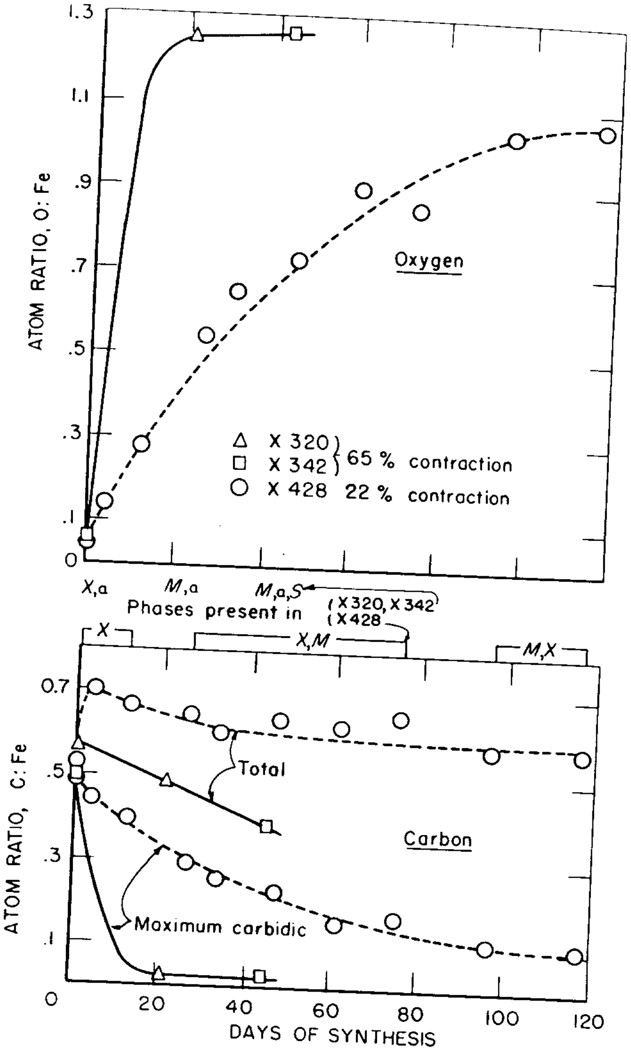


FIGURE 10.—Composition Changes of Carbided Catalyst, D3001, in Synthesis With $1H_2+1CO$ Gas at 21.4 Atmospheres. Symbols representing phases are defined in tables 1 and 3.

version of residual metallic iron in the fresh catalyst to Hägg carbide. In experiments at 7.8 atmospheres diffraction lines of metallic iron in the fresh catalyst disappeared during this period of synthesis. Usually the initial increase in carbon exceeded by only a small amount the value corresponding to complete conversion of promoters to carbonates. After the initial increase, the carbon content either remained constant or decreased slowly. The estimated values for maximum carbidic carbon decreased more rapidly than total carbon due to the formation of magnetite. The oxygen content of the catalyst increased continuously during the synthesis, and catalyst deterioration, in the moderate temperature range, 200° to 260° C., was probably due to structural changes accompanying oxidation rather than to carbon deposition.

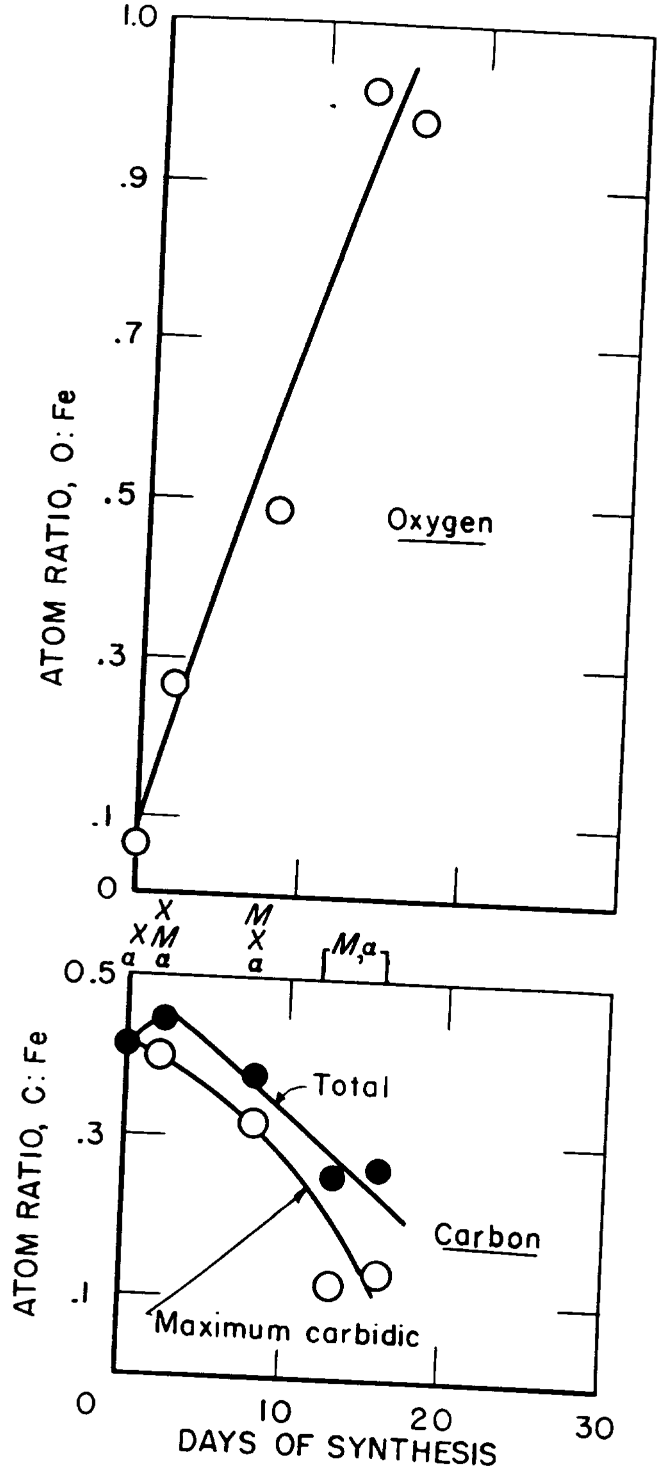


FIGURE 11.—Composition Changes of Carbided Catalyst, D3008, in Synthesis With $1H_2+1CO$ Gas at 21.4 Atmospheres (Test X416). Symbols representing phases are defined in tables 1 and 3.

The observed composition changes must result from several competitive reactions, some limited by kinetic and others, by thermodynamic factors. Under most synthesis conditions the ratio, CO_2:CO, is sufficiently low to reduce magnetite, and to produce carbide or elemental carbon. Furthermore, carbides or elemental carbon can be produced by reactions of carbon monoxide and hydrogen. On the other hand the ratio of H_2O: H_2 is usually sufficiently large to oxidize iron and carbides; the carbides may be oxidized according to the equations

$$3Fe_2C+8H_2O \rightarrow 2Fe_3O_4+3C+8H_2, \text{ and} \quad (1)$$
$$3Fe_2C+8H_2O \rightarrow 2Fe_3O_4+3CH_4+2H_2. \quad (2)$$

Also, the ratio $CH_4:(H_2)^2$ is low enough to permit the hydrogenation of carbides or elemental carbon to methane. Removing elemental carbon as carbon monoxide by water or carbon dioxide is not thermodynamically possible. Thus the component responsible for oxidizing and possibly removing carbon appears to be water vapor reacting according to equations (1) and (2). Thermodynamic tendency for equation (2) as well as for hydrogenation of elemental and carbidic carbon increases with operating pressure, which may account for the progressive decrease of total carbon and the presence of metallic iron in samples from tests at the higher operating pressures. Typical data for partial pressures of H_2, CO, H_2O, CO_2, and CH_4 and significant ratios of these concentrations in the exit gas are given in table 4. These data represent the maximum values for products and minimum values for reactants, as observed in the main gas stream in synthesis tests. In all experiments the ratio $H_2O:H_2$ is large enough for oxidizing iron or carbide. It appears that oxidation by water is possible at all conversions more than about 5 percent. The ratio CO_2:CO exceeds that required for oxidation only in the test at conversions of about 80 percent. In all cases the ratio $CH_4:(H_2)^2$ is sufficiently low to permit the hydrogenation of carbides and elemental carbon.

TABLE 4.—*Partial pressures of significant products in exit gas from typical experiments*

Test X—	Operating pressure, atmospheres	Apparent contraction, percent	Partial pressures, atmospheres [1]					Ratios of partial pressures [2]		
			H_2	CO	H_2O	CO_2	CH_4	$\frac{H_2O}{H_2}$	$\frac{CO_2}{CO}$	$\frac{CH_4}{(H_2)^2}$
294	7.8	65	2.94	1.66	0.93	1.97	0.29	0.316	1.19	0.033
399	7.8	80	2.39	.33	1.90	2.61	.56	.795	7.91	.098
342	21.4	65	7.98	5.24	2.10	5.42	.65	.263	1.03	.010
428	21.4	22	9.44	9.96	1.08	.75	.17	.115	.07	.0019

[1] Other gaseous components are present in minor amounts and are not included. Water is determined by difference, and these values are slightly high.

