TABLE 55.—*Effect of nitriding on synthesis with fused catalyst D3001*

6- to 8-mesh; synthesis at 100 atmospheres of $1H_2 : 1CO$ gas

Pretreatments:									
Reduction with H_2 at:									
Temperature ° C	450	450	--------	385	450	385	--------	550	550
Time hours	43	40	--------	4	40	4	--------	40	20
Space velocity, $hr.^{-1}$ [1]	2, 500	2, 500	--------	1, 000	2, 500	5, 000	--------	2, 500	2, 500
Extent of reduction percent	92	96	--------	--------	100	--------	--------	98	100
Nitrided with NH_3 at:									
Temperature ° C	--------	450	385	--------	385	--------	385	--------	385
Time hours	--------	5	4	--------	4	--------	4	--------	4
Space velocity, $hr.^{-1}$ [1]	--------	5, 000	5, 000	--------	5, 000	--------	1, 000	--------	5, 000
N:Fe	0	0. 032	--------	--------	0. 44	--------	--------	0	0. 46
Initial iron phases present	α–Fe	α–Fe γFe_4N	--------	Hägg Fe_2C	ϵ Fe_2N	Fe_3C	--------	αFe	ϵ Fe_2N
Synthesis conditions:									
Test number	X–152	X–207A	X–207B	X–207C	X–214A	X–214B	X–214C	X–173	X–215
Weeks, averaged	5	5	5	3	5	5	3	5	27
Average temperature ° C	263	240	221	239	225	238	224	259	227
Contraction percent	65	65	68	71	64	64	63	65	64
Activity A_{Fe}	14	37	83	50	62	40	64	18	50
Usage ratio, H_2: CO	0. 72	0. 75	0. 80	0. 77	0. 75	0. 75	0. 79	0. 72	0. 74
Products, gm./$m.^3$:									
H_2O	24. 8	27. 6	48. 4	20. 8	26. 0	33. 1	24. 2	24. 0	22. 6
CO_2	340. 2	329. 8	335. 3	315. 4	293. 6	279. 9	297. 5	325. 4	310. 7
Total hydrocarbons	120. 6	107. 2	72. 7	99. 8	101. 9	97. 5	90. 0	110. 9	96. 5
Distribution of hydrocarbons, weight-percent:									
CH_4	17. 8	12. 5	32. 0	13. 9	20. 5	11. 3	25. 0	16. 2	22. 3
C_2	9. 5	7. 2	19. 2	9. 1	10. 3	9. 1	8. 3	11. 1	11. 8
C_3+C_4	19. 9	19. 4	30. 2	25. 8	25. 3	21. 1	29. 7	18. 1	23. 8
C_5+ [2]	52. 8	60. 9	18. 6	51. 2	43. 9	58. 5	37. 0	54. 6	49. 1
Distillation and infrared analysis, weight-percent:									
<185° C	38. 1	26. 5	58. 4	31. 6	61. 7	38. 7	56. 5	31. 2	61. 9
Bromine number	66	62	21	55	39	59	10	59	10
OH	0. 2	1. 3	9. 1	1. 5	7. 8	1. 1	14. 6	0. 6	13. 5
CO+COOH	. 6	. 5	1. 4	. 5	--------	. 6	1. 0	. 8	1. 5
α–olefins (C=C)	4. 9	4. 8	2. 0	5. 5	5. 2	4. 3	1. 5	2. 6	1. 5
Other olefins (C=C)	5. 1	4. 5	1. 2	2. 7	. 7	4. 6	--------	6. 3	--------
185°–352° C.:	35. 5	38. 7	35. 0	38. 4	34. 1	31. 9	32. 9	38. 4	34. 5
Bromine number	33	29	16	28	29	28	12	28	9
OH	--------	--------	0. 8	0. 1	1. 0	0. 1	1. 4	0. 1	2. 0
CO+COOH	0. 3	0. 2	. 8	. 3	--------	. 3	. 7	. 4	. 8
α-olefins (C=C)	1. 1	--------	. 8	1. 6	2. 3	. 8	1. 0	. 6	. 4
Other olefins (C=C)	3. 9	1. 9	1. 5	2. 6	2. 0	3. 4	0. 8	3. 6	. 9
352°–464° C	14. 9	16. 8	5. 1	12. 9	3. 5	12. 0	10. 6	14. 4	2. 9
>464° C	11. 4	18. 0	1. 5	17. 1	. 7	17. 4	--------	16. 0	. 7
Acid number [3]	. 8	0. 8	2. 4	1. 0	1. 0	1. 0	2. 9	1. 2	1. 3

[1] Volumes of gas at standard temperature and pressure per volume of catalyst space per hour.
[2] Total hydrocarbons and liquids+solids including oxygenated compounds dissolved in hydrocarbon phases.
[3] Acid number of liquids+solids.

which converted the free iron to ϵ-iron nitride, after which it was possible to decrease the operating temperature to 224° C. for a peak activity of 79.

A life test of catalyst D3001 reduced at 550° C. and nitrided to a nitrogen: iron atom ratio of 0.46 in test X–215 is compared with the corresponding reduced catalysts (X–173) in figure 50 and table 55. The activity of the nitrided catalyst remained high throughout the six months of the test. At the end of this period the nitrided catalyst dropped freely from the reactor and was found to be in the same mechanical condition as when charged to the unit. This is a marked contrast to tests of reduced catalysts, in which catalyst disintegration usually cakes the catalyst in the reactor tube, often tightly enough to prevent the flow of gas in tests of only 6 to 12 weeks.

These experiments at 7.8 atmospheres demonstrated that a mild nitriding treatment, producing the γ'-phase in iron catalysts, was

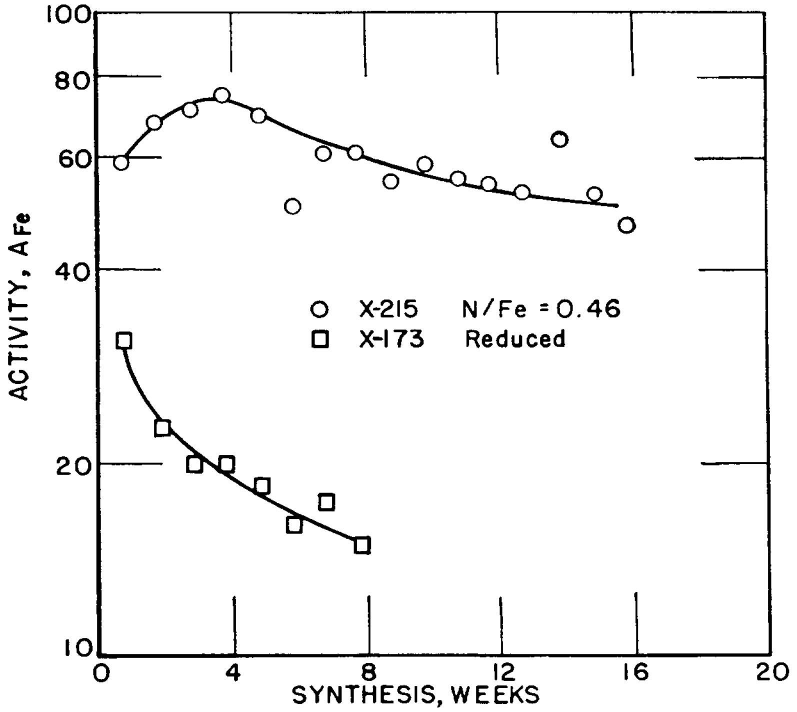


FIGURE 50.—Activities of Fused Catalyst D3001 With $1H_2$: 1CO Gas at 7.8 Atmospheres.

enough to increase the activity significantly above that of the corresponding reduced (unnitrided) catalysts. Nitriding to the ε-phase increased the activity still further.

Figure 51 compares the activities at 7.8 atmospheres and 21.4 atmospheres of $1H_2+1CO$ gas (expressed as volumes of synthesis gas converted at 240° C.) of 2 nitrided fused catalysts—D3001 (Fe_3O_4–MgO–K_2O) and D3008 (Fe_3O_4–Al_2O_3–K_2O).[96] The magnesia-promoted catalyst was more active than the alumina-promoted preparation, both reduced and nitrided. The activity of the nitrides at 21.4 atmospheres was about twice as great as at 7.8 atmospheres. The selectivity data for these tests (fig. 52) show that although the fraction of liquid products in the total hydrocarbons plus oxygenates was about the same, the composition of the liquids was very different. The condensed fractions from nitrided catalysts contained large concentrations of alcohols (expressed as weight-percent OH-group in fraction), aldehydes and ketones (weight-percent of CO-group), and esters (not indicated in block diagram), compared with reduced catalysts; however, the concentration of olefins (indicated by bromine numbers, Br) in these fractions from nitrided catalysts was lower than from reduced catalysts. Nitrogen was slowly displaced by carbon during synthesis to form a carbonitride; ε-nitrides are converted largely to ε-carbonitrides. Nitrided catalysts oxidize very slowly at 7.8 atmospheres and somewhat more rapidly at 21.4 atmospheres, but at all pressures the rate of oxidation of nitrides was considerably less than for the corresponding reduced catalyst. Hydrogenation of the ε-carbonitride produced in synthesis (for example, tests X-337A and X-337B of figs. 51 and 52) converted the catalyst to a mixture of α-iron, cementite, and magnetite. Although removal of nitrogen caused essentially no change in activity, the average molecular weight and olefin content of the product were greatly increased, and the fraction of oxygenated molecules was decreased.

PRECIPITATED-IRON CATALYSTS

For routine testing of precipitated-iron catalysts by the Bureau of Mines the pretreatment, based on German results, consisted of passing synthesis gas ($1H_2$:1CO) over the catalyst at atmospheric pressure for 24 hours at 260° C. for catalysts that contained little or no copper and at 235° C. for preparations with sizable amounts of copper. These pretreatment procedures have been shown to be satisfactory in a previous section on composition of catalysts.

To determine the influence of pretreatment on precipitated iron catalysts, samples of P3003.24 (100Fe:10Cu:0.5K_2CO_3) were tested in the synthesis with $1H_2+1CO$ gas at 7.8

---

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

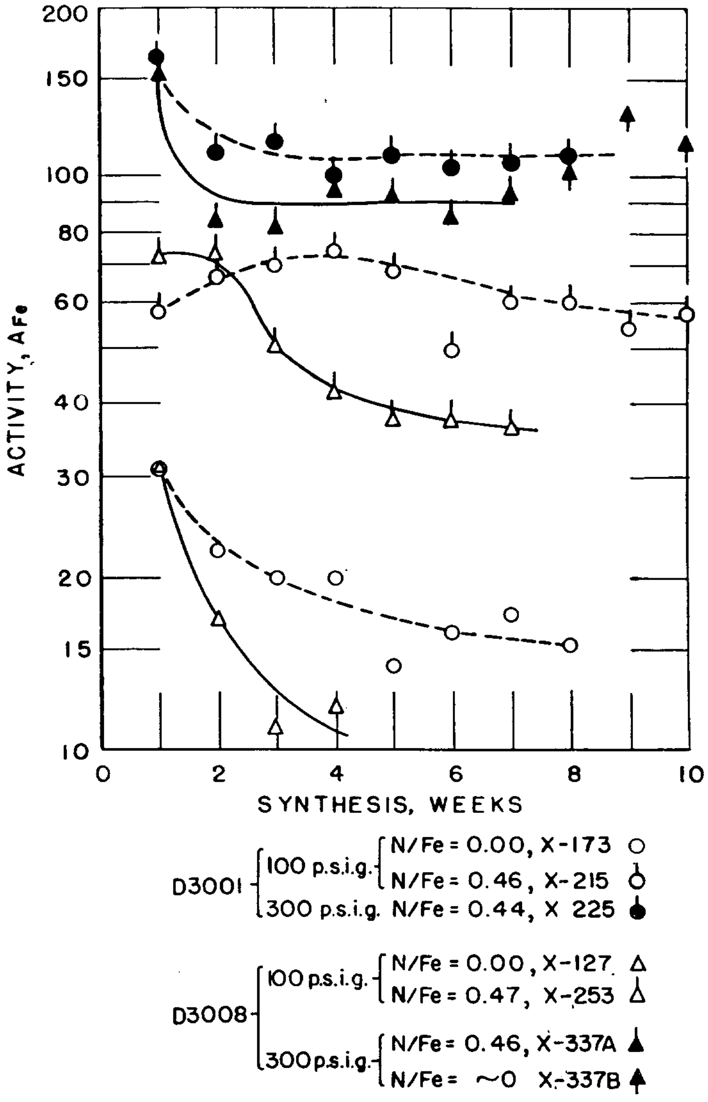


FIGURE 51.—Activities of Reduced and Reduced- and-Nitrided Catalysts D3001 and D3008.

