Tropsch Synthesis. Addition of Radioactive Alcohol: Jour. Am. Chem. Soc., vol. 73, 1951, pp. 564-569.

[64] Kummer, J. T., and Emmett, P. H., Fischer-Tropsch Synthesis Mechanism Studies. The Addition of Radioactive Alcohols to the Synthesis Gas: Jour. Am. Chem. Soc., vol. 75, 1953, pp. 5177-5182.

[65] Hall, W. K., Kokes, R. J., and Emmett, P. H., Mechanism Studies of the Fischer-Tropsch Synthesis. The Addition of Radioactive Methanol, Carbon Dioxide, and Gaseous Formaldehyde: Jour. Am. Chem. Soc., vol. 79, 1957, pp. 2983-2989.

[66] Kokes, R. J., Hall, W. K., and Emmett, P. H., Fischer-Tropsch Synthesis Mechanism Studies. The Addition of Radioactive Ethanol to the Synthesis Gas: Jour. Am. Chem. Soc., vol. 79, 1957, pp. 2989-2996.

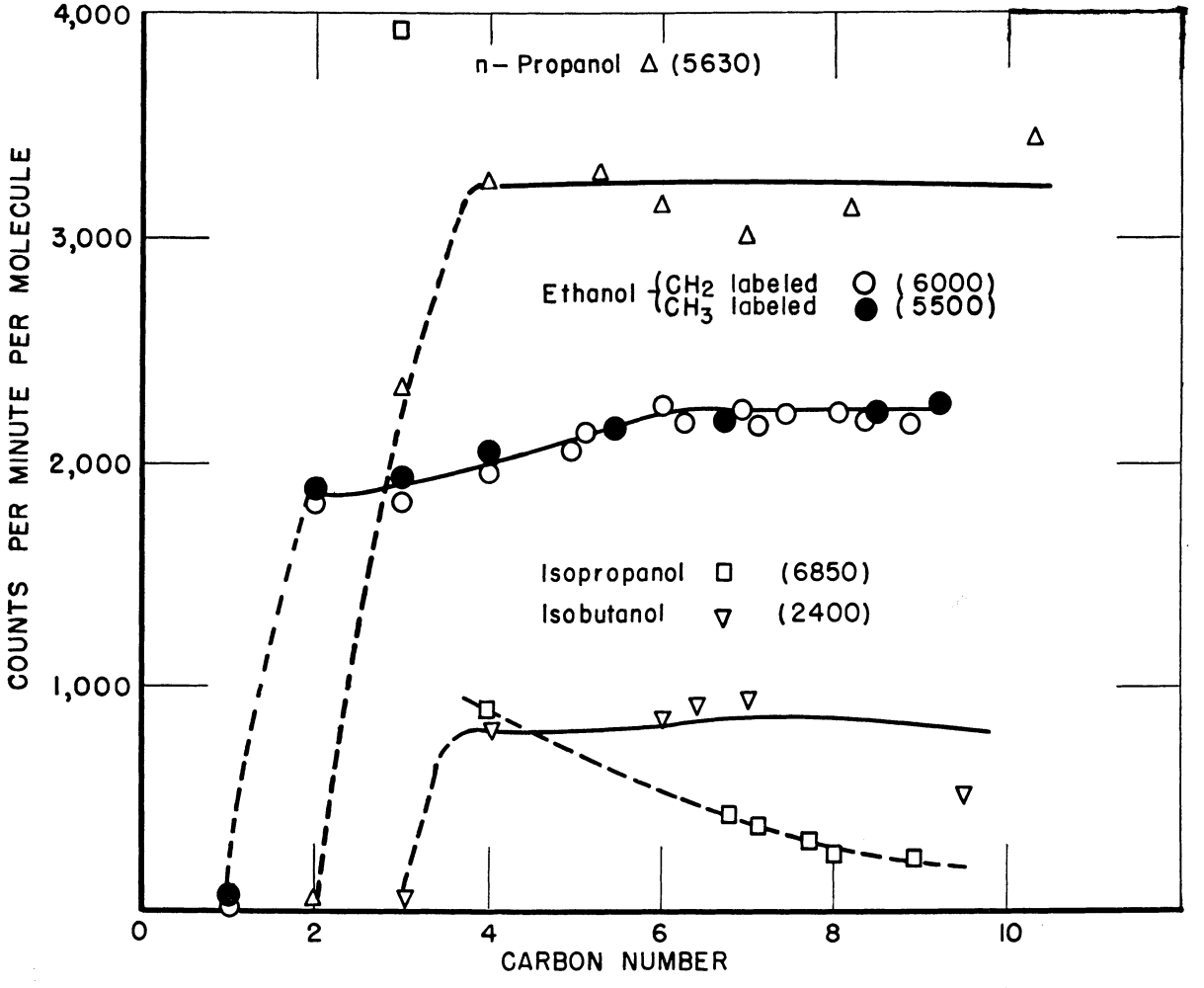


FIGURE 12.—Incorporation of Radioactive Alcohols in Synthesis on Iron Catalysts. (The radioactivity of alcohol is shown in parenthesis.)

about 1 percent of the hydrocarbon chains. Thus, Kokes, Hall, and Emmett [67] concluded that the oxygenated intermediate postulates of Storch, Anderson, and Golumbic [68] may not apply to the synthesis on cobalt.

Eidus and coworkers [69] also questioned the validity of the "alcohol" intermediate hypothesis. They cited experiments showing that radioactive ethylene (in concentrations of 0.78 and 1.45 volume-percent in synthesis gas at atmospheric pressure) was incorporated into synthesis products on cobalt to give a constant molar radioactivity in the C_3^+ hydrocarbons. About one-fourth of the ethylene was incorporated, and half was hydrogenated to ethane. For the higher ethylene concentration about 20 percent of the hydrocarbon chains were initiated by ethylene. Similarly, tagged acetaldehyde and methyl formate were incorporated to give a constant molar activity in higher hydrocarbons. Recently Hall, Kokes, and Emmett [70] measured the incorporation of 1.25 volume-percent radioactive ethylene on a singly promoted iron catalyst at atmospheric pressure and obtained constant molar radioactivity of the higher hydrocarbons. About 12 percent of the hydrocarbon chains were initiated by ethylene, compared with about 50 percent for ethanol.

At present, despite the great progress made in the last decade, many aspects of reaction mechanism require resolution. Many basic ideas of the earlier carbide theories have been

[67] See footnote 66, p. 23.
[68] See footnote 54, p. 19.
[69] Golovina, O. A., Dokukina, E. S., Roginskii, S. Z., Sakharov, M. M., and Eidus, Ya. T. [The Role of Flat Chains in Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen]: Doklady Akad, Nauk S.S.S.R., vol. 112, 1957, pp. 864-867.

[70] Hall, W. K., Kokes, R. J., and Emmett, P. H., Mechanism Studies of the Fischer-Tropsch Synthesis: The Incorporation of Radioactive Ethylene, Propionaldehyde, and Propanol: Jour. Am. Chem. Soc., in press.

shown to be unsound. Chain-growth hypotheses involving one-carbon additions to the first or second carbon atom at one end of the growing chain are capable of predicting the isomer and carbon-number distributions from iron and cobalt catalysts satisfactorily. The hypothesis of an alcohol-type intermediate provides a satisfactory simple explanation of most observed phenomena on iron catalysts; but with cobalt catalysts other mechanisms, possibly involving olefinic intermediates, may be required.

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