[2] Thermodynamic data: Oxidation of iron to magnetite at 250° C. requires $H_2O:H_2$ and CO_2:CO in excess of 0.025 and 2.2, respectively (*80*). Hydrogenation of graphite to methane requires $CH_4:(H_2)^2$ less than 1,200. The free energy of formation of Hägg carbide at 250° C. is +3.7 kcal./mole (*21*). Thus, thermodynamics would favor oxidation or hydrogenation of the carbide rather than the corresponding reactions with iron or graphite, respectively.

Thus the increased rate of oxidizing and removing carbon at the higher operating pressures and larger conversions must be related to the influence of the higher partial pressures of products, principally water vapor.

In the Fischer-Tropsch synthesis using porous catalysts the partial pressures of oxidizing components of the gas stream may represent only minimum values of these molecules in contact with the catalyst surface, for the gas in the pores very likely contains considerably greater concentrations of product molecules. Each pore may act like a long reactor, and possibly the gas entering a pore continues to react until hydrocarbons and iron oxide are formed. Within the pores these processes and the synthesis are impeded by the large amount of wax (liquid at synthesis temperature) adsorbed on the catalyst.

In the initial period, catalysts converted to Hägg carbide are more active than reduced catalysts at all synthesis pressures. Thus, the presence of Hägg carbide, as well as other interstitial phases of iron, nitrides, and carbonitrides (*16*), increases the catalytic activity. In the case of nitrides and carbonitrides the activity data are difficult to interpret, because the enhanced activity may result from either an increase in the intrinsic activity or an increase in the accessible surface owing to the lower molecular weight product from the nitride or carbonitride synthesis. Since the present carbided catalysts have essentially the same selectivity as reduced preparations, the relative accessibility of the catalyst surface should be approximately equal for the reduced and the carbided catalyst. Surface areas of reduced, carbided, or nitrided catalysts before synthesis are approximately equal (*44*).

At pressures of 7.8 to 14.5 atmospheres, the activity of carbides remained constant or increased with time, but at 21.4 atmospheres the activity of carbides decreased rapidly. Although the rapid decrease in activity at 21.4 atmospheres is probably related to the rapid oxidation and simultaneous destruction of the carbide and modification of the physical structure of the catalyst, the explanation is not simple. For example, the carbided catalyst used at 14.5 atmospheres had a constant activity, even when more than 80 percent of the iron had been converted to magnetite. Similarly, although the reduced catalysts oxidize less rapidly at 7.8 atmospheres than at 21.4 atmospheres, the activities at the lower pressure usually decreased with time (X152, fig. 1) but remained essentially constant at the higher pressure (X515, fig. 2). Thus, other factors, such as changes in physical structure accompanying oxidation, are probably important in determining catalytic activity. The activities of nitrided-iron catalysts which oxidize at a slower rate than corresponding reduced catalysts, remained essentially constant for long periods of synthesis (*16*).

SYNTHESIS WITH FUSED-IRON OXIDE CATALYSTS CONVERTED TO CEMENTITE

Synthesis tests were made on 6- to 8-mesh samples of fused-iron oxide catalyst D3001 converted to cementite at 7.8 and 21.4 atmospheres of $1H_2+1CO$ gas to determine the influence of method of preparation and operating pressure on activity and selectivity (*71*).

The reducing and carbiding conditions and the principal phases, determined by X-ray diffraction, in the pretreated catalysts are given in table 5. Details of preparing cementite are given in an earlier section. Three methods were used:

A. Reaction of Hägg iron carbide and iron at 475° C. to form cementite.

B. Direct preparation by carbiding the reduced catalyst with $2H_2+1CO$ gas at 310° C.

C. Direct preparation by treating the reduced catalyst with methane at 500° C.

TABLE 5.—*Pretreatment of catalysts* [1]

Test X—	Reduction in hydrogen				Carbiding				Phases from X-ray diffraction [2]
	Temperature, ° C.	Space velocity, hour −1	Time, hour	Extent of reduction, percent	Gas	Temperature, ° C.	Time, hour	Atom ratio, C:Fe	
152	450	1,000	43	90.2	None				α
173	550	1,980	24	98.0	None				α
515	500	1,180	24	97.8	None				α
249	450	2,110	60	97.7	CO	[3] 240	12	0.30	α, C
317	450	2,000	62	96.1	CO	[3] 200–276	10	.36	C
343	500	2,200	24	100	CO	[3] 245–252	12	.31	C, α
329	500	2,390	40	98.3	$2H_2+1CO$	310	6	.42	C, α
294	500	2,500	24	96.6	CO	150–350	18	.58	χ, α
342	500	1,990	24	97.2	CO	150–350	18	.43	χ, α
268	550	2,850	20	96.0	CH_4	500	4	.24	α, C
276	550	2,050	20	97.2	CH_4	500	6	.40	C

[1] All steps at atmospheric pressure.

[2] Phases listed in order of decreasing intensity of X-ray diffraction pattern: α—metallic iron; C—cementite; χ—Hägg carbide.

[3] After carbiding, the catalyst was heated in helium at 475° C. for two hours.

Activities of reduced and carbided iron at 7.8 and 21.4 atmospheres (absolute) are compared in figures 12 and 13, respectively. Activity, A_{Fe}, was corrected to standard synthesis conditions (240° C. and 65-percent conversion) by an empirical rate equation and is expressed as cubic centimeters of synthesis gas consumed per gram of iron per hour. Although surface areas were determined on some of these samples, and could be estimated for the remainder, the activity per gram is usually independent of surface area; hence, activity was not expressed per unit of surface area. For catalyst D3001 the surface areas per gram of unreduced catalyst are principally a function of reduction temperature (*43*, *44*) as follows: 450° C., 9.3 m. ^{2}; 500° C., 6.4 m. ^{2}; and 550° C., 3.5 m. ^{2}.

Figure 14 compares product distributions of reduced and reduced and carbided catalysts at 7.8 and 21.4 atmospheres, corresponding to data in figures 12 and 13. The histograms present distribution of total hydrocarbons, including oxygenated molecules dissolved in condensed hydrocarbons, water-soluble oxygenated molecules being excluded. Symbols in histograms were defined in the preceding section. The relative usage of H_2 and CO is given in table 6.

Reduction procedures for the catalysts described were not always the same (table 5). These differences, however, do not seriously complicate the interpretation, since (*a*) synthesis behavior is relatively independent of reduction conditions in the temperature range, 450° to 550° C., and (*b*) sufficient data are presented to permit cross comparison.