atmospheres and space velocities of 100 hr.^{1} after the following pretreatments:[97]

Test	Gas	Space velocity, hour,	Temp., ° C.	Hours	Atom ratio, N:Fe
X-149	$1H_2+1CO$	100	230	23	0.0
X-245	H_2	1,480	300	18	.0
X-220	H_2	1,420	300	16	.25
	NH_3	1,000	300	8	
X-273A	H_2	1,350	300	25	.48
	NH_3	900	300	15	
X-273B	H_2	1,000	300	9	0

In the pretreatment with synthesis gas (X-149) the ferric oxide was converted to magnetite and part of this to Hägg carbide. In tests X-245, X-220, and X-273A the catalyst was fairly completely reduced in the hydrogen treatment. After six weeks of testing in X-273A the catalyst was hydrogenated at 300° C. to remove nitrogen, and the subsequent portion of the test was designated as X-273B.

The average activities in these experiments were about equal, as shown in figure 53; however, the activity of the nitrided catalysts decreased with time while the activity of the sample pretreated with synthesis gas increased. Although the average activity was about the same, the selectivity changed remarkably, as shown in figure 54. The sample inducted in synthesis gas (X-149) yielded a high-molecular-weight product, of which 92 percent was C_3+ and 51 percent boiled above 464° C. In the products from the reduced catalyst 84 percent was C_3+ and 18 percent boiled above 464° C. The reduced and nitrided catalysts (X-220 and X-273A) produced a still lower molecular

---

[97] Work cited in footnote 96, p. 94.

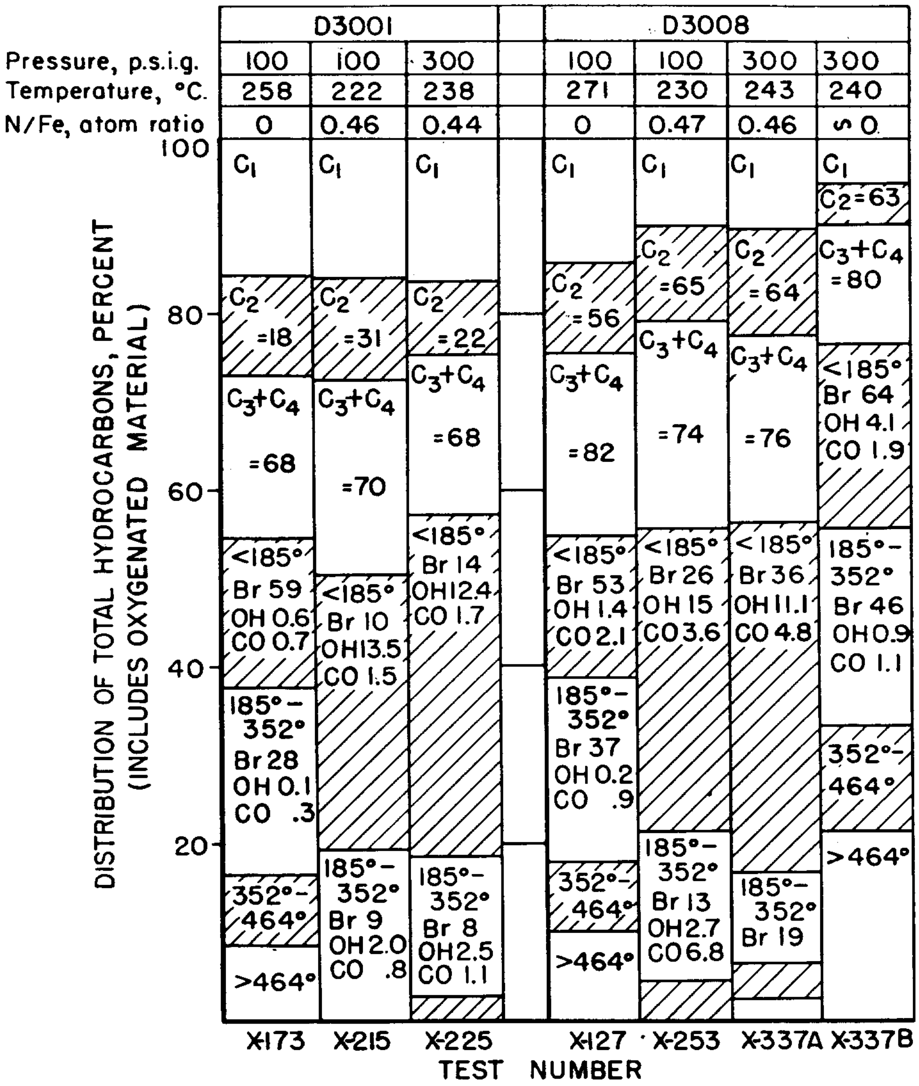


FIGURE 52.—Average Compositions of Products Obtained From Reduced and Reduced-and-Nitrided Catalysts D3001 and D3008.

weight product, with practically no wax boiling above 464° C. Hydrogenation of the catalyst in X–273A after 6 weeks produced no significant change in activity but increased the average molecular weight of the products so that these products appear intermediate between those from the inducted (X–149) and reduced (X–245) samples. The liquid products from nitrided catalysts contained larger quantities of alcohols and correspondingly smaller amounts of olefins than nonnitrided samples.

Attempts were made to nitride the raw Fe_2O_3–CuO–K_2CO_3 catalyst directly with ammonia, a process analogous to the preparation of carbides by treating iron oxide with carbon monoxide. However, at 300° to 400° C. ammonia only reduced the precipitated catalysts from Fe_2O_3 to Fe_3O_4.

TABLE 56.—*Activity of precipitated-iron catalyst P3003.24 after treatment with various gases during the hydrocarbon synthesis (experiment X–101)*

Treatment at 250° C.		Activity after treatment	
Gas	Time, hours	Temp., ° C.	Contraction, percent
Original activity	--------	251	64
Nitrogen	24	250	65
Natural gas	16	250	67
Hydrogen	17	250	65
Carbon dioxide	21	250	69
Air	16	248	67

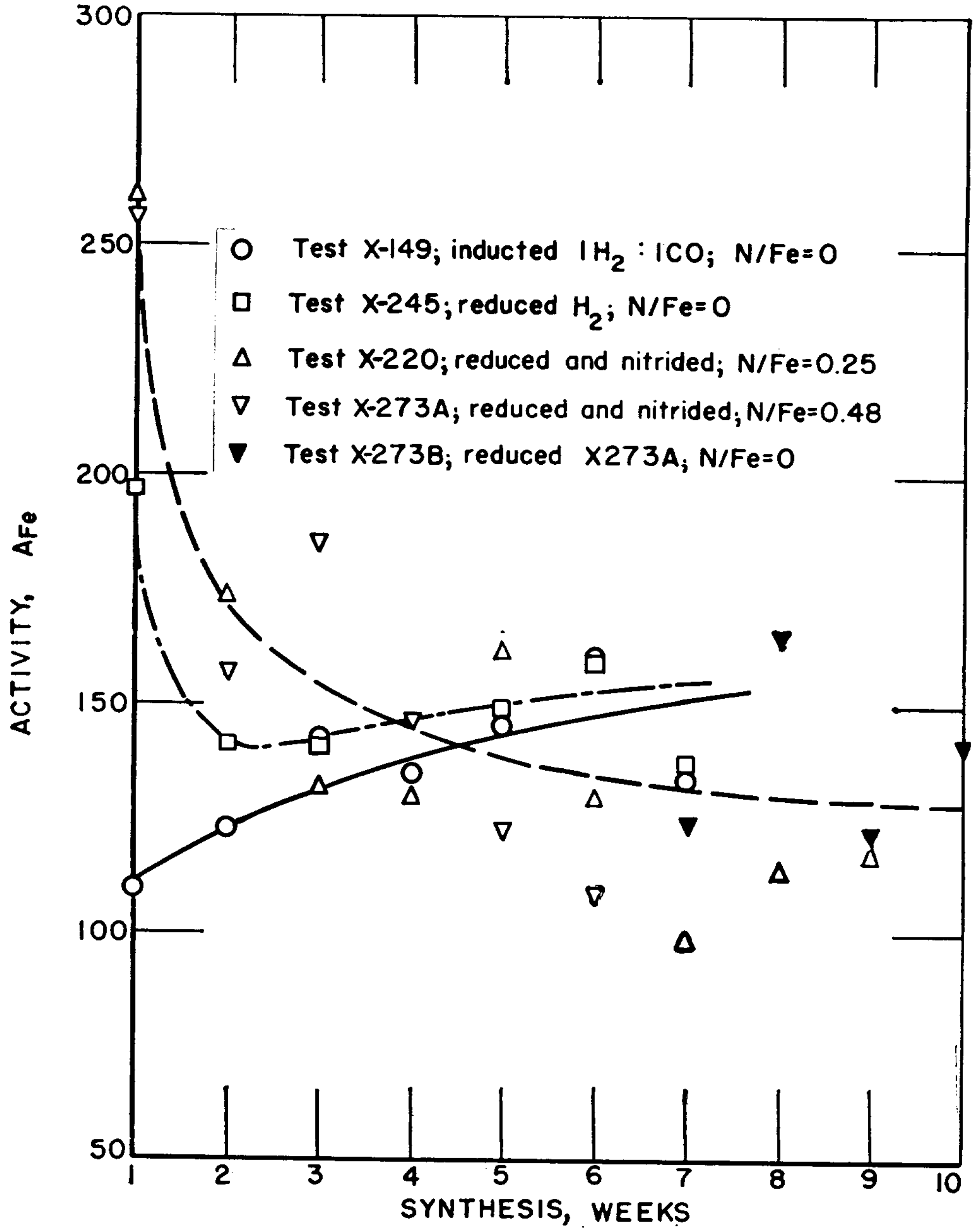


FIGURE 53.—Variation of Activity of Precipitated Catalyst P3003.24 With Method of Pretreatment.

After 7 weeks of operation in the hydrocarbon synthesis, a precipitated-iron catalyst, P3003.24 (100Fe:10Cu:0.5K_2CO_3), was treated with various gases at atmospheric pressure and retested in the synthesis after each treatment to determine the effect on activity of exposure to any of these gases. Data for these experiments are summarized in table 56. None of the gases tested appeared to have any significant effect on the catalyst. These results are surprising. Apparently this catalyst is adequately covered with heavy wax, so that neither oxidizing nor reducing gases at atmospheric pressure react with it.

ALKALIZED GOETHITE ORE

Although fused, sintered, and cemented catalysts are more active when reduced with hydrogen than when inducted with hydrogen-carbon monoxide gas mixtures, Bureau of Mines tests with catalyst A2103 (goethite ore + K_2O) showed that its activity increased with temperature of induction. Table 57 summarizes these results and shows that the sample inducted at 325° C. was nearly as active as the one reduced in hydrogen.