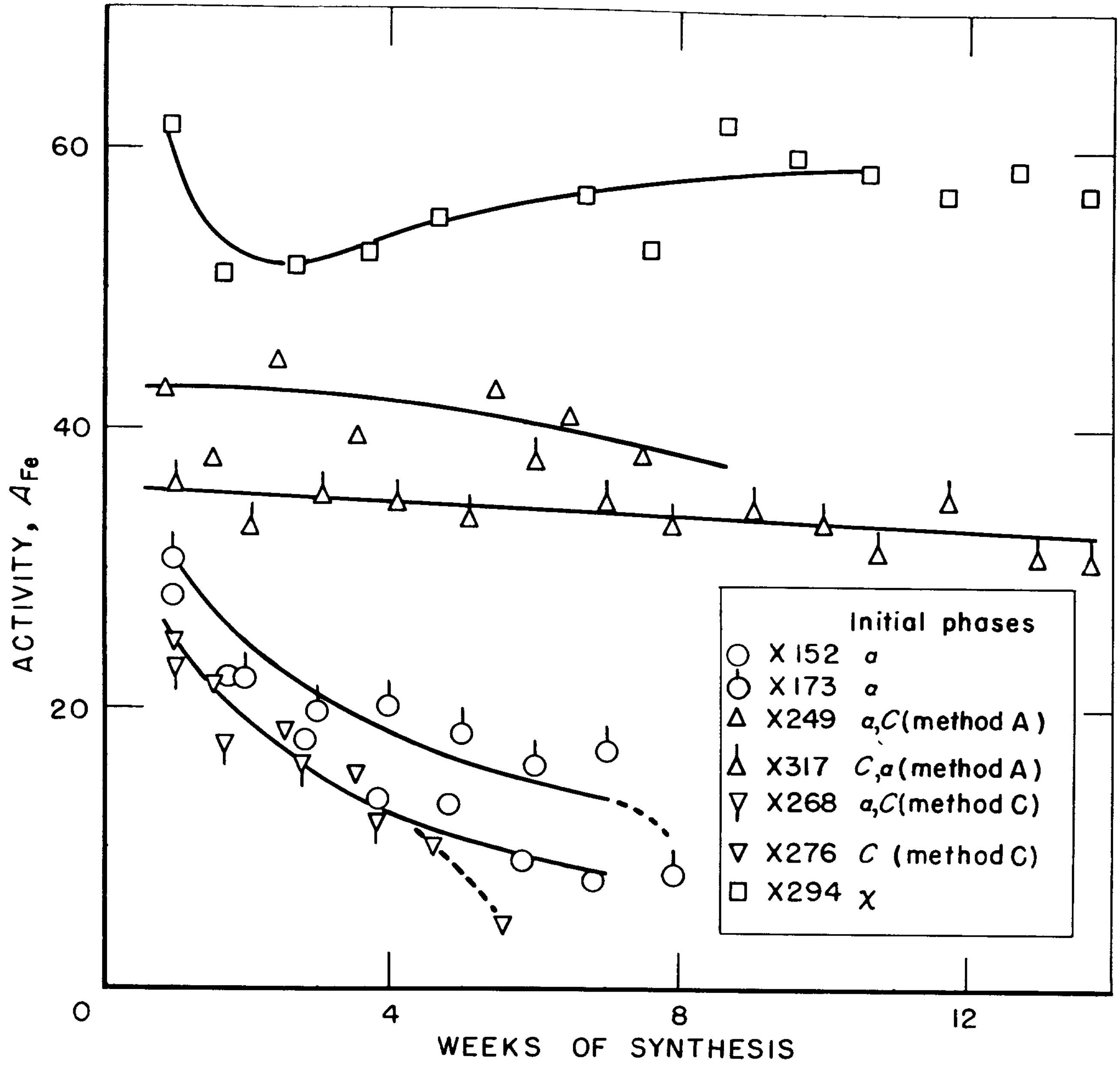


FIGURE 12.—Activities of Reduced and Carbided Catalysts at 7.8 Atmospheres as a Function of Time. Symbols representing phases are defined in table 5.

At 7.8 atmospheres, the catalysts converted to cementite by thermal treatment of Hägg carbide and iron (X249 and X317) had high constant activities for as long as 14 weeks (fig. 12). The average activity of these preparations was about twice that of the corresponding reduced sample (X152), and the activity of the reduced sample decreased sharply with time. The behavior of cementite was similar to that observed for Hägg carbide (X294), except that Hägg carbide was more active. The activity of cementite prepared from methane (X268 and X267) decreased rapidly with time, and the average activity was somewhat less than that observed for the corresponding reduced catalyst (X173).

In the synthesis at 21.4 atmospheres, however, the activity of the carbides decreased steadily with time, whereas the activity of the reduced catalyst remained essentially constant (fig. 13). Hägg carbide (X342) was most active at this pressure. The activity of cementite prepared by method *B* (X329) was intermediate between the activities of Hägg carbide (X342) and reduced catalyst (X515). Cementite prepared from Hägg carbide and metallic iron (X343) had a lower activity than reduced catalyst (X515).

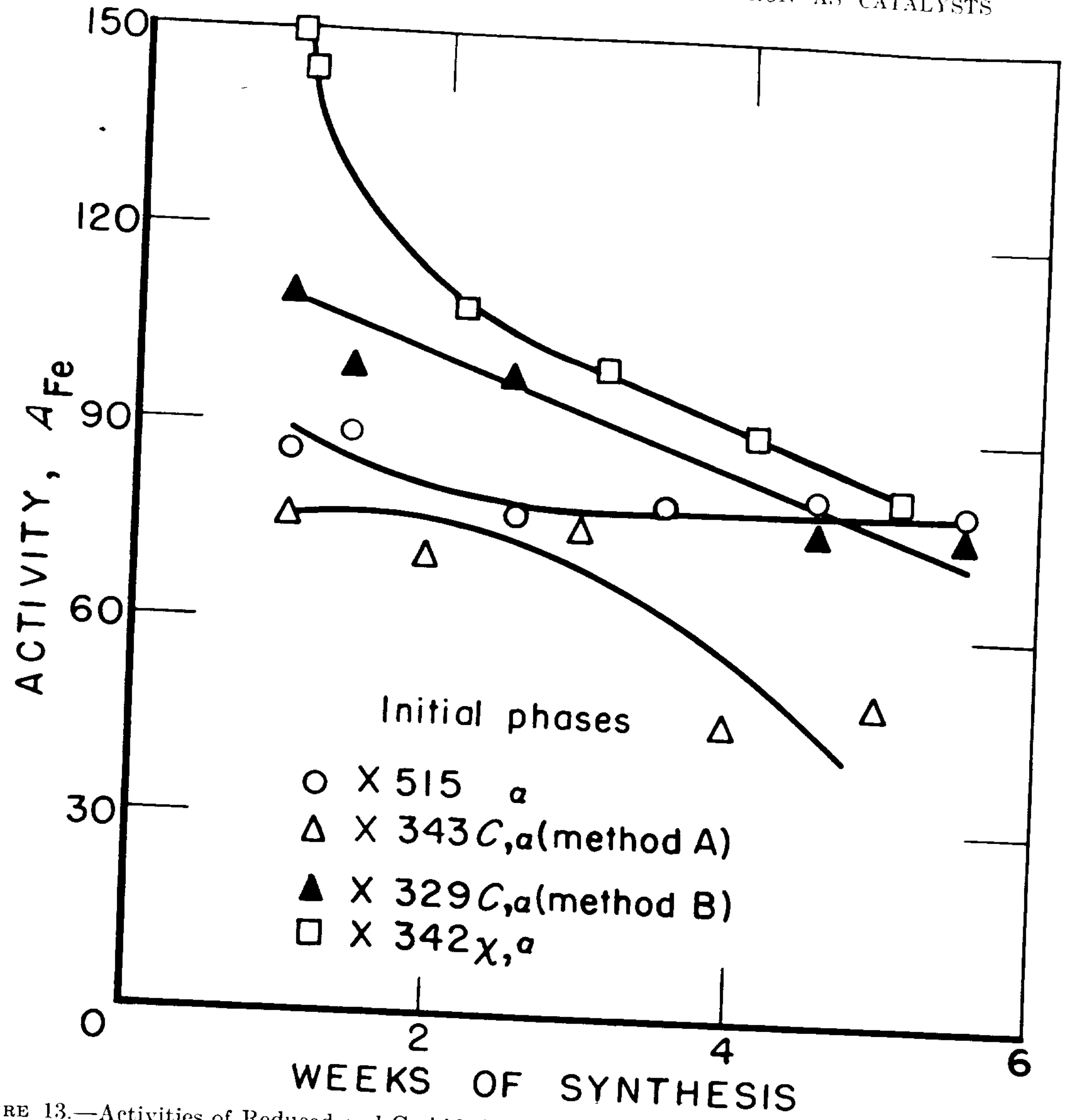


FIGURE 13.—Activities of Reduced and Carbided catalysts at 21.4 Atmospheres as a Function of Time. Symbols representing phases are defined in table 5.

TABLE 6.—*Usage ratios* (H_2 : CO) *for tests of fused catalysts with* $1H_2 : 1CO$[1]

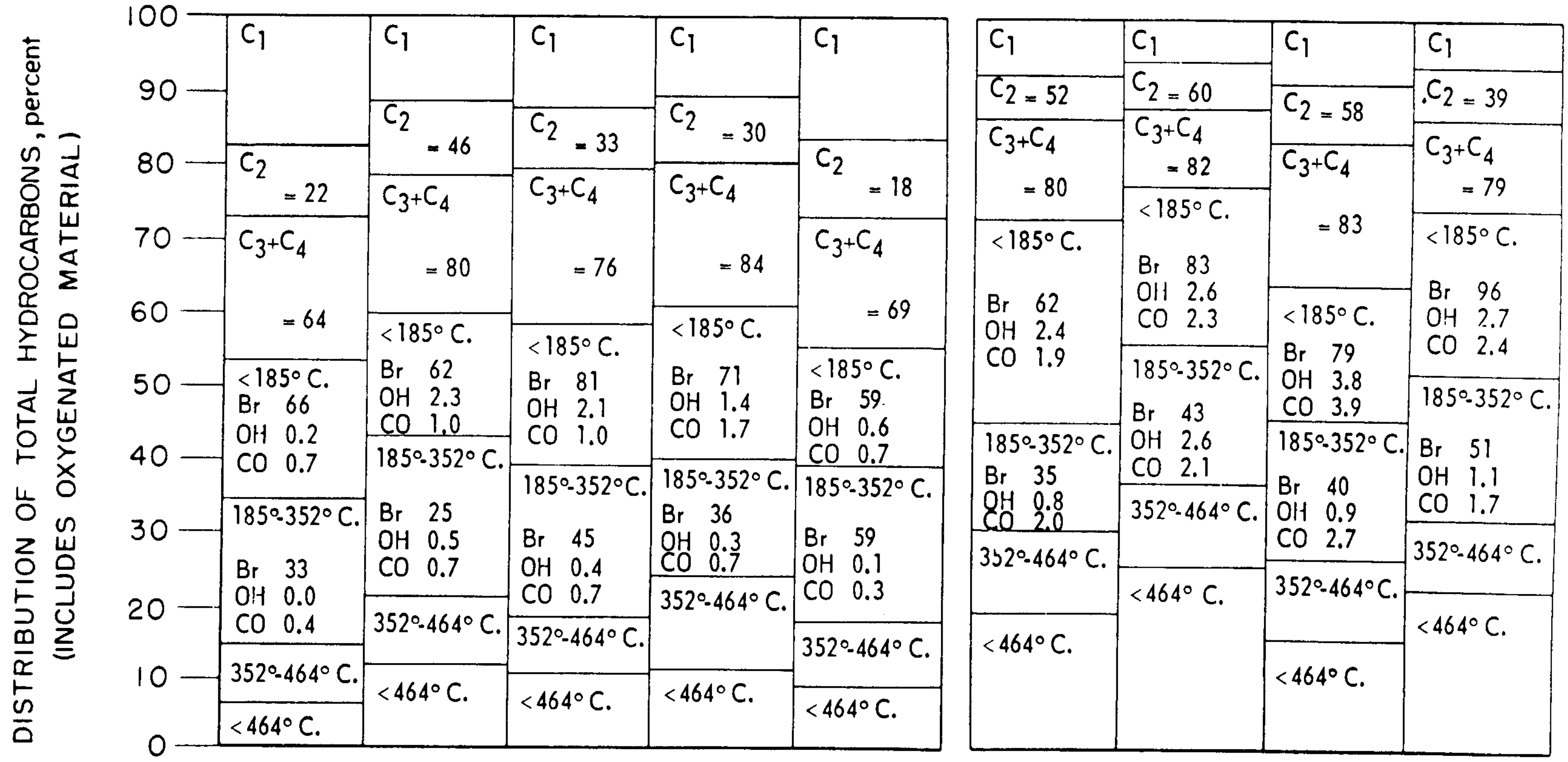
Test X—	Carbiding gas	Usage ratio,[2] H_2 : CO	Initial[3] phases
	7.8 atmospheres (absolute)		
152	None	0.72	α
173	None	.70	α
249	CO	.81	α, C
268	CH_4	.77	α, C
276	CH_4	.79	C
294	CO	.75	χ, α
317	CO	.83	C
	21.4 atmospheres (absolute)		
329	$2H_2+1CO$	0.85	C, α
342	CO	.79	χ, α
343	CO	.76	C
515	None	.76	α

[1] Average contraction 62 to 65 percent.
[2] Averages of weeks 2 to 6.
[3] Phases listed in order of decreasing intensity of X-ray diffraction pattern: α=metallic iron; C=cementite; χ=Hägg carbide.

At 7.8 atmospheres, the selectivity of catalysts converted to cementite (fig. 14) appears to be essentially independent of operating temperature; however, the catalysts operating at the higher temperatures (X268 and X276) were those carbided with methane, the other two (X249 and X317) having been prepared by thermal reaction of Hägg carbide with iron. The carbided catalysts produced a material of higher average molecular weight than that from reduced catalyst (X152 and X173). Usually for a given catalyst with the same pretreatment, the average molecular weight decreases with increasing temperature and the only positive statement that can be made from this group of data is that the catalysts carbided with methane yield a higher molecular weight product than reduced catalysts.

At 21.4 atmospheres, the average molecular weight of the product was greater than in corre-

	7.8 atm.					21.4 atm.			
Test number	X152	X317	X294	X276	X173	X342	X343	X329	X515
Carbiding gas	None	CO	CO	CH_4	None	CO	CO	$2H_2+1CO$	None
Phases present	α	C	χ,α	C	α	χ,α	C,α	C,α	α
* Temperature, °C.	270	235	229	270	259	243	257	247	248
* Space velocity, $hr.^{-1}$	97	83	106	100	97	334	287	322	303
* Contraction, percent	65	63	64	63	63	63	62	64	65
* Activity, A_{Fe}	14	34	53	14	20	104	55	89	80



* Average synthesis conditions.

FIGURE 14.—Selectivity of Reduced and Carbided Catalyst. Symbols representing initial phases are defined in table 5. Total hydrocarbons includes oxygenated material dissolved in liquid phase.

sponding tests at 7.8 atmospheres. However, no simple explanation can be offered for these data based on initial phases or operating temperature.

At 7.8 atmospheres, the usage ratios, H_2:CO, with carbided catalysts (table 6) were significantly higher than with reduced catalysts, but in most tests at 21.4 atmospheres the usage ratios were about the same. In these experiments, the usage ratio is principally determined by the relative production of water and carbon dioxide and probably reflects the relative rates of a primary synthesis reaction producing water and a subsequent water-gas shift reaction.

TABLE 7.—*Composition and phase changes during synthesis*

Test X—	Time, days	Atom or mole ratios				Phase from X-ray analyses [2]
		O:Fe	CO_2:Fe	Total C:Fe	Computed maximum carbidic C:Fe [1]	
		7.8 atmospheres (absolute)				
249	0	(3)	(3)	(3)	(3)	α, *C*
	55	0.395	(3)	0.354	0.234	*C*, *M*
268	0	.033	(3)	.237	.237(?)	α, *C*
	26	.415 [4] (.351)	0.031	.318 [4] (.287)	.229 (.246)	*C*, α, *M*
276	0	.022	(3)	.401	.327	*C*
	40	.632 [4] (.561)	.036	.559 [4] (.523)	.178 (.193)	*C*, *M*
294	0	.024	(3)	.573	.491	χ, α
	96	.357	(3)	.710	.364	χ, *M*
317	0	.108	(3)	.363	.306	*C*
	105	.562 [4] (.528)	.018	.428 [4] (.410)	.193 (.202)	*C*, α, *M*
173	0	.027	(3)	.000	0	
	54	.716	(3)	.292	.061	*M*, α, χ
		21.4 atmospheres (absolute)				
329	0	0.049	(3)	0.420	0.321	*C*, α, *M*
	40	1.298	(3)	.351	.011	*M*, α
342	0	0.061	(3)	.573	.477	χ, α
	37	1.47 [4] (1.255)	0.110	.487 [4] (.377)	0 (.030)	*M*, α, *S*
343	0	0.051	(3)	.308	.308	*C*, α
	35	1.300 [4] (1.047)	.126	.299 [4] (1.73)	.008 (.071)	*M*, α, *C*
515	0	0.017	(3)	0	0	α
	39	1.069	(3)	.258	.100(?)	*M*, α, χ

[1] Maximum carbide content assuming that all of the iron is present as Fe_3O_4.

[2] Phases present in order of decreasing intensity of diffraction pattern α=metallic iron; *M*=magnetite; *C*=cementite; χ=Hägg carbide; *S*=magnesite ($MgCO_3$) or siderite ($FeCO_3$).

[3] Not determined.

[4] Calculated, assuming carbon dioxide is present as $MgCO_3$.

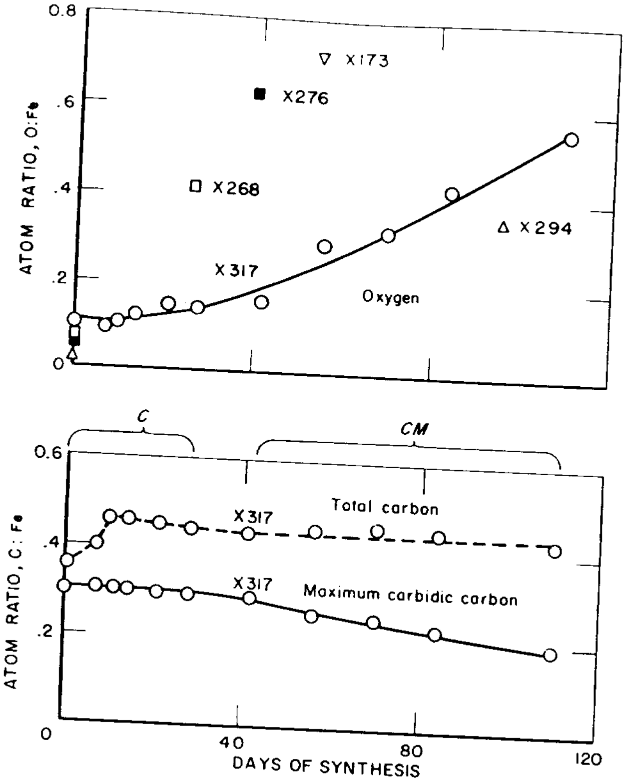


FIGURE 15.—Composition Changes of Catalyst D3001, (Converted to Cementite by Thermal Reaction of Hägg Carbide With Iron) in Synthesis at 7.8 Atmospheres, Test X317. For comparison the oxygen content is shown for catalysts containing initially metallic iron (X173), Hägg carbide (X294), and cementite from methane (X268 and X276).

Analytical data for catalyst samples before and after synthesis are presented in table 7, and figure 15 shows composition changes during the course of a 7.8-atmosphere test of a catalyst converted to cementite by method *A*. For comparison, typical data for oxygen contents of reduced catalysts and samples converted to cementite by two different methods are included in this figure. Samples that had been used in synthesis were extracted with boiling toluene before analyses. The phases present were determined by X-ray diffraction. Chemical analyses were made for total content of iron and carbon, and oxygen was estimated by difference. Analyses for carbonates were made on a few representative samples by measuring the amounts of carbon dioxide evolved on acidifying the catalyst. The carbon dioxide evolved was 1 to 2 weight-percent, at 7.8 atmospheres and 6.4 weight-percent at 21.4 atmospheres.