PHASE CHANGES DURING SYNTHESIS

The phase changes in the catalyst during synthesis were studied in experiment X–194

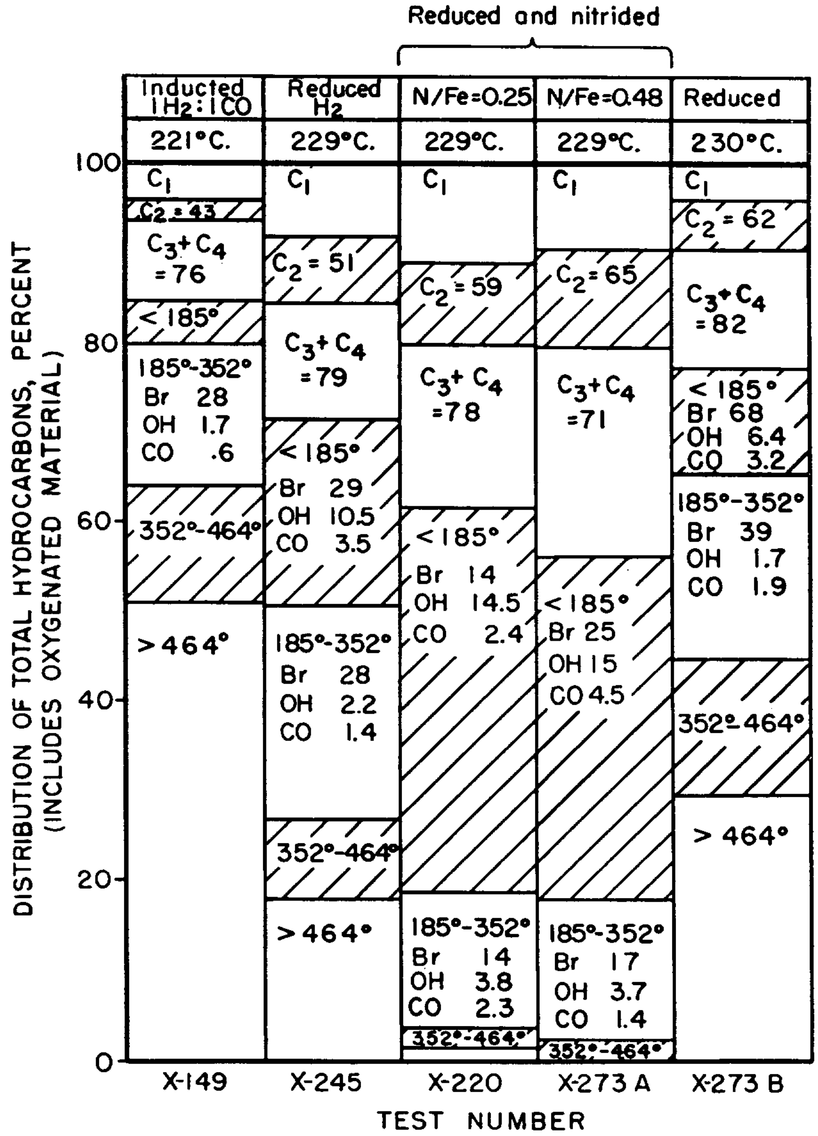


FIGURE 54.—Effect of Pretreatment of Precipitated Catalyst P3003.24 on Composition of Products Obtained From It.

using a fused, synthetic-ammonia-type catalyst, D3001.[98] Samples of catalyst were withdrawn periodically during operation in the hydrocarbon synthesis and subjected to X-ray, thermomagnetic, and chemical analyses. This catalyst had previously been reduced in hydrogen at a space velocity of 1,000 hr.$^{-1}$ for 40 hours at 450° C. After thermomagnetic analysis the total weight of iron in each sample was determined by chemical analysis, and the amount of magnetically measurable iron in the different phases was computed independently from the magnetic moments of the sample. Differences between calculated and analytical values represent the portion of iron not detectable magnetically. The presence of nonmagnetic iron—that is, iron that is not detected by magnetic analysis—may be attributed largely to magnetic unsaturation of the iron due to the low field strength (2,160 gauss) used. At higher field strengths a larger fraction of the iron could be measured by magnetic analysis.

The results of experiment X–194 are shown in table 58 and figure 55. In the first 46 hours the temperature was held at 235° C., and from 46 to 1,870 hours the temperature was maintained at 257° C. From 1,870 to 2,300 hours the temperature was increased, in several steps, to 300° C. In the initial 200 hours the fraction of iron present as Hägg carbide increased to its maximum—29.2 percent. In subsequent testing at 257° C. (200 to 1,800 hours) the amount of iron present as Hägg carbide decreased to 21.2 percent. The α-iron phase decreased rapidly in the first 200 hours, with the formation

---

[98] Anderson, R. B., Hofer, L. J. E., Cohn, E. M., and Seligman, B., Studies of the Fischer-Tropsch Synthesis. IX. Phase Changes of Iron Catalysts in Synthesis: Jour. Am. Chem. Soc., vol. 73, 1951, pp. 944–946.

TABLE 57.—*Influence of pretreatment of 6- to 8-mesh goethite catalyst A2103 (100Fe : 0.42 K_2O)*

Pretreatment at atmospheric pressure for 24 hours; synthesis at 7.8 atmospheres of $1H_2$:1CO gas

Test number	X-181	X-183	X-188	X-216
Pretreatment:				
Gas	H_2	$1H_2+1CO$	$1H_2+1CO$	$1H_2+1CO$
Space velocity	2,000	100	100	104
Temperature ° C	450	270	282	325
Testing data:				
Weeks, average	4	4	5	5
Temperature ° C	231	270	264	234
Average activity A_{Fe}	75	19	22	52
Usage ratio, H_2:CO	0.83	0.73	0.71	0.82
Products, gm./m.³:				
CO_2	238.4	327.6	346.3	275.6
H_2O	37.4	16.0	48.6	26.2
Total hydrocarbons	102.3	104.0	114.0	105.9
Distribution of hydrocarbons,[1] weight-percent:				
C_1	8.3	20.4	18.2	14.3
C_2	7.8	12.6	11.2	9.3
C_3+C_4	17.1	23.4	27.9	17.1
C_5+[1]	66.8	43.6	42.7	59.4
Distillation of liquids + solids,[1] weight-percent:				
<185° C	28.1	45.1	50.3	26.8
185°-352° C	29.7	37.4	35.1	37.3
352°-464° C	16.7	10.9	9.5	16.2
>464° C	25.5	6.6	5.1	19.7

[1] Includes oxygenated molecules dissolved in oil phase.

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, and the carbide phase may be more resistant to oxidation than α-iron. The fraction of nonmagnetic iron remained essentially constant throughout the experiment, despite 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.

In the period 1,870 to 2,300 hours the temperature of operation was increased to 278° C., then to 300° C. With testing at 300° C. carbon increased, although the iron as Hägg carbide fell from 21.2 percent to 12.8, whereas the iron as magnetite increased from 38.0 percent to 47.4.

In the synthesis with nitrided-iron catalysts, composition changes occur less rapidly. Although iron nitride is hydrogenated very rapidly in pure hydrogen at synthesis temperatures, nitrogen is removed very slowly in the synthesis. Presumably hydrogenation of the nitride is strongly inhibited by carbon monoxide. In the synthesis the nitrides are transformed to carbonitrides by carbon atoms replacing nitrogen. The carbonitrides are isomorphic with nitrides and the transformation requires no change in the positions of iron atoms in the crystallites. X-ray diffraction patterns of samples taken during the synthesis of nitrided catalysts show principally the lines of ε-phase. Oxidation proceeds very slowly with nitrided catalysts. Analyses for carbon and nitrogen in used nitrided catalysts (table 59) indicate that carbon replaced nitrogen and that the sum of the carbon plus nitrogen atoms remained relatively constant.

In test X-218[99] with nitrided, fused catalyst D3001 (Fe_3O_4-MgO-K_2O) using $1H_2+1CO$ gas

TABLE 58.—*Composition and activity of fused-iron catalyst D3001*

$1H_2$: 1CO gas at 7.8 atmosphere

Testing data			Total carbon		Magnetic analysis, percent Fe as—			
Time, hours	Temp., ° C.	Activity, cc./gm./hr.[1]	C:Fe[2]	Max. Fe as Fe_2C, percent[3]	Fe_2C Hägg	α-Fe	Fe_3O_4	Nonmagnetic
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
1,000	256	47.9	.210	42.0	23.0	11.3	33.9	31.8
1,200	257	41.2	.212	42.4	22.3	10.1	35.6	32.0
1,400	257	43.7	.214	42.8	21.8	9.2	36.9	32.1
1,600	255	67.0	.215	43.0	21.7	8.8	37.2	32.3
1,800	257	50.9	.216	43.2	21.2	8.2	38.0	32.6
2,000	266	57.3	.218	43.6	20.3	7.8	39.1	32.8
2,200	300	[4] 21.0	.275	55.0	16.9	7.2	42.9	33.0
2,300	300	(4)	.313	62.6	12.8	6.8	47.4	33.0

[1] Volume (cubic centimeters) of H_2+CO converted per gram of iron per hour at 240°.

[2] Atom ratio.

[3] This value assumes that all of the carbon is present as Fe_2C.

[4] Very high percentage conversions of synthesis gas, for which the method of computing activities is not valid.

---

[99] Shultz, J. F., Seligman, B., Lecky, J. A., 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.

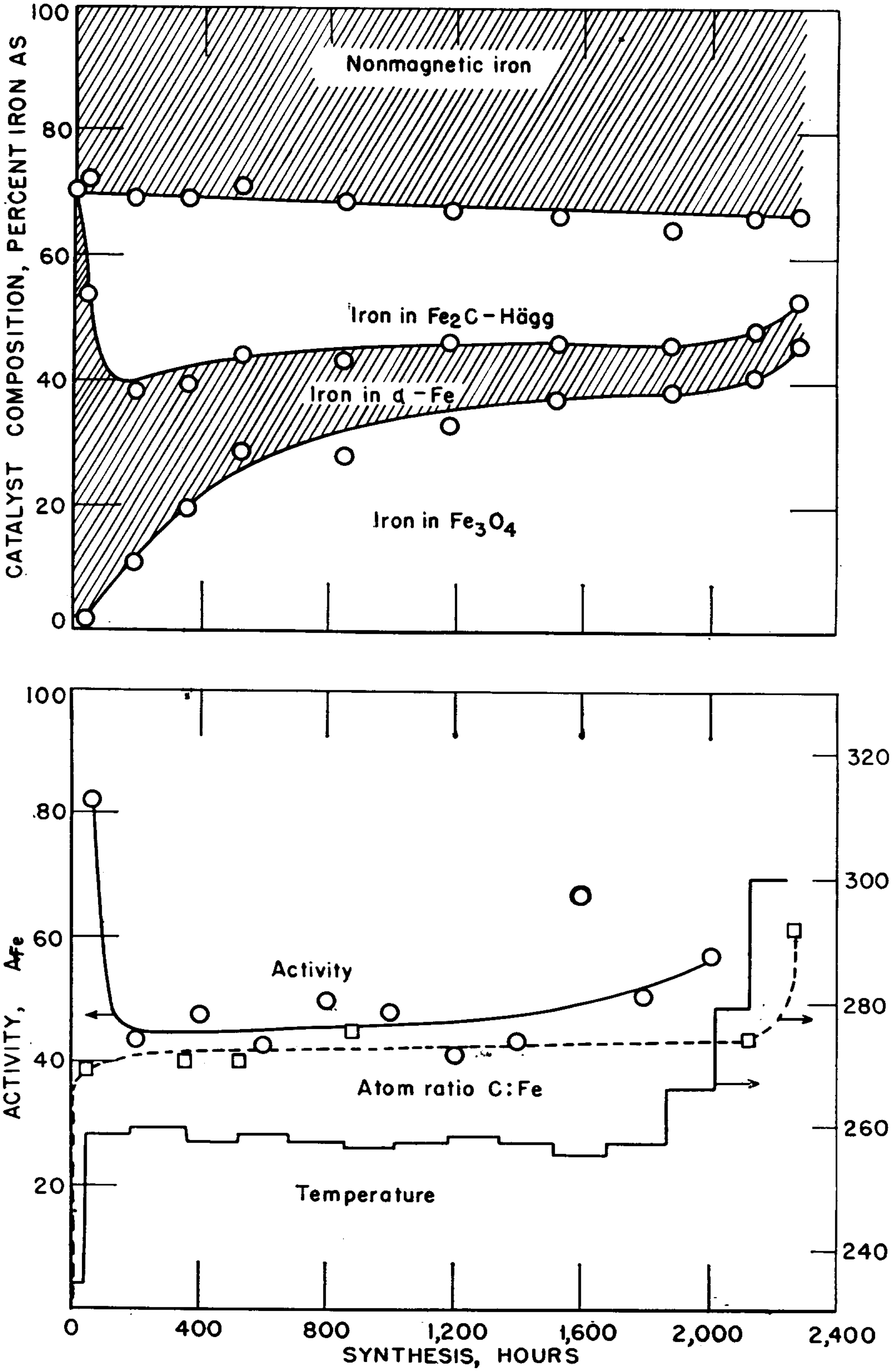


FIGURE 55.—Variation of Composition of Catalyst, Activity, and Temperature With Time: Fe_3O_4–MgO–KO_2 Catalyst at 7.8 Atmospheres of $1H_2$:CO.