In used carbided catalysts, the concentration of metallic iron is usually very small, and an estimate could be made of the maximum amount of carbidic carbon by assuming that iron was present only as carbide or magnetite. Previous work suggested that carbon dioxide was present principally as magnesium carbonate (*16*, *75*), and the data in parentheses in table 7 were adjusted on this basis.

Pertinent results of table 7 and figure 15 may be summarized as:

1. Atom ratios O:Fe increased during synthesis, approaching the value for magnetite in tests at 21.4 atmospheres. Catalysts converted to cementite by treatment with carbon monoxide or $2H_2+1CO$ oxidized at about the same rate as those made from Hägg carbide and iron; however, cementite prepared from methane

(X268 and X276) oxidized more rapidly. Its higher rate of oxidation may have resulted from operation at higher temperatures, required to maintain constant conversions. These preparations oxidized at about the same rate as the corresponding reduced catalyst.

2. At 7.8 atmospheres (X317) atom ratios, total C:Fe, increased in the first 10 days of synthesis and then remained about constant. At 21.4 atmospheres, atom ratios, total C:Fe, for samples converted to cementite, were lower after 35 to 40 days of testing than before synthesis. These results are similar to those obtained with Hägg carbide, mentioned previously.
3. Although values for maximum carbidic carbon are only approximate, in most cases they show the same trends as phases found in X-ray and thermomagnetic analyses.
4. After synthesis with catalysts converted to cementite, this phase was the only carbide identified by X-ray diffraction.
5. Formation of carbonates during synthesis increased sharply with pressure, and the results were similar to those with catalysts converted to Hägg carbide (see previous section), or iron nitride (*75*).
6. At the temperature studied, deposition of elemental carbon from synthesis gas does not appear to be an important factor in disintegration of catalyst during synthesis. Disintegration parallels oxidation and appears to be related to structural changes involved in forming magnetite.
7. Explanations advanced for composition changes of Hägg carbide during synthesis are adequate for cementite: (*a*) Water is the principal oxidant, and (*b*) the decrease in carbon content of catalyst in synthesis at 21.4 atmospheres may result from direct hydrogenation of carbide or reaction of water with carbide to produce methane and magnetite.

The data indicate that fused-iron catalysts, converted to cementite, are active in the Fischer-Tropsch synthesis and that their behavior is qualitatively similar to that of preparations containing Hägg iron carbide or metallic iron. Cementite prepared with carbon monoxide was more active than cementite from methane; the reason for the difference is not known. In synthesis at 7.8 atmospheres, catalysts converted to Hägg carbide or cementite by treatment with carbon monoxide were more active and oxidized less rapidly than reduced catalysts. At 21.4 atmospheres, carbide catalysts had little or no advantage over reduced catalysts with respect to either activity or rate of oxidation. The selectivity of fused catalysts containing metallic iron, Hägg carbide, or cementite as the initial phase was about the same, except that the carbides often had a slightly higher usage ratio, H_2:CO, than reduced catalysts.

These and older data demonstrate that cementite, Hägg iron carbide, iron nitride, and iron carbonitride are at least as active in the Fischer-Tropsch synthesis as the metal. This behavior of interstitial compounds of iron is in sharp contrast to that of carbides of cobalt (*9*, *86*) and nickel (*51*, *65*), which have very low activities, compared with the metals.

THERMOMAGNETIC ANALYSES OF FUSED-IRON OXIDE CATALYSTS

Several samples of carbided catalyst D3001 reported in the previous sections and samples of reduced D3001 were analyzed by thermomagnetic methods (*49*), based on the difference of specific magnetization of the sample above and below the Curie temperature of the carbide. Metallic iron and magnetite cannot be determined in this manner, but can be estimated by using magnetic and X-ray-diffraction data. Specifically the magnetic analysis measures total magnetization of metallic iron plus magnetite above the Curie temperature of the carbide, and the X-ray-diffraction pattern provides an estimate of relative amounts of these two phases. The X-ray estimate is the least accurate part in the analysis, and the values for metallic iron and magnetite must be regarded as approximate.

In most of the magnetic analyses all of the iron compounds could not be accounted for, presumably because of the form and crystallite size of the magnetic phases and the relatively low magnetic field used. In all of the present calculations these undetected compounds are assumed to exist in the same proportions as in the magnetically measurable portion of the specimen.

Results from the magnetic analysis may be compared with estimates from elemental analyses. After extraction of wax the catalysts were analyzed by standard methods for iron and carbon, and oxygen was estimated by difference. From these data and the ratio of promoters to iron, an estimate was made of the amount of iron as metallic iron, magnetite, and carbide. All of the oxygen was assumed to be present as Fe_3O_4, and the remaining iron as metallic iron or carbide. The carbon was assumed to be present as Fe_2C except for catalysts converted to cementite for which Fe_3C was used. Carbon in excess of the amount required for the carbide was assumed to be elemental carbon. Any iron remaining was assumed to be metallic iron. Uncertainties in these estimates include determination of oxygen by difference, assumptions regarding phases present and their composition, and the postulate that all carbon is carbidic up to the amount required to account for all of the iron not present as magnetite.

Tables 8 and 9 compare composition changes by chemical and magnetic analyses during synthesis for catalyst D3001 pretreated to Hägg carbide (X294 and X320) and cementite (X317). These tests were described in detail previously. In general the results from the

TABLE 8.—*Composition changes during synthesis with catalyst, D3001, converted to Hägg carbide*

Days of synthesis	Temperature, ° C.	Iron, percent as—						Phases from X-ray diffraction [2]
		Metallic Fe		Fe_2C		Fe_3O_4		
		Chem.[1]	Mag.[1]	Chem.[1]	Mag.[1]	Chem.[1]	Mag.[1]	
	A.—Test X294, 7.8 atmospheres and hourly space velocity of 100							
0	--------	0	7.8	97.2	92.2	2.8	0	χ, α
1	205	0	5.9	91.1	94.1	8.9	0	χ, α
20	229	0	6.6	92.4	93.3	7.6	0	χ
27	228	0	5.0	92.0	95.0	8.0	0	χ
41	229	0	5.8	85.5	94.2	14.5	0	χ
55	229	0	0	81.0	89.8	19.0	10.2	χ, *M*
62	229	0	0	80.2	84.5	19.8	15.5	χ, *M*
69	229	0	0	80.6	83.9	19.4	16.1	χ, *M*
76	227	0	0	76.2	82.8	23.8	17.2	χ, *M*
90	230	0	0	73.8	79.3	26.2	20.7	χ, *M*
97	230	0	0	73.2	79.5	26.8	20.5	χ, *M*
	B.—Test X320, 21.4 atmospheres and hourly space velocity of 300							
0	--------	0	0	97.0	100	3.0	0	χ, *M*
21	256	0	20	6.0	0	94.0	80	*M*, α

[1] Chem.=estimate from chemical analyses; Mag.=estimate from magnetic analyses.
[2] Phases from X-ray diffraction in order of decreasing intensity of patterns: χ=Hägg carbide; α=metallic Fe; *M*=magnetite.

TABLE 9.—*Composition changes during synthesis, with catalyst, D3001, converted to cementite, test X317*

Days of synthesis	Temperature, ° C.	Iron, percent as—						Phases from X-ray diffraction [2]
		Metallic Fe		Fe_3C		Fe_3O_4		
		Chem.[1]	Mag.[1]	Chem.[1]	Mag.[1]	Chem.[1]	Mag.[1]	
0	--------	0	0	91.9	93.3	8.1	6.7	*C*
1	201	0	0	92.8	87.3	7.2	12.7	*C*
6	230	0	0	92.0	89.4	8.0	10.6	*C*
10	230	0	0	90.6	88.8	9.4	11.2	*C*
17	231	0	0	88.7	91.6	11.2	8.4	*C*, *M*
18	232	0	0	88.9	89.7	11.1	10.3	*C*
38	235	0	0	87.6	88.6	12.4	11.4	*C*, *M*
101	237	0	0	57.8	73.6	42.2	26.4	*C*, *M*

[1] Chem.=estimate from chemical analyses; Mag.=estimate from magnetic analysis.

[2] Phases in order of decreasing intensity of X-ray diffraction patterns; *C*=cementite; *M*=magnetite.

two analytical methods are in satisfactory agreement, especially in view of the assumptions which were made in calculations from chemical analyses. That the results of two different methods are approximately the same suggests that both methods are fairly reliable. In all cases values for iron as carbide by the two methods were in best agreement.