at 7.8 atmospheres, the catalyst was sampled by the method described for test X–194. Only X-ray diffraction patterns of ϵ-iron nitride or carbonitride were observed, except for weak patterns of magnetite in a few samples. The changes in atom ratios of nitrogen, total carbon, elemental carbon, and oxygen to iron, as well as the fraction of iron as ϵ-carbonitride and magnetite, are given in figure 56. In this figure the carbonitride phase was arbitrarily assumed to be composed of Fe_2C and Fe_2N to show the relative quantities of carbon and nitrogen in the ϵ-phase. During the first 98 days of synthesis the temperature was maintained at 217°C., and the activity was essentially constant. The nitrogen content decreased while the carbon content increased at rapid rates in the beginning of the synthesis and thereafter at lower rates. In this period the atom ratio of elemental carbon to iron increased from 0 to 0.10. The amount of iron present as magnetite was only about one-fourth as large as in the test of the reduced catalyst in figure 55 (p. 100). From 99 to 139 days the temperature was increased to 240° and finally to 258°C. The elimination of nitrogen and the deposition of both interstitial and elemental carbon were accelerated, but the rate of oxidation remained about constant.

TABLE 59.—*Composition of nitrided catalysts after synthesis*

Test No.	Total weeks of testing	Phases present[1]	Atom ratios		
			N : Fe	C : Fe	(C+N) : Fe
X-214A	8	ϵ, M	0.149	0.260	0.409
X-214C		ϵ, M	.160	.333	.493
X-215	28	ϵ	.194	.325	.519

[1] Phases from X-ray diffraction listed in order of decreasing intensity of lines: ϵ=ϵ-nitride or carbonitride, M=magnetite.

INFLUENCE OF OPERATING VARIABLES

Data relating conversion and selectivity to operating variables are meager, and most of the experiments of this type were not arranged in a manner that permits simple interpretation. Data available in German documents may be summarized as follows:

1. The conversion decreases as flow increases.
2. The conversion increases as temperature increases. From data of Pichler[1] over-all apparent activation energies of 20 kcal./mole were estimated.
3. The conversion increased with operating pressure.
4. The rate of synthesis appears to increase with hydrogen content up to about $2H_2$:1CO.

VARIATION OF CONVERSION WITH SPACE VELOCITY AND TEMPERATURE

The influence of flow and temperature was studied on a reduced sample of 6- to 8-mesh fused catalyst D3001.[2] The variation of the fraction of hydrogen and carbon monoxide converted (real contraction) with the reciprocal of the space velocity on fused catalyst D3001 is given in figure 57. At constant temperature as the flow was decreased, the fractional conversion increased to a value of about 0.85. At the higher temperature, the conversion at the same space velocity was greater. The data may be approximated by the simple empirical equation

$$-\log(-C)=AS^{-1}\text{exp.}^{(-E/RT)}, \tag{28}$$

where C is the percentage of hydrogen-carbon monoxide consumed (the real contraction); A a constant; S the space velocity of a gas containing equal parts of hydrogen and carbon monoxide; and E the apparent over-all activation energy of the synthesis, as shown by the plots of the log (1–C) against 1,000/S in figure 57. The value of E computed from these data was 20 kcal./mole. In other tests of this fused catalyst and of a precipitated catalyst, Arrhenius plots were made of the logarithm of the total volume of hydrogen-carbon monoxide reacted in the synthesis per hour (space-time-yield) against reciprocal of temperature, the flow being varied to maintain essentially constant fractional conversions; these plots are shown in figure 58. From the slope of the straight lines, apparent over-all activation energies of 20.0 and 20.9 kcal./mole were computed. The equation for computing activity, which was described on page 73, is derived from equation (28). In this series of experiments the usage ratio varied with flow. These results will be discussed in a later section.

PRESSURE

The influence of pressure is considered in two ways: (1) The over-all differences in activity and selectivity in tests of moderately long duration; and (2) the variation of activity with pressure over short periods of synthesis (2 to 6 hours). The tests of long duration show the influence of progressive changes in catalyst composition, as well as pressure, on catalyst behavior.

Figure 59 presents plots of the activities (A_{Fe}) of several types of iron catalyst against weeks of operation in hydrogen-carbon monox-

---

[1] Pichler, H., Lecture and Discussion on Iron Catalysts for the Middle-Pressure Synthesis: TOM Reel 101, Doc. PG 21, 574-NID; trans. in TOM Reel 244 by M. Leva.

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

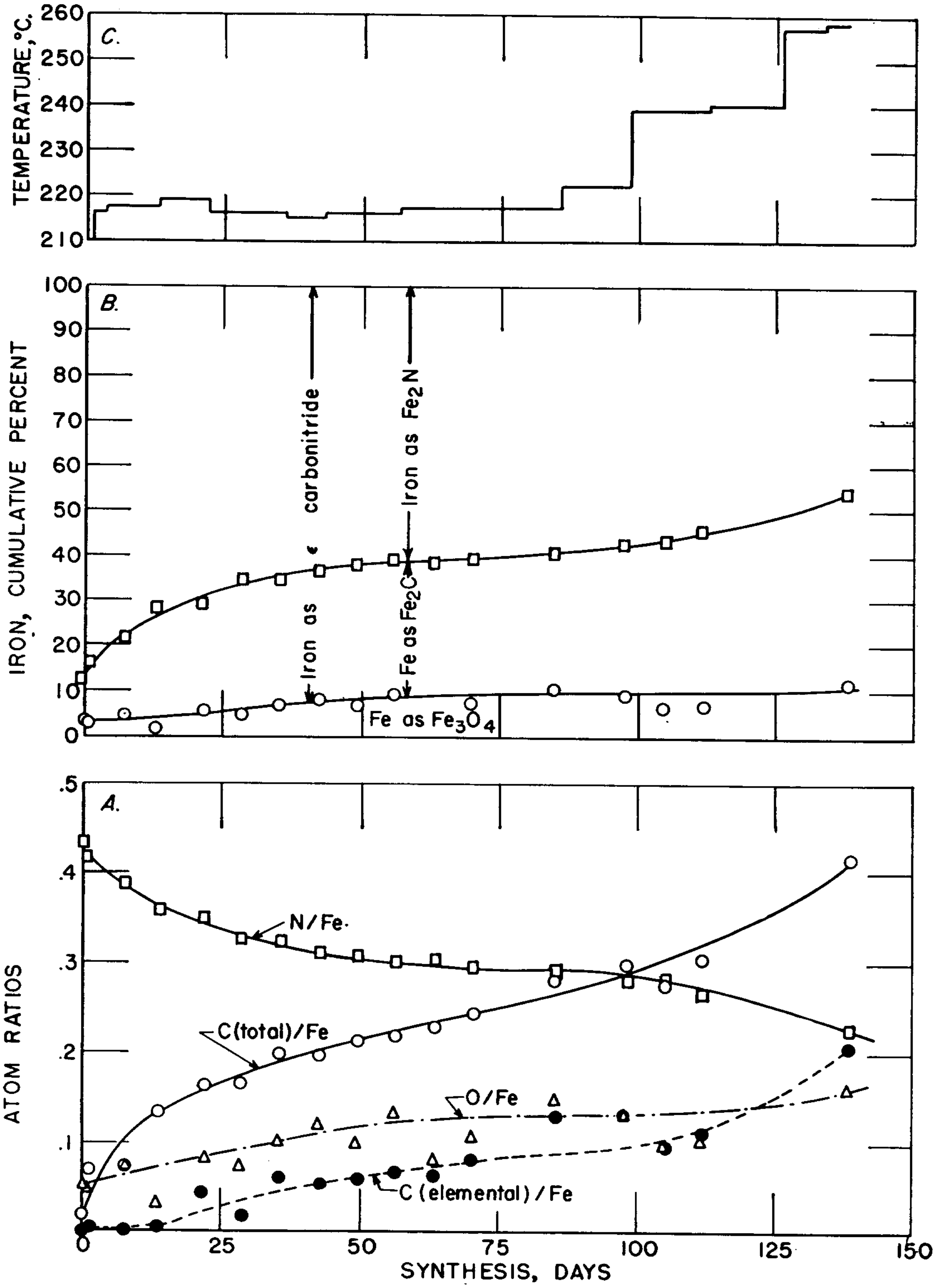


FIGURE 56.—Composition Changes of Catalyst D3001 During Synthesis With $1H_2$: 1CO Gas at 100 p.s.i.g. in Test X-218.

A, Atom ratios of nitrogen, total carbon, elemental carbon, and oxygen to iron; *B*, distribution of iron as carbonitride and magnetite; *C*, temperature.

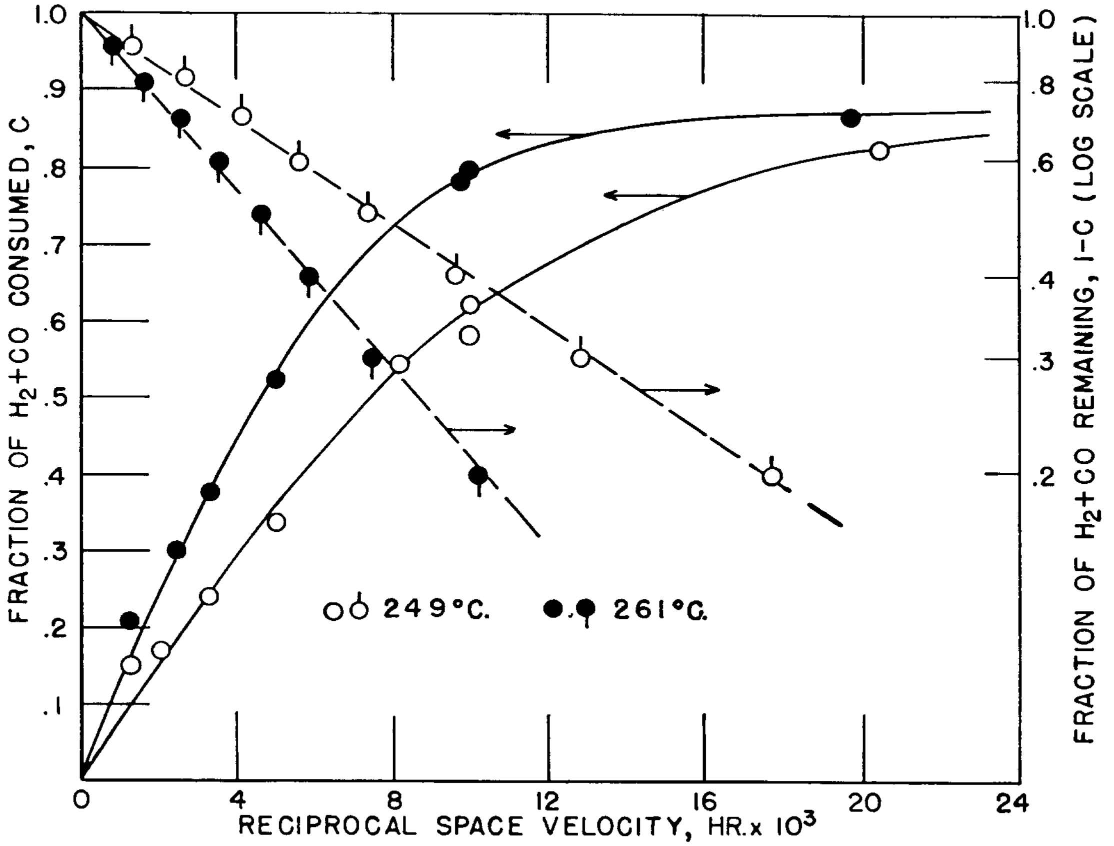


FIGURE 57.—Variation of Conversion With Reciprocal of Space Velocity; Fused Fe_3O_4-MgO-K_2O Catalyst, $1H_2$: 1CO Gas; 7.8 Atmospheres.

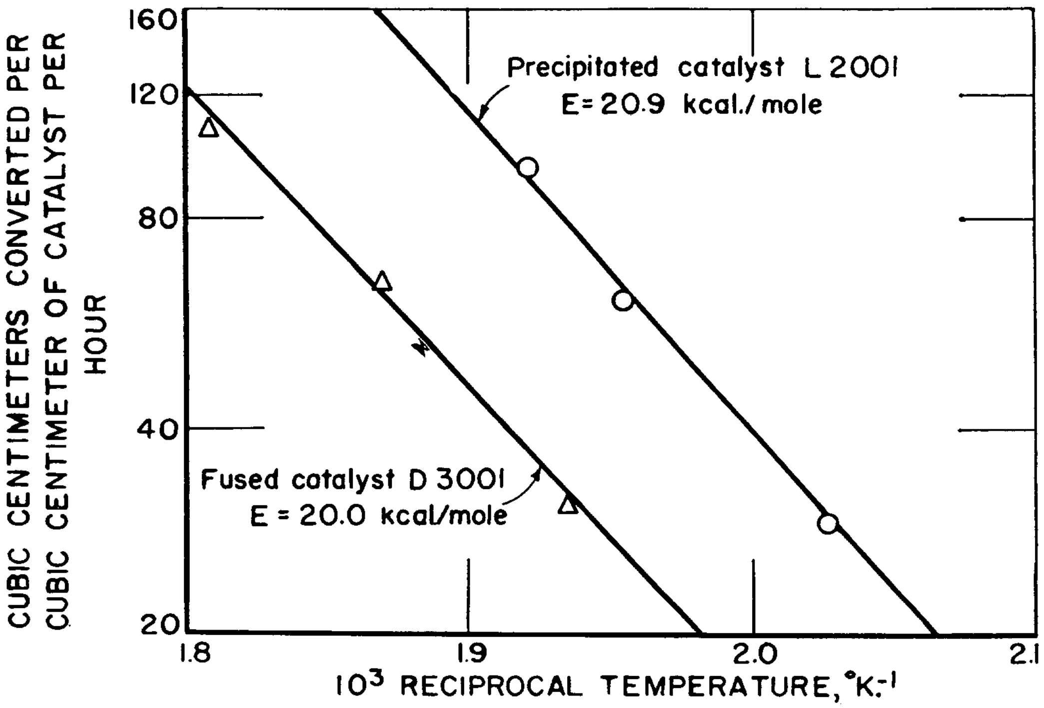
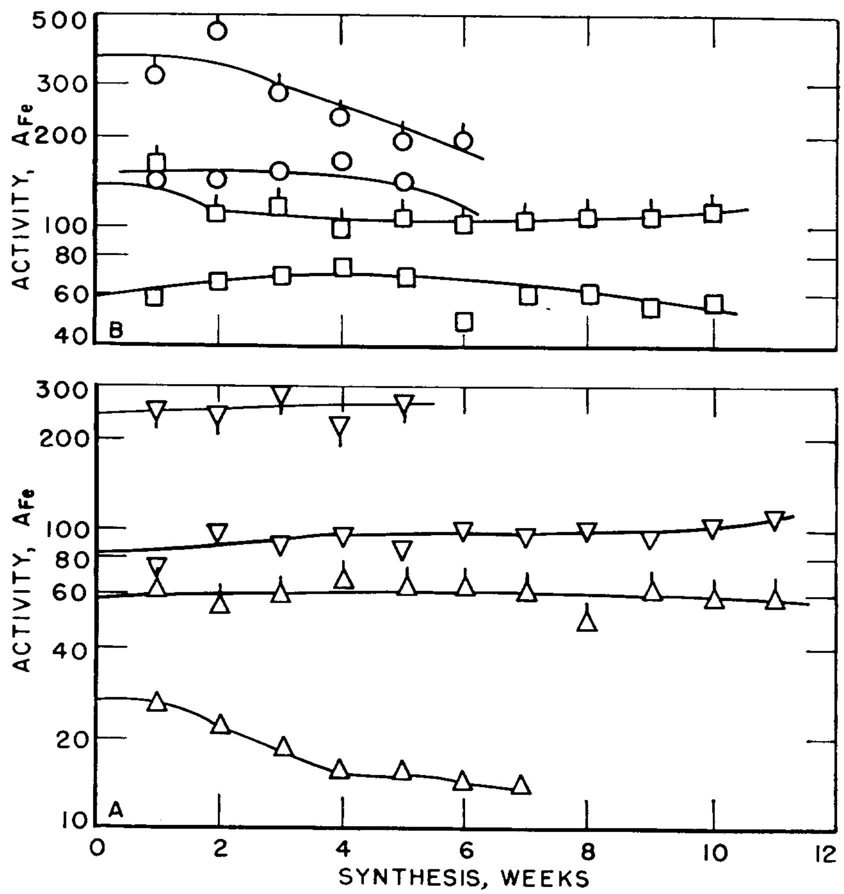


FIGURE 58.—Arrhenius Plots of Space-Time-Yield (in Terms of Volume of Synthesis Gas Converted); Flow Varied to Maintain Apparent Contractions of 65 Percent.



PART A. Sintered catalysts A2101, ▽ X-160, 100 p.s.i.g.; A2106, ▽ X-228, 300 p.s.i.g. Fused catalyst D3001 (reduced) △ X-152, 100 p.s.i.g.; △ X-200, 300 p.s.i.g.

PART B. Precipitated catalyst P3003.24 ○ X-101, 100 p.s.i.g.; ○ X-204, 300 p.s.i.g. Fused catalyst D3001 (nitrided) □ X-215, 100 p.s.i.g.; □ X-225, 300 p.s.i.g.

FIGURE 59.—Activity of Iron Catalysts With $1H_2$:1CO Gas at 7.8 and 21.4 Atmospheres.

ide gas at 7.8 and 21.4 atmospheres. The average activities at 21.4 atmospheres were 1.8 to 3.3 times greater than those observed at 7.8 atmospheres. For the reduced, fused catalysts, the activity remained essentially constant at 21.4 atmospheres but decreased continuously at 7.8 atmospheres. The activity of the precipitated catalyst decreased more rapidly at 21.4 than at 7.8 atmospheres. The activities of the nitrided, fused catalyst and the sintered catalysts remained essentially constant at both pressures.

Table 60 presents the distribution of products in the tests shown in figure 59. For precipitated catalysts, the distribution into gaseous and liquid-solid products was the same at both pressures; however, the average molecular weight of the condensed fraction was lower at the higher pressure. Similarly, for the sintered catalysts, the average molecular weight of the products was lower at 21.4 atmospheres. On the other hand, for the fused catalysts, both reduced and reduced and nitrided, the average molecular weight of the products increased with increasing operating pressure. Except for the nitrided catalysts, for which the yields of oxygenated products were high at both pressures, the fraction of oxygenated products increased with pressure from 7.8 to 21.4 atmospheres. The olefin content was essentially the same at both pressures.

The variation of the synthesis rate, shown in figure 59, results from the effect of pressure on the kinetics as well as from the effect of progressive changes in catalytic activity that may occur at different rates at different synthesis pressures. Hence, to study the effect of pressure on kinetics, a number of tests of short duration were made with fused catalyst D3001, in which the synthesis rate was determined at pressures varying from 4.4 to 16.3 atmospheres for periods of 3 to 5 hours. The pressures were varied in a manner designed to minimize the effect of any progressive change in activity. Data for experiments at 237° and 249° C. in terms of A_v are given in figure 60. For this catalyst the synthesis rate was proportional to the first power of the operating pressure (P), and equation 28 may be modified to

$$-\log(1-C)=A'PS^{-1}\exp(-E/RT). \qquad (29)$$

COMPOSITION OF SYNTHESIS GAS

Bureau of Mines data for reduced- and nitrided-fused catalyst D3001 (table 61) indicated very little change in the amount of gas converted per unit time when $2H_2$:1CO gas was used in place of $1H_2$:1CO gas at about the same temperature; but these results were obtained

TABLE 60.—*Effect of operating pressure on activity and selectivity* [1]

$1H_2+1CO$ gas

Catalyst:								
Composition	Fe_2O_3–CuO–K_2CO_3		Fe_3O_4–K_2CO_3		Fe_3O_4–MgO–K_2O			
Type	Precipitated [2]		Sintered [3]		Fused [3]			
Number	P3003.24		A2101	A2106.05	D3001			
Test number	X–101	X–204	X–160	X–228	X–152	X–200	X–215	X–225
Pretreatment:								
Gas	$1H_2+1CO$	$1H_2+1CO$	H_2	H_2	H_2	H_2	[4] NH_3	[4] NH_3
Space velocity [5]	135	135	1, 000	1, 000	600	2, 700	5, 000	1, 000
Time, hours	24	24	43	24	43	40	4	6
Temperature ° C.	230	230	400	400	450	450	385	350
Testing data:								
Pressure atm	7. 8	21. 4	7. 8	21. 4	7. 8	21. 4	7. 8	21. 4
Temperature ° C.	232	241	221	226	263	257	226	238
Average activity A_{Fe} [6]	148	337	89. 7	254	18. 4	62. 1	67. 8	120. 4
Usage ratio, H_2:CO	. 59	. 68	. 61	. 74	. 73	. 72	. 74	. 79
Composition of products:								
Hydrocarbons,[7] weight-percent as:								
C_1	4. 7	5. 0	4. 8	6. 7	13. 2	11. 3	16. 0	16. 4
C_2	5. 3	4. 4	4. 7	6. 2	8. 8	8. 3	10. 6	8. 3
C_3+C_4	8. 5	9. 1	11. 6	13. 9	20. 6	12. 2	22. 5	17. 9
C_1-C_4	18. 5	18. 5	21. 1	26. 8	42. 6	31. 8	49. 1	42. 6
Liquids+solids	81. 5	81. 5	78. 9	73. 1	57. 4	68. 1	50. 9	57. 4
Acid number [8]	----------	2. 1	6. 2	10. 4	. 8	7. 7	. 3	3. 0
Distillation of liquids+solids, weight-percent:								
<185° C.	2. 6	14. 0	12. 1	32. 1	36. 5	36. 8	61. 9	67. 3
185°–352° C.	19. 6	27. 0	26. 6	33. 8	36. 5	29. 8	34. 5	25. 0
352°–464° C.	17. 5	14. 0	10. 8	11. 1	15. 3	13. 2	2. 9	5. 2
>464° C.	60. 3	45. 0	50. 5	23. 0	11. 7	20. 2	. 7	2. 5
Infrared analysis, weight-percent of functional group:								
<185° C.:								
CO+COOH	1. 6	2. 8	3. 7	4. 0	. 6	1. 7	1. 5	1. 4
COO	. 5	. 5	1. 3	1. 3	. 1	. 5	. 2	. 3
OH	3. 1	7. 9	4. 5	7. 5	. 2	3. 4	13. 5	11. 7
α-olefins (C=C)	2. 8	4. 1	5. 7	6. 2	4. 9	7. 0	1. 5	1. 7
Other olefins (C=C)	1. 0	. 3	0	0	5. 1	. 9	0	0
Bromine number	25	29	38	41	66	53	10	12
185°–352° C.:								
CO+COOH	1. 0	1. 0	1. 5	1. 7	. 3	. 8	. 8	1. 3
COO	0	1. 2	2. 0	2. 8	. 1	. 9	. 6	1. 0
OH	. 7	1. 9	. 9	2. 2	0	. 7	2. 0	2. 7
α-olefins (C=C)	1. 9	1. 8	3. 8	4. 2	1. 1	4. 0	. 4	. 6
Other olefins (C=C)	1. 4	. 6	. 4	. 5	3. 9	1. 3	. 9	. 5
Bromine number	22	16	28	28	33	35	9	8

---

[1] From Anderson, R. B., Catalysts for the Fischer-Tropsch Synthesis: Chap. 2, Catalysts, vol. 4 (ed. by P. H. Emmett), Reinhold Publishing Corp., New York, N. Y., pp. 230–231.