Phase changes determined by magnetic analysis during the synthesis with reduced catalyst D3001 at 7.8 atmospheres were reported previously (*10*). A similar experiment was made at 21.4 atmospheres, and the estimates by magnetic and chemical analyses are given in table 10. Here the two analytical methods gave widely diverging results for metallic iron and magnetite. Part of this difference may be attributed to formation of $MgCO_3$ or $FeCO_3$, which was not determined for this sample. Figure 16 presents magnetic analyses for samples from synthesis tests with reduced catalysts at 7.8 and 21.4 atmospheres. At both

TABLE 10.—*Phase changes during synthesis with reduced catalyst, D3001, test X361*

($1H_2+1CO$ gas at 21.4 atmospheres, hourly space velocity=300)

Days of synthesis	Temperature °C.	Iron, percent as—						Phases from X-ray diffraction [2]
		Metallic Fe		Fe_2C		Fe_3O_4		
		Chem.[1]	Mag.[1]	Chem.[1]	Mag.[1]	Chem.[1]	Mag.[1]	
0	--------	92.8	95.0	0	0	7.2	5.0	*α, M*
1	230	44.8	74.3	40.2	19.7	15.0	6.0	*α, M*
8	255	0	41.7	30.1	28.1	69.9	30.2	*M, α*
21	254	0	21.6	20.3	16.0	84.4	63.9	*M, α*
36	255	0	21.3	16.7	17.3	83.3	61.4	*M, α*
43	252	0	22.1	15.6	14.0	84.4	63.9	*M, α*

[1] Chem.=estimate from chemical analyses; Mag.=estimate from magnetic analyses.

[2] Phases in order of decreasing intensity of X-ray diffraction patterns: α=metallic iron; $M=Fe_3O_4$.

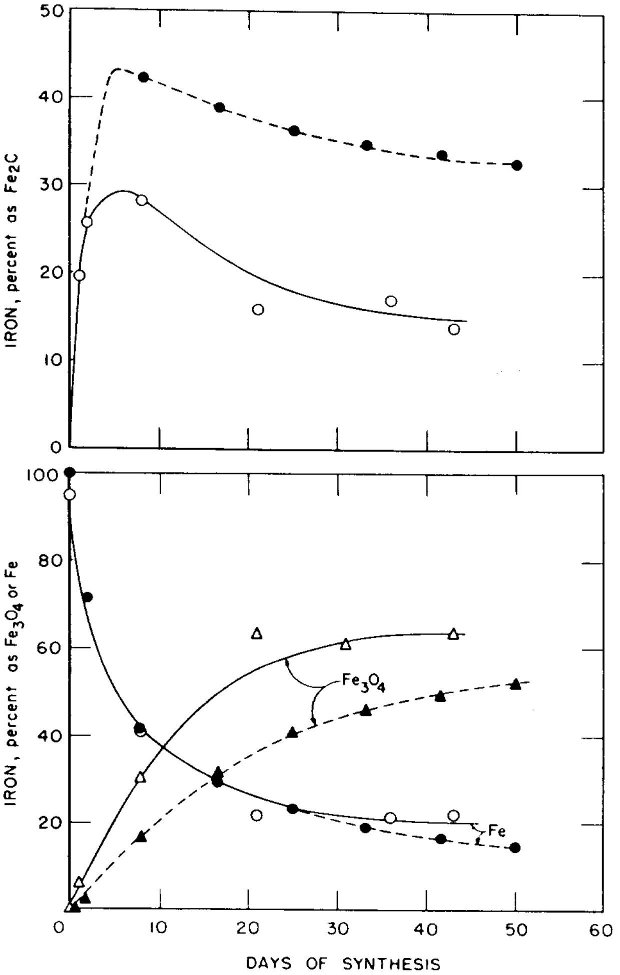


FIGURE 16.—Phase Changes During Synthesis With Reduced Catalyst D3001 in Tests at 7.8 and 21.4 Atmospheres with $1H_2+1CO$ Gas. Solid symbols denote test at 7.8 atmospheres, and open points, 21.4 atmospheres.

pressures the iron as carbide increased rapidly at the start of the test, then decreased slowly. Metallic iron decreased rapidly initially, and then the rate decreased with time. Magnetite increased rapidly initially, and its rate decreased with time. The curves for metallic iron were about the same at both pressures, but more magnetite and less Hägg carbide were present at any given time at 21.4 atmospheres than at 7.8.

SYNTHESIS TESTS OF CARBURIZED PRECIPITATED-IRON CATALYSTS

The effect of a variety of pretreatments on 6- to 10-mesh precipitated-ferric oxide catalyst P3003.24 ($Fe:Cu:K_2CO_3=100:10:0.5$) was studied. Some of these tests, including nitriding experiments, were reported previously (*15, 76*). Pretreatment conditions are described in table 11, and synthesis data and composition of used catalyst, in table 12. Selectivity data are given in figure 17. No correlation can be found between the carbide

TABLE 11.—*Pretreatment of precipitated-iron catalyst, P3003.24*

(All steps at atmospheric pressure)

Test X—	Pretreatment				Phases from X-ray diffraction [1]
	Gas	Space velocity, hour $^{-1}$	Temperature, °C.	Duration, hours	
149	$1H_2+1CO$	98	230	23	(2)
101	$1H_2+1CO$	100	230	24	(2)
304	$2H_2+1CO$	2,500	310	6	(2)
825	$2H_2+1CO$	2,480	310	6	(2)
341	CO	100	[3] 200-250	16	*M*
245	H_2	1,480	313	17	α, Cu
324	H_2 CO	1,940 98	296 [3] 185-300	25 13	χ
324C [4]	H_2	220 190	298 391	24 24	α, Cu

[1] Phases in decreasing order of intensity of diffraction pattern: $M=Fe_3O_4$; α=metallic iron; Cu=copper; χ=Hägg carbide.

[2] Not determined, catalyst pretreated in synthesis reactor.

[3] Temperature increased as required to maintain CO_2 concentration of about 20 percent in exit gas.

[4] Catalyst from X324.

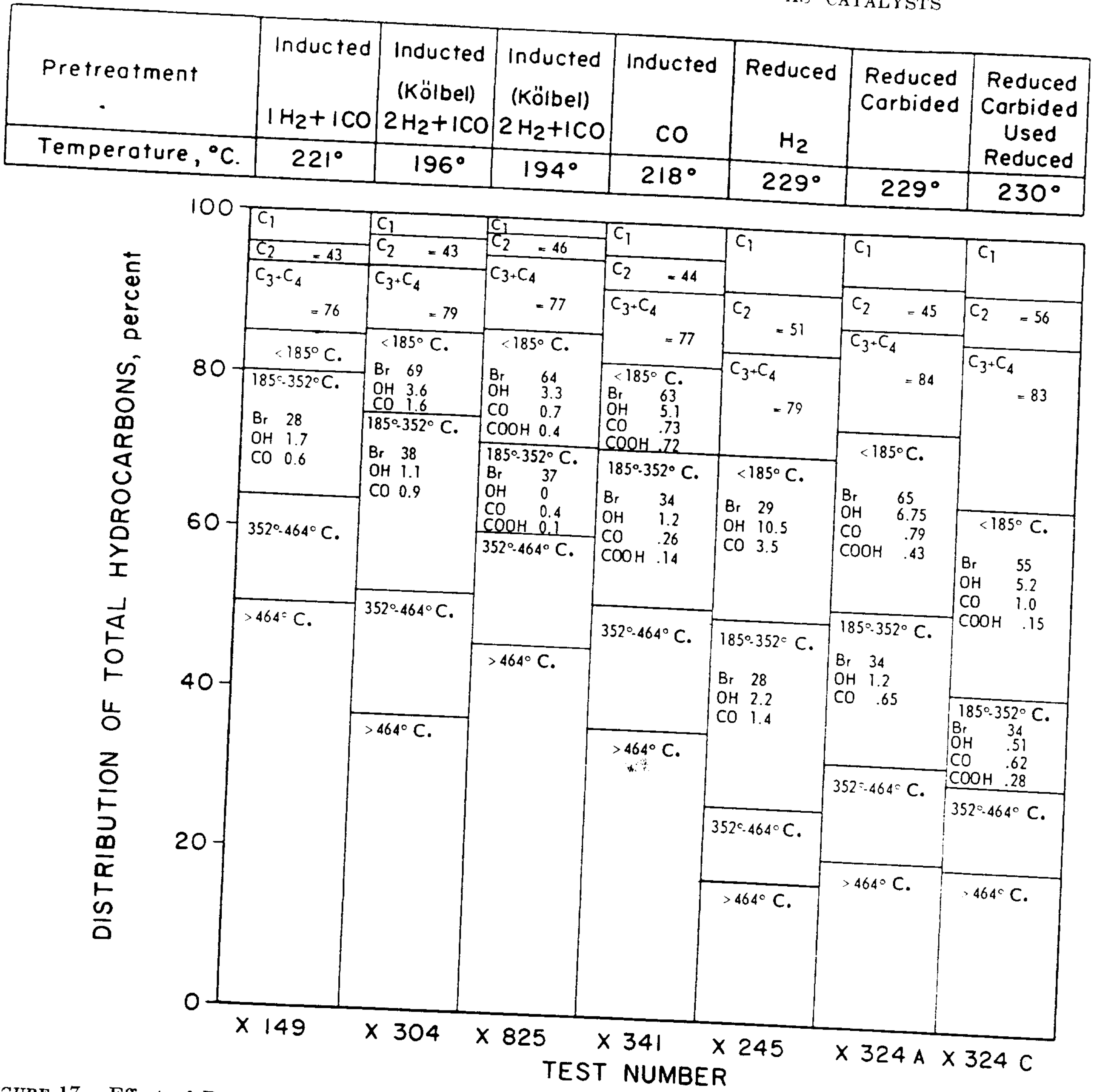


FIGURE 17.—Effect of Pretreatment of Precipitated Catalyst, P3003.24, on Composition of Products. Total hydrocarbons includes oxygenated material dissolved in liquid phase.