[2] 6- to 14-mesh granules.

[3] 6- to 8-mesh granules.

[4] Reduced in hydrogen at space velocity of 2,500 and at 550° C. for 20 hours and converted to ε-phase nitride by the ammonia treatment.

[5] Volumes of gas at standard temperature and pressure per volume of catalyst space per hour.

[6] Average activity of weeks 1 to 5.

[7] Total hydrocarbons and liquids+solids include oxygenated compounds dissolved in hydrocarbon phases.

[8] Acid number of liquids+solids.

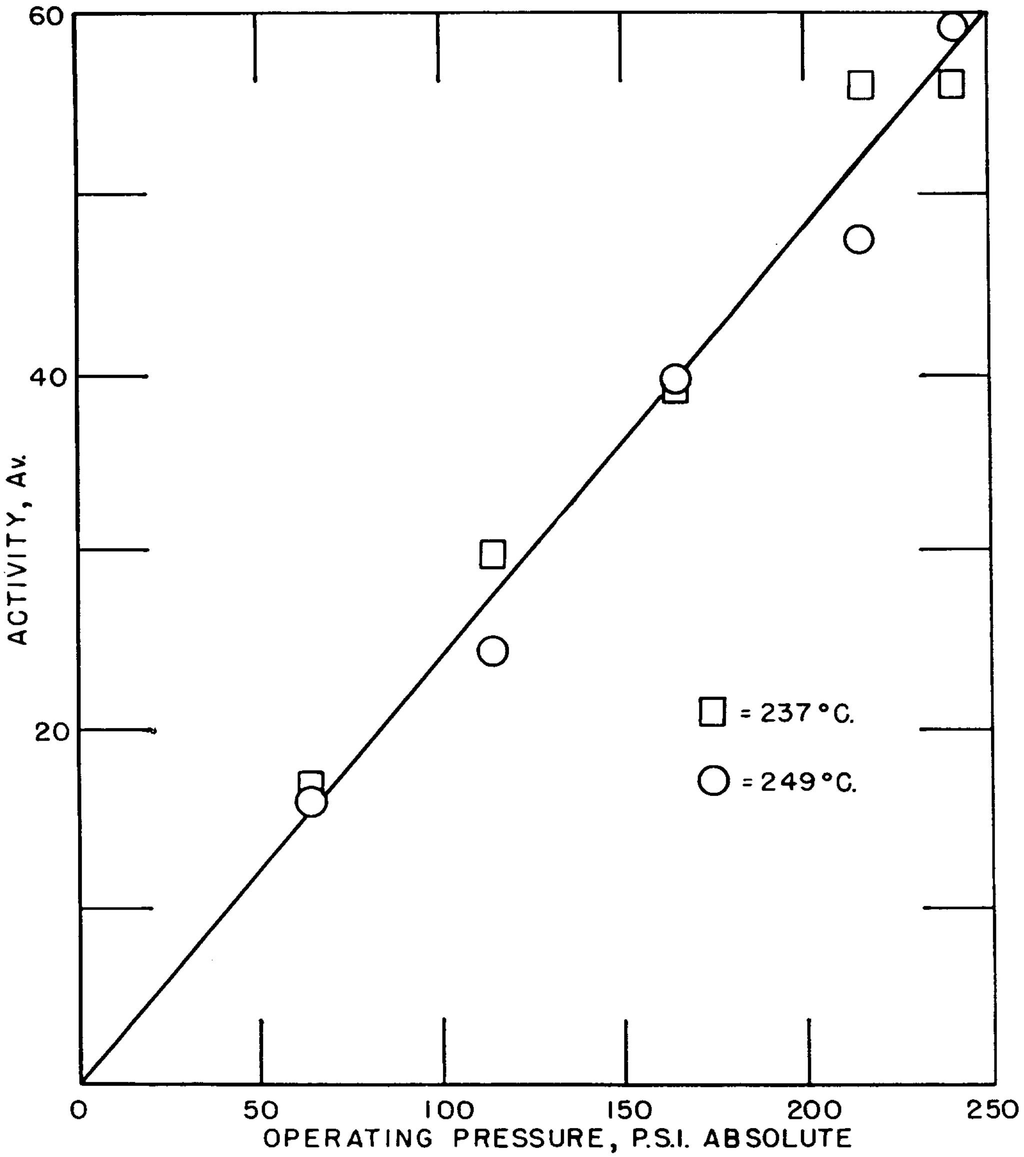


FIGURE 60.—Variation of Activity With Operating Pressure on Fused Catalyst D3001 With $1H_2 : 1CO$ Gas.

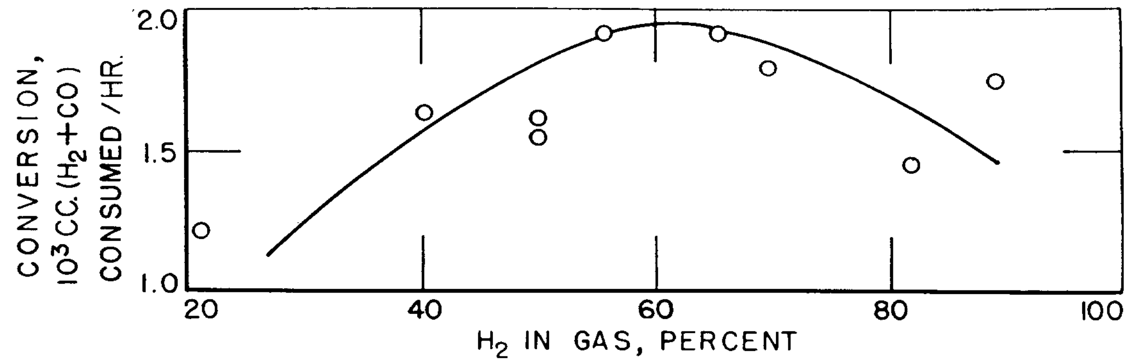


FIGURE 61.—Rate of Synthesis as a Function of Gas Composition; Constant Flow of Feed Gas, Varying Contractions,

Constant flow of feed gas; varying compositions; temperature, 219° C.; catalyst D3001; experiment 217.

at fairly high conversions. Similar results were obtained when $1H_2$:1CO and $1H_2$:1.5CO gases were used on nitrided catalysts. In all instances the average molecular weight of the product decreased with increasing hydrogen content of the feed gas.

In special experiments designed to furnish unambiguous information concerning the effect of synthesis-gas composition on the rate of synthesis, fused-iron catalyst D3001 was reduced in hydrogen and operated with $1H_2$: 1CO gas at 7.8 atmospheres for about 2 months (test X-217) at low conversion and at less than 230° C. In the subsequent parts of the experiments, conversion was maintained low enough (less than 30 percent) so that only relatively small percentages of hydrogen or carbon monoxide were consumed, and observations were made over a short period of time so that changes in catalyst composition were minimized. The composition of the feed gas was varied by two methods: (1) The flows of hydrogen and carbon monoxide were adjusted to maintain a constant total flow, and the contraction was permitted to vary with feed-gas composition; (2) the total flow of feed gas was varied, with the contraction maintained constant. Figures 61 and 62 show maximum activity with between 60 and 70 percent of hydrogen in the feed gas. Methane production (grams per cubic meter of synthesis gas consumed) (fig. 63) increases rapidly with hydrogen content of the feed gas.

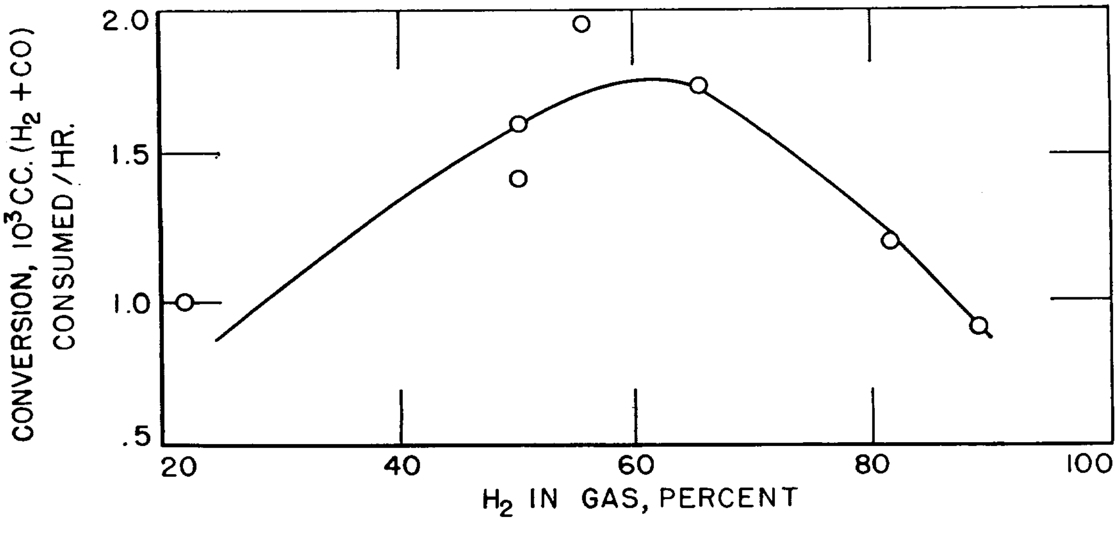


FIGURE 62.—Rate of Synthesis as a Function of Gas Composition; Varying Flow of Feed Gas, Constant Contractions.

Varying flow of feed gas: constant contraction (22 percent); temperature, 219° C.; catalyst D3001; experiment 217.

TABLE 61.—*Effect of feed-gas composition on activity and selectivity of nitrided synthetic-ammonia-type catalyst*

Catalyst D3001; 6- to 8-mesh

Pretreatments:				
Reduction with H_2 at:				
Temperature ° C	550	550	550	550
Time hours	20	20	20	20
Space velocity hr.$^{-1}$	2, 500	1, 000	2, 500	1, 000
Extent of reduction percent	98	100	100	100
Nitrided with NH_3 at:				
Temperature ° C	350	350	385	350
Time hours	6	6	4	6
Space velocity hr.$^{-1}$	1, 000	1, 000	5, 000	1, 000
N : Fe	0. 44	0. 5	0. 46	0. 46
Initial iron phases present	ϵ–Fe_2N	ϵ–Fe_2N	ϵ–Fe_2N	ϵ–Fe_2N
Synthesis conditions:				
Test number	X–225	X–226	X–215	X–236
Pressure atm	21. 4	21. 4	7. 8	7. 8
Type of gas used	$1H_2$: 1CO	$2H_2$: 1CO	$1H_2$: 1CO	$1H_2$: 1.5CO
Weeks, average	5	5	5	5
Average temperature ° C	238	240	221	230
Contraction [1] percent	65	54	62	64
Space velocity hr.$^{-1}$	297	351	99	105
Usage ratio, H_2 : CO	0. 73	1. 03	0. 73	0. 65
Products, gm./m.^{3}:				
H_2O	25. 4	51	18	8
CO_2	281. 4	214	323	311
Total hydrocarbons [2]	106. 5	93	103	95
Distribution of hydrocarbons, weight-percent:[2]				
CH_4	17. 0	28. 5	17. 7	13. 9
C_2	8. 0	25. 1	10. 9	8. 9
C_3+C_4	17. 8	11. 9	21. 8	20. 3
C_5+[2]	57. 2	34. 5	49. 6	56. 9
Distillation and infrared analysis, weight-percent:[3]				
<185° C	67. 6	74. 0	61. 9	61. 0
OH	12. 4	15. 8	13. 5	13. 3
CO+COOH	. 4	1. 3	1. 5	1. 6
α-olefins (C=C)	2. 1	. 5	1. 5	3. 0
Other olefins (C=C)	0	0	0	0
185°–352° C	27. 2	20. 3	34. 5	32. 1
OH	2. 5	4. 0	2. 0	1. 3
CO+COOH	1. 1	. 6	. 8	1. 1
α-olefins (C=C)	. 9	. 4	. 4	1. 7
Other olefins (C=C)	. 3	. 2	. 9	1. 0
352°–464° C	5. 2	4. 3	2. 9	5. 6
>464° C	0	1. 4	. 7	1. 3

[1] CO_2-free apparent contraction.
[2] Includes oxygenated molecules dissolved in oil phase
[3] Weight-percent of C_5+.

INFLUENCE OF OPERATING VARIABLES AND COMPOSITION OF CATALYST ON USAGE RATIO

The usage ratio (H_2 : CO) for the synthesis on iron catalysts varies from 0.5 to 3.0. In this section a number of variables influencing usage ratio are discussed. Variation of conversion and feed-gas compositions produces the largest changes in usage ratio. These data add support to the postulate that water is the primary oxygenated product and that carbon dioxide is produced by a subsequent water-gas-shift reaction.

The influence of feed composition is considered first. Data in figure 64 were obtained from the special experiments described in the previous section. The usage ratios were somewhat higher than those in tests at higher conversions. The usage ratios for feed gases containing over 80 percent of hydrogen exceeded 2. The high value of 4.3 obtained for a feed gas containing 89 percent hydrogen probably is incorrect, but such high values could result from hydrocracking of hydrocarbons or hydrogenation of carbide or oxide. That this may occur is indicated by the unusually low usage ratio of 0.4 obtained when a feed gas containing 21 percent hydrogen was used immediately following the feed gas containing 89 percent hydrogen. The usage ratio increased with hydrogen content of the feed gas over the composition range studied. Similar results were obtained in tests at 65-percent conversion given in table 62.

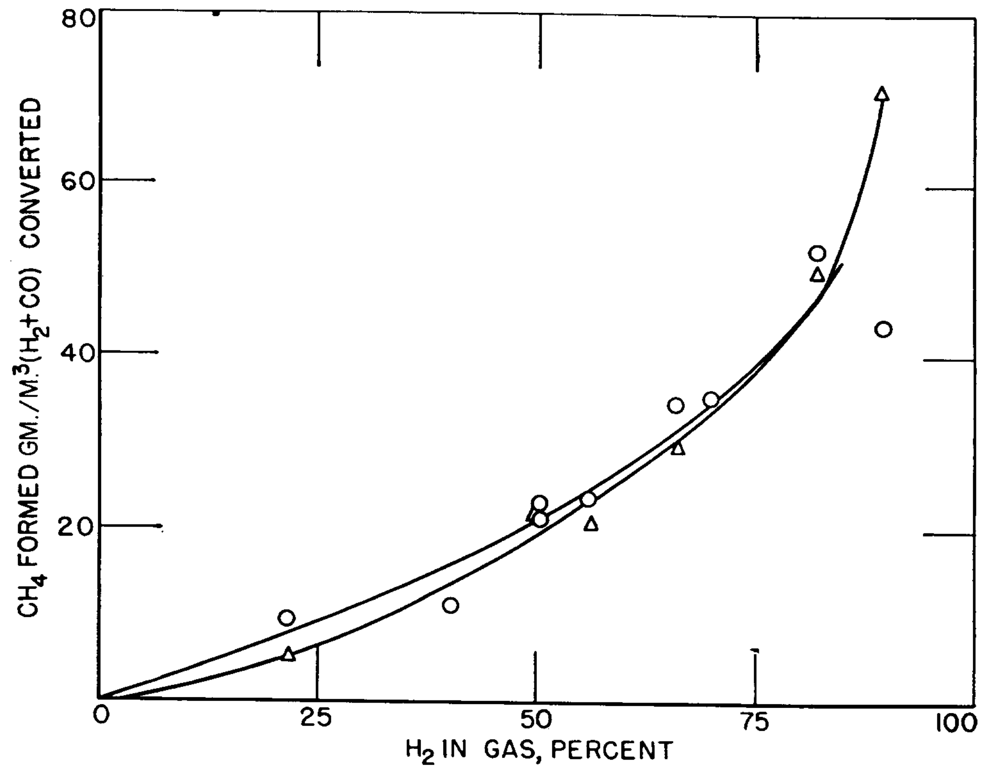


FIGURE 63.—Methane Production as a Function of Gas Composition.

○, Constant flow of feed gas; varying contraction; temperature, 219° C. △, Varying flow of feed gas; constant contraction (22 percent); temperature, 219° C.; catalyst D3001; experiment 217.

TABLE 62.—*Effect of synthesis-gas ratio on usage ratio*

Synthetic-ammonia-type catalyst D3006, 4- to 6-mesh; 300 p. s. i. g.; hourly space velocity of 300

Experiment No.	Synthesis gas, H_2:CO	Usage ratio, H_2:CO	Average temperature for 65-percent, CO_2 free contraction, °C.
RA-24	0. 962	0. 700	261
RA-41	. 820	. 679	260
RA-60	. 725	. 659	263

For experiments at constant temperature the usage ratio varied with the flow of synthesis gas, principally because of changes in the extent of conversion. Figure 65 shows the variation of usage ratio as a function of conversion for experiments with reduced, fused-iron catalysts in which the flow was varied at constant temperature. Conversion data for these experiments have been described previously (fig. 57, p. 103). The H_2 : CO usage ratio was high at low conversions, passed through a minimum at about 40-percent conversion, and then increased with increasing conversions.

Available data, including those of Kölbel and Engelhardt[3] as well as those of the Bureau of Mines, suggest that water may be the principal primary oxygenated product formed on iron catalysts and that a large fraction of the carbon dioxide is produced by a subsequent water-gas reaction. Bureau of Mines experiments described in this section show that the usage ratio increased with increasing hydrogen-carbon monoxide ratio in the feed gas. These observations suggest an explanation of figure 65:

1. At low fractional conversions of synthesis gas, the partial pressure of water vapor in the gas stream is

---

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

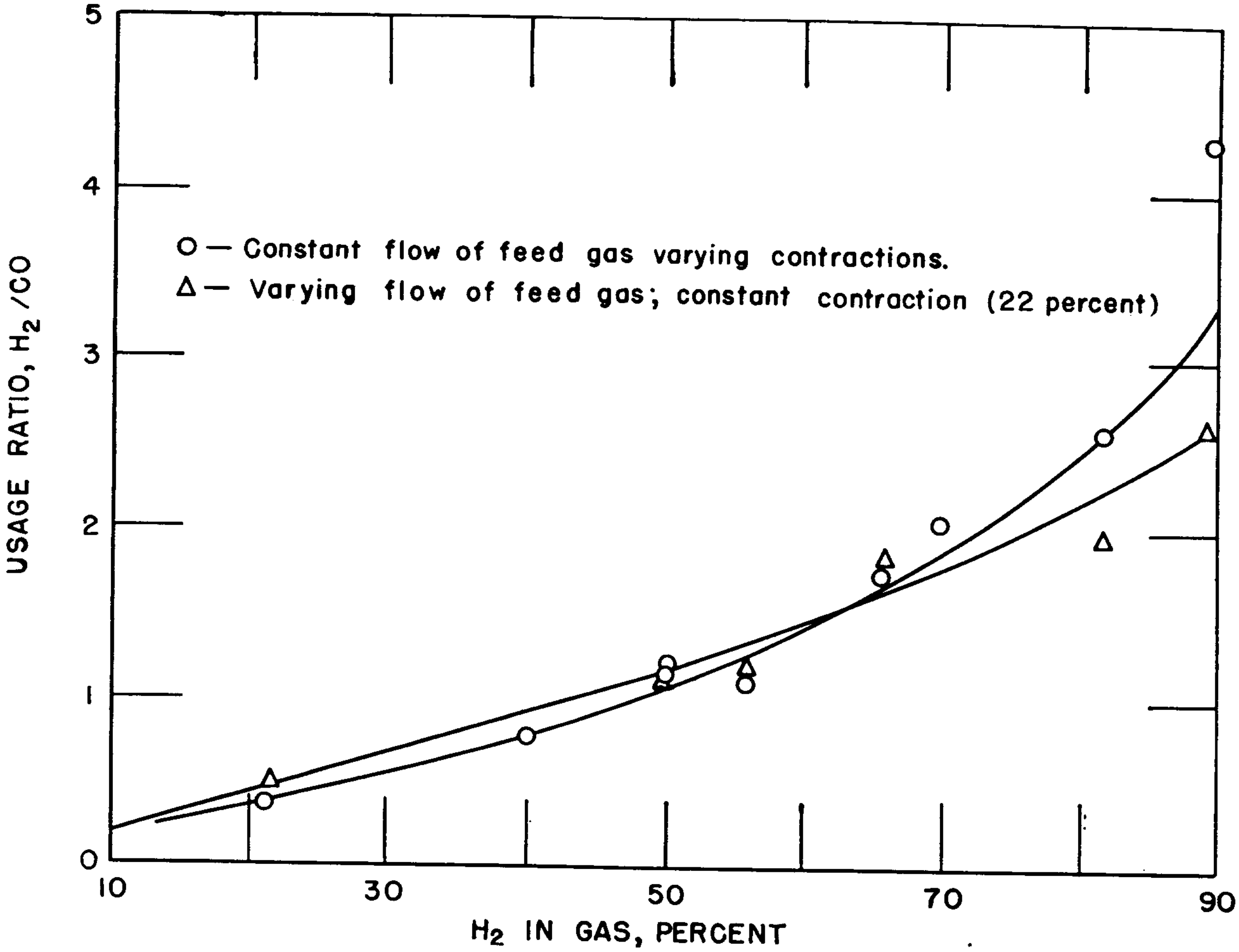


FIGURE 64.—Usage Ratio as a Function of Gas Composition; Experiment 217.