TABLE 12.—*Synthesis with pretreated, precipitated-iron catalyst, P3003.24*

($1H_2+1CO$ gas at hourly space velocities from 100 to 139 and at 7.8 atmospheres. Apparent CO_2 free contraction maintained at 62 to 65 percent)

Test X—	Synthesis temperature, ° C.		Average activity, A_{Fe}[1]	Usage ratio, H_2:CO	Phases in used catalyst [2]	Composition of used catalyst, iron as—			Free carbon, percent based on Fe [3]
	2d week	6th week				Metal	Fe_2C	Fe_3O_4	
149	229	219	136	0.57	M, ϵ–C, Cu	---	---	---	---
101	226	230	148	.59	M, ϵ–C	0	31	69	4.3
304	203	195	479	.76	χ, M	0	66	34	13.2
825	190	197	398	.73	χ, M	0	69	31	19.6
341	224	214	217	.62	M, Cu	0	10	90	6.2
245	228	229	145	.66	ϵ–C, M, Cu, χ	4	82.5	13.5	0
324A	222	233	120	.72	χ, S	---	81.5	18.5	5.0
324C	233	---	87	.66	χ, M	0	84	16	3.9

[1] Activity expressed as cubic centimeters (S.T.P.) of H_2+CO consumed per gram Fe at 240° C.

[2] Phases in decreasing order of intensity of X-ray diffraction pattern: M=magnetite; ϵ–C=hexagonal Fe_2C; Cu=metallic copper; χ=Hägg Fe_2C; S=siderite ($FeCO_3$).

[3] Grams of elemental carbon per 100 grams Fe.

content of the used catalyst and activity or selectivity. Catalysts containing the largest quantities of elemental carbon had the highest activity, and those containing the larger amounts of oxide yielded products of the higher molecular weight. The induction procedure described by Ackermann (*1*), used in X304 and X825, produced the most active conventional iron catalysts that we have tested to date—producing high yields of hydrocarbons at temperatures less than 200° C. Apparently pretreatment of the oxide under conditions that deposit substantial quantities of elemental carbon in the catalyst is required for preparing precipitated catalysts of high activity. This carburization step would probably adversely affect the mechanical properties of the catalyst, but no difficulties were observed in the catalyst tests.

Catalysts that were reduced in hydrogen as a part of their pretreatment (X245, X324A, and X324C) yielded products containing lower amounts of wax and higher amounts of gaseous hydrocarbons than the catalysts treated directly with carbon monoxide or synthesis gas. The catalysts that were pretreated only with carbon monoxide or synthesis gas contained the largest amounts of oxygen after use in the synthesis, and these catalysts yielded the products of higher molecular weight, despite the presence or absence of substantial quantities of Fe_2C carbides.

SYNTHESIS TESTS WITH NITRIDES AND CARBONITRIDES OF IRON

Study of the preparation of iron nitrides and of their properties in the synthesis have been described in previous Bureau publications (*15*, *73*) and elsewhere (*5*, *14*, *16*, *70*, *75*, *76*). In the Fischer-Tropsch synthesis nitrided-iron catalysts showed improved stability against the deterioration caused by oxidation and free carbon deposition, and they preferentially catalyze the synthesis of alcohols, other oxygenated products, and lower boiling liquid hydrocarbons. After a short period of operation the nitride acquires appreciable amounts of carbon and becomes essentially carbonitride. Therefore, as the catalyst spends most of its lifetime in the carbonitride stage, this is the most important form to consider.

The usual form of freshly nitrided iron is ϵ-iron nitride. This phase is isomorphous with ϵ-iron carbide, and a continuous series of solid solutions in the ϵ phase, ranging from pure carbide to pure nitride, is theoretically possible. But while phases corresponding to the two terminal compositions have been realized, compositions of carbonitride have been prepared only in the range of atomic ratios of carbon to nitrogen from zero to about 2 (*6*, *52*, *53*, *54*). Not only are ϵ-carbonitrides with a wide range of carbon-nitrogen ratios experimentally realizable, but the ratio of iron to total interstitial elements (nitrogen plus carbon) can also vary between 2 to 1 and 3 to 1.

There is apparently a critical carbon-nitrogen ratio that, when exceeded, causes decomposition of ϵ-carbonitride to χ-iron carbide. In this transformation the nitrogen from the ϵ-iron carbonitride (1) may go into the χ-phase which then would really be χ-iron carbonitride, (2) may go into a phase of such small crystallite diameter that the diffraction pattern is too diffuse to be detected, or (3) may be eliminated as gas. This critical ratio ranges from about 2 to 1 at 450° C. to ∞ at 180° C. This conclusion is based on the following experimental facts.

Jack (*53*) and Hall, Dieter, Hofer, and Anderson (*42*) have shown that ϵ-iron nitride is converted to carbonitride by substituting carbon atoms for nitrogen atoms when treated with carbon monoxide. At 400° C. carburization proceeds in this way until the ratio of carbon to nitrogen is about 2. Further carburization leads to formation of χ-iron carbide.

Direct carbiding of iron catalysts at 190° C. with carbon monoxide leads to the formation of ϵ-iron carbide, isomorphous with ϵ-iron nitride (*50*, *52*, *54*).

Thermal conversion of pure ϵ-iron carbide to χ-carbide proceeds at a measurable rate at 240° C. and probably at lower temperatures. The critical carbon-iron ratio is not affected by gas-phase composition, as the reactions involved can proceed entirely in the solid state.

This section describes, first, composition changes that occur when catalysts converted to ϵ-iron nitride are used in the synthesis, second, synthesis tests with catalysts nitrided only to α or γ' phase, and, third, tests of iron carbonitrides prepared in several ways.

COMPOSITION CHANGES OF ϵ-IRON NITRIDES DURING SYNTHESIS

In the first series of experiments catalysts of the fused, sintered, and precipitated types were analyzed after extended periods of synthesis (*75*). For chemical analyses, samples of the used catalysts were extracted with boiling toluene to remove adsorbed synthesis products, and the extracted material was analyzed for total iron, carbon, and nitrogen. Particular care was taken to remove the solvent and to prevent atmospheric oxidation of the catalyst. Oxygen values, determined by difference, are the most uncertain as they contain the combined errors of all of the other determinations. From weight percentages of iron, carbon, nitrogen, and oxygen, the atom ratios of carbon to iron, nitrogen to iron, and oxygen to iron were computed.

The phases present in pretreated and in used catalysts were identified by X-ray diffraction photograms (*50*, *52*, *53*, *54*), which showed that the used, nitrided catalysts usually contained ϵ-carbonitride and magnetite but no metallic iron. For quantitative estimation, the phases containing iron were assumed to be magnetite and ϵ-carbonitride,[8] the latter being arbitrarily assumed to be a mixture of Fe_2C and Fe_2N.[9] From the atom ratios of total carbon, of nitrogen, and of oxygen to iron the percentages of iron as Fe_2C, Fe_2N, and Fe_3O_4 were computed. When the sum of the percentages of iron in these phases exceeded 100, the apparent excess

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[8] The possibility that used catalysts may contain ferrous or promoter carbonates was examined by determining the carbon dioxide liberated when the sample was digested in hydrochloric acid. Less than 1 percent CO_2 by weight was found except for samples of tests X349 and X226 (table 14), for which the carbon dioxide was 4.36 and 4.92 percent, respectively. Carbon dioxide values of about 1 percent produced no significant variations of the calculated composition data. However, in the calculations of X349 and X226, the carbon dioxide was assumed to be present as $MgCO_3$, since sizable CO_2 values were obtained only for catalyst containing magnesia.

[9] These formulas correspond to the upper limit of the ϵ-carbonitride phase.

TABLE 13.—*Pretreatment of nitrided catalysts* [1]

Catalyst No.	Type	Principal components	Test X—	Reduction in hydrogen: Hourly space velocity	Reduction in hydrogen: Temperature, ° C.	Reduction in hydrogen: Duration, hours	Nitriding in ammonia: Hourly space velocity	Nitriding in ammonia: Temperature, ° C.	Nitriding in ammonia: Duration, hours
D3001	Fused	Fe_3O_4-MgO-K_2O	215	1, 000	550	20	5, 000	385	4
			218	1, 000	550	20	4, 000	380	8
			226	1, 000	550	20	1, 000	350	6
			236	1, 000	550	20	1, 000	350	6
D3008	do	Fe_3O_4-Al_2O_3-K_2O	253	1, 000	550	40	1, 000	350	6
			337	2, 000	555	41	1, 000	350	6
L3028	do	Fe_3O_4-ZrO_2-K_2O	355	2, 300	450	30	1, 000	350	6
A2106.11	Sintered	Fe_3O_4-K_2O	266	2, 000	400	24	1, 800	350	7
P3003.24	Precipitated	Fe_2O_3-CuO-K_2CO_3	273	1, 000	300	25	1, 000	300	15
								325	7

[1] Both reduction and nitriding at atmospheric pressure.

TABLE 14.—*Composition changes in nitrided catalyst, D3001, during synthesis*

Test X—	Previous treatment [1]	Total days of synthesis	Conditions of previous period of testing: Temperature, ° C.	Conditions of previous period of testing: Space velocity [2]	Conditions of previous period of testing: Contraction, percent [3]	Phases from X-ray diffraction [4]	Atom ratios to iron: Carbon: Total	Atom ratios to iron: Carbon: Elemental	Atom ratios to iron: Nitrogen	Atom ratios to iron: Oxygen	Percent iron as—: Fe_2C	Percent iron as—: Fe_2N	Percent iron as—: Fe_3O_4
	Operating pressure=7.8 atmospheres (absolute)												
215	*RN*	0	----	----	----	ε	0	0	0.46	0	0	92.0	----
	RNU	203	227	99	65	ε	.324	.090	.194	.192	46.8	38.8	14.4
	$RNUN^5U$	238	217	100	64	ε	.355	.175	.266	.146	35.9	53.2	10.9
	$RNUN^5UN^5U$	252	223	101	63	ε	.358	.186	.276	.140	34.3	55.2	10.5
236 [6]	*RN*	0	----	----	----	ε	0	0	.46	0	0	92.0	----
	RNU	50	230	104	64	ε	.257	.103	.302	.117	30.2	60.4	8.8
	Operating pressure=21.4 atmospheres (absolute)												
349	*RN*	0	----	----	----	ε	0	0	0.432	0.082	0	86.4	6.2
	RNU	37	241	309	64	ε, *M*, α	.239	.059	.138	.487	36.0	27.6	36.4
226 [7]	*RN*	0	----	----	----	ε	0	0	.452	.068	0	90.4	5.1
	RNU	64	241	347	54	ε, *M*, α	.224	.000	.140	.329	44.8	28.0	27.2

[1] *R*=reduced in hydrogen; *N*=nitrided with ammonia; *U*=used in synthesis.

[2] Space velocity defined as volumes of synthesis gas (S.T.P.) per volume of catalyst space per hour.

[3] Apparent carbon dioxide free gas contraction.

[4] α=metallic iron; ε=ε-nitride or ε-carbonitride; *M*=magnetite. Phases are listed in order of decreasing amounts.

[5] Renitrided at 350° C. and a space velocity of ammonia of 1,000 for 6 hours.

[6] Synthesis with $1H_2$ to 1.5 CO gas.

[7] Synthesis with $2H_2$ to 1 CO gas.

was attributed to the presence of elemental carbon, and an atom ratio of elemental carbon to iron was computed. The above calculation was made only for samples containing essentially ε-carbonitride and magnetite.

The pretreatments of catalysts are described in table 13, and the analyses of catalysts after synthesis are given in tables 14 and 15.

Table 14 presents analytical data for tests of catalyst D3001 at 7.8 and 21.4 atmospheres. In test X215 after 203 days of operation, the catalyst still showed only an X-ray diffraction pattern of ε-carbonitride and contained small amounts of elemental carbon and oxide. The catalytic activity remained essentially constant throughout this period. Nevertheless, the catalyst was renitrided after 203 days and again after 238 days with ammonia at 350° C. and a space velocity of 1,000 for 6 hours. After renitriding and using it in synthesis, the catalyst still produced an X-ray pattern of only ε-carbonitride. However, the fraction of nitrogen in the carbonitride phase was increased, the oxygen to iron ratio was decreased, and the elemental carbon to iron ratio was increased.

In test X349 at 21.4 atmospheres with $1H_2+1CO$ gas, the nitrogen content of the catalyst decreased more rapidly than at 7.8 atmospheres, and oxidation and elemental carbon deposition were faster. After synthesis,

TABLE 15.—*Composition changes in nitrided catalysts during synthesis*

(All tests with $1H_2$ to 1CO synthesis gas)

Test X—	Catalyst No.	Previous treatment[1]	Total days of synthesis	Conditions of previous period of testing			Contraction, percent[3]	Phases from X-ray diffraction[4]	Atom ratios to iron				Percent iron as—		
				Pressure, atmospheres	Temperature, ° C.	Space velocity[2]			Carbon		Nitrogen	Oxygen	Fe_2C	Fe_2N	Fe_3O_4
									Total	Elemental					
355	L3028	*RN*	0					ε, (?)	0	0.	0.454	0.082	0	90.8	6.1
		RNU	40	21.4	222	313	66	ε, (?)	.186	.055	.286	.219	26.4	57.2	16.4
253	D3008	*RN*	0					ε	0	0	.434	.090	0	86.8	6.7
		RNU	49	7.8	230	98	63	ε	.178	.060	.334	.131	23.6	66.8	9.6
337	D3008	*RN*	0					ε	0	0	.438	.099	0	87.6	7.4
		RNU	50	21.4	243	277	65	ε, *M*, α	.254	.066	.261	.178	37.6	52.2	13.4
		RNUR[5]	50					α, *C*, *M*	.239	(6)	.002	.138	(6)	0.4	10.4
		RNURU	70	21.4	238	297	65	*M*, α, *C*	.559	(6)	.009	.670	(6)	1.8	50.2
266	A2106.11	*RN*	0					ε, *M*	0	0	.470		0	94.0	
		RNU	60	7.8	216	102	65	ε	.160	.074	.369	.120	17.2	73.8	9.0
273	P3003.24	*RN*	0					ε, Cu, *M*	0	0	.463	.130	0	92.6	9.7
		RNU	39	7.8	229	138	64	ε, Cu	.230	.109	.318	.163	24.2	63.6	12.2
		RNUR[7]	39					α, Cu, χ	.241	(6)	0	.120	(6)	0	9.0
		RNURU	67	7.8	230	137	65	*M*, χ	.327	(6)	.002	.749	(6)	.4	56.1

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[1] *R*=reduced in hydrogen; *N*=nitrided with ammonia; *U*=used in synthesis.

[2] Space velocity defined as volumes of synthesis gas (S.T.P.) per volume of catalyst space per hour.

[3] Apparent carbon dioxide free gas contraction.

[4] α=metallic iron; ε=ε-nitride or ε-carbonitride; χ=Hägg carbide; *C*=cementite; *M*=magnetite; Cu=metallic copper. Phases are listed in order of decreasing amounts—(?) denotes presence of diffuse lines that could not be identified.

[5] Used catalyst reduced at 385° C. and a space velocity of hydrogen of 1,000 for 4 hours.

[6] Estimates of carbidic and elemental carbon could not be made on these samples.

[7] Used catalyst reduced at 300° C. and a space velocity of hydrogen of 1,000 for 9 hours.

the samples gave X-ray patterns of ε-carbonitride, magnetite, and metallic iron. About 36 percent of the iron was present as magnetite, and the elemental carbon to iron ratio was 0.059.

In test X226 with $2H_2+1CO$ gas, the amounts of magnetite and elemental carbon found in the used catalyst were less than those observed in X349 with $1H_2+1CO$ gas. Although in 37 days of test X349, the nitrogen had decreased to about the same value as found after 64 days of test X226, removal of nitrogen was relatively independent of synthesis gas composition. In experiments at both 7.8 and 21.4 atmospheres, the nitrogen content decreased rapidly in the first 20 days of synthesis, but it usually did not decrease appreciably after 30 to 40 days of synthesis. Thus in test X225 (table 16), which was a duplicate of X349 except for duration, the nitrogen to iron atom ratio was the same (0.139) after 102 days as in X349 (37 days) and X226 (64 days).

Table 15 presents analytical data for nitrided fused catalysts containing alumina and zirconia as structural promoters and data for nitrided sintered and precipitated catalysts. Nitrided catalysts D3008 (Fe_3O_4-Al_2O_3-K_2O) differ from D3001 in being more resistant to oxidation during synthesis at 21.4 atmospheres. Nitrogen was removed from D3008 at a greater rate at 21.4 atmospheres (X337) than at 7.8 atmospheres (X253). Analyses of nitrided sintered catalyst A2106.11 (Fe_3O_4-K_2O) and nitrided precipitated catalyst P3003.24 (Fe_2O_3-CuO-K_2CO_3) (table 15) again demonstrated that nitrided-iron catalysts are resistant to oxidation in the synthesis at 7.8 atmospheres.

The nitrided catalysts in tests X273 and X337 were reduced with hydrogen after 39 and 50 days of testing, respectively. This treatment removed virtually all of the nitrogen, whereas the carbon was essentially unchanged, and the oxygen decreased only slightly. The used fused catalysts in X337 and in X214 (*16*) contained metallic iron, cementite, and magnetite (in order of decreasing amounts), after reduction at 385° C. The used precipitated catalyst in X273 contained metallic iron, copper, and Hägg carbide after reduction at 300° C. After reduction, the products of the synthesis changed from the relatively low molecular weight, highly oxygenated products characteristic of nitrided catalysts to a high molecular weight, slightly oxygenated material characteristic of reduced or carbided catalysts. After several weeks of testing, the principal phase in the reduced nitrides was magnetite—more than 50 percent of the iron.

When ε-iron nitrides were treated with carbon monoxide at 450° C. and atmospheric pressure, ε- or ζ-iron carbonitrides were formed (*53*) in which carbon replaced nitrogen, with the