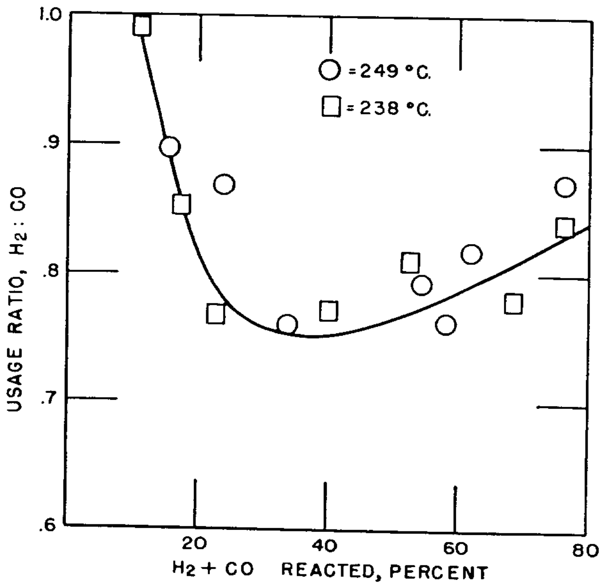


FIGURE 65.—Variation of Usage Ratio With Conversion; Fused Catalyst D3001 at 100 p. s. i. g. With $1H_2$:1CO.

low; hence, the water-gas reaction proceeds only very slowly, and the usage ratio at low fractional conversions may exceed 1.5.

2. As the fractional conversion is increased, the partial pressure of water vapor increases, and a greater fraction of it is consumed in the water-gas reaction, causing the usage ratio to decrease.

3. Except at very low conversions, with $1H_2$: 1CO feed gas, carbon monoxide is consumed at a greater rate than hydrogen; thus, the ratio of hydrogen to carbon monoxide in the gas phase increases as the gas passes through the catalyst bed. At some point, the H_2:CO ratio becomes high enough so that the usage ratio in that increment of the bed begins to increase in spite of effect 2. These effects increase with bed length or conversion, and eventually the usage ratio in this part of the bed is large enough to cause the overall usage ratio, (based on feed gas) to increase with increasing bed length or conversion.

Thus, (1) predicts the high usage ratios at low fractional conversions; (2) predicts the decrease in usage ratio with increasing fractional conversion; and (2) and (3) predict the minimum and the increase of the usage ratio at higher fractional conversions.

TABLE 63.—*Usage ratios in synthesis tests at 7.8 atmospheres with* $1H_2 : 1CO$ *gas*

Usually 6- to 8-mesh particles

Catalyst: Number	Catalyst: Promoter: K_2O/100Fe	Catalyst: Promoter: Other	Test No.	Average temperature, ° C.	Contraction (CO_2-free), percent	Usage ratio, H_2:CO	Remarks
Fused catalysts							
D3001	0.91	$MgO-Cr_2O_3-SiO_2$	X-105	256	63	0.79	
			X-107	310	63	.67	
			X-118	239	62	.77	14- to 18-mesh.
			X-121	238	65	.71	
			X-126	263	64	.75	
			X-144	248	64	.76	
			X-140	257	63	.74	
D3004	2.8	Al_2O_3	X-114	298	65	.70	
			X-125	309	55	.68	
D3006	.83	$MgO-Cr_2O_3-SiO_2$	X-124	252	62	.68	
D3008	1.4	Al_2O_3	X-127	271	64	.69	
D3005	2.1	Al_2O_3	X-136	262	65	.76	
A3212	.50	Al_2O_3	X-129	281	63	.68	From electrolytic iron.
A3217	.45	Al_2O_3	X-148	266	63	.68	
Synol	.94	Al_2O_3-CaO	X-113	219	66	.61	German catalyst.
A1000	None	None	X-147	285	66	.69	
P3003.262	.34	CuO	X-109	277	63	.74	Fused precipitated catalyst.
			X-132	250	65	.71	
Sintered and cemented catalysts							
A1003	None	Minor impurities	X-145	265	65	.81	Alan Wood magnetite as glomerules or powder.
A2101	0.6	do	X-160	221	64	.61	
			X-166	224	64	.58	
A3211	.6	Al_2O_3	X-123	233	65	.66	
A3213.24	.6	Al_2O_3	X-131	232	64	.62	
A3215	.5	Al_2O_3	X-138	242	65	.68	
A3218.05	.5	Al_2O_3	X-153	232	65	.70	
A3218.00	None	Al_2O_3	X-167	280	66	.81	
L1002.2	-----	$Na_2B_4O_7$	X-165	249	66	.63	
L3009	.5	Al_2O_3	X-156	237	65	.69	Mill scale.
A3210	.8	Al_2O_3	X-134	236	65	.68	Fe_2O_3 powder.
P3003.2511	.34	CuO	X-112	300	18	.64	Sintered precipitated catalyst.
Precipitated catalysts							
P3003.24	0.34	CuO	X-101	232	63	0.59	
			X-149	221	65	.57	
			X-143	236	64	.61	
P3003.04	None	CuO	X-130	268	67	.89	
L2001	.13	None	X-104	238	63	.74	
L2002	.13	None	X-119	244	63	.75	
L3004	.13	CuO	X-115	229	66	.68	From $FeCl_2$–$FeCl_3$.
L3006	.13	CuO	X-141	282	37	1.52	From $FeCl_3$.
L6005	.34	CuO	X-122	261	65	.88	Contains natural kieselguhr.
L6006	.34	CuO	X-106	261	65	.73	Contains flux-calcined kieselguhr.

TABLE 64.—*Relative usage of hydrogen and carbon monoxide on nitrided and reduced fused catalysts*

$1H_2+1CO$ gas; conversion, about 65 percent

Test	Pressure, atm.	Average temperature, ° C.	Initial atom ratio, N : Fe	Usage ratio, H_2 : CO
Catalyst D3001 (Fe_3O_4-MgO-K_2O)				
X-173	7.8	258	0	0.72
X-200	21.4	257	0	.72
X-214A	7.8	225	.44	.75
X-214B	7.8	238	0	.75
X-215	7.8	222	.46	.74
X-218	7.8	218	.43	.71
X-219	21.4	242	.26	.77
X-225	21.4	238	.44	.79
Catalyst D3008 (Fe_3O_4-Al_2O_3-K_2O)				
X-127	7.8	271	0	0.69
X-253	7.8	230	.47	.69
X-337A	21.4	243	.46	.73
X-337B	21.4	240	~0	.72

The data just described indicate that the usage ratio depends strongly on feed-gas composition and conversion but is relatively independent of operating temperature and pressure. Data on iron catalysts at 7.8 atmospheres in table 63 demonstrate that the usage ratio is also relatively independent of the type and composition of the catalysts. Alkali (K_2CO_3) was the only promoter that produced any significant change in usage ratio. The usage ratios of catalysts with low alkali content were significantly larger than those of corresponding preparations containing amounts of alkali adequate for high activity. The usage ratios of catalysts L6005 and L6006 (table 63) suggest that catalyst containing natural kieselguhr was alkali-deficient; the active high area support apparently effectively removed the alkali added to the catalyst. Table 64 compares usage ratios for two fused catalysts, both reduced and nitrided, at 7.8 and 21.4 atmospheres.

SELECTIVITY OF THE FISCHER-TROPSCH SYNTHESIS

The hydrocarbons, alcohols, and other oxygenated molecules produced in the Fischer-Tropsch synthesis are not in thermodynamic equilibrium with respect to type of molecules and carbon number and isomer distributions. This observation suggests that, by changing the nature of the catalyst or operating conditions, major changes in product composition may be obtained and that valuable information regarding the mechanism of the synthesis may be obtained from a study of the composition of synthesis products. The synthesis products have predominantly straight carbon chains, together with a small but significant amount of monomethyl isomers and smaller amounts of dimethyl isomers. In hydrocarbons up to C_8, molecules containing quaternary carbon atoms or chains substituted with ethyl or higher hydrocarbon radicals have not been found. The structures with straight carbon chains are present in amounts greatly exceeding those corresponding to thermodynamic equilibrium between these molecules. Olefins are present in much greater amounts than would be predicted for equilibrium between olefins and the corresponding paraffins in the presence of hydrogen. In addition 1-olefins are present in significantly larger amounts than internal olefins. Alcohols and other oxygenated organic molecules are present in significantly larger amounts than would be anticipated for equilibrium between these molecules and hydrocarbons. On this basis the following statements can be made regarding the mechanism of the synthesis:

(1) Alcohols or other oxygenated molecules may be intermediates in the synthesis, and this statement applies equally well to 1-olefins.

(2) Straight carbon chains are the principal primary product of the synthesis reaction, and any synthesis mechanism must explain their presence.

CARBON-NUMBER DISTRIBUTION

Friedel and Anderson[4] determined the carbon-number distribution of products from a cobalt catalyst and extended the chain growth hypothesis of Herington.[5]

The distribution of hydrocarbon products from tests of precipitated-cobalt catalysts in small reactors with $2H_2 : 1CO$ gas at atmospheric pressure (space velocity of 100 and about 190°) was obtained by fractional distillation of the liquids and mass-spectrometer analysis of the gases. The liquid products were fractionated in a 6-foot, 25-mm.-diameter, Podbielniak column, at atmospheric pressure up to C_{13} and at 40 mm. pressure from C_{13} to C_{20}. Plate values for the atmospheric distillation varied between about 50 and 80 theoretical plates. Fractionations were carried out on both the original sample and on a hydrogenated portion. The molecular weight distributions obtained from the boiling-point curves were identical for the two distillations. Estimated accuracies for the distribution vary from 5 percent at C_6 to 25 percent at C_{20}. Qualitative tests by ferrox paper, 2,4-dinitrophenylhydrazone, and spectrometric methods showed the presence of oxygenated compounds in various fractions. For the over-all distribution to C_{20} no further separation or analysis was undertaken.

The distribution according to carbon number is given in figure 66. The yield of methane was large, followed by a minimum at C_2, a broad maximum from C_5 to C_{11}, and a gradual decrease. Ten percent of the products was above C_{20}, the average molecular weight of this residue being 309. This distribution is similar to that reported by Craxford[6] for C_1 to C_{13}, but differs considerably from those reported by Underwood[7] for C_1 to C_{32} and by Herington[8] for C_5 to C_{11}, in which the weight fraction decreased continually with increasing carbon number above C_5.

Olefin percentages in the C_2, C_3, C_4, and C_5 fractions were, respectively, 0 (none detectable), 39, 47, and 43 percent. The percentages of olefins in the higher fractions decreased steadily with molecular weight, similar to the data of Herington.

Approximate analyses of olefin types in the C_6–C_8 range were carried out on the olefin portion from the silicagel separation (table 65). The infrared spectrometric method used was essentially that described in recent publications.[9] [10] Results showed the predominance of internal double-bond olefins over the alpha form; this predominance increased with molecular weight. Further, the transconfiguration was found in greater concentration than the cis-form of internal olefins (table 65). Without all the necessary calibration compounds, chain branching is detectable in olefins only if the substituents are on the carbon atoms of the double bond; such isomers were not detected.

---

[4] Friedel, R. A., and Anderson, R. B., Composition of Synthetic Liquid Fuels. I. Product Distribution and Analysis of C_5–C_8 Paraffin Isomers From Cobalt Catalyst: Jour. Am. Chem. Soc., vol. 72, 1950, pp. 1212-1215, 2307.

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

[6] Craxford, S. R., The Chemistry of the Fischer-Tropsch Synthesis: Fuel, vol. 26, 1947, pp. 119–123.

[7] Underwood, A. J. V., Industrial Synthesis of Hydrocarbons From Hydrogen and Carbon Monoxide: Ind. Eng. Chem., vol. 32, 1940, pp. 449–454.

[8] Work cited in footnote 5, p. 112.

[9] Johnston, R. W. B., Appleby, W. G., and Baker, M. O., Determination of Olefins in Gasoline. Application of Infrared Spectroscopy: Anal. Chem., vol. 20, 1948, pp. 805–812.

[10] Anderson, J. A., Jr., and Seyfried, W. D., Determination of Oxygenated and Olefin Compound Types by Infrared Spectroscopy: Anal. Chem., vol. 20, 1948, pp. 998–1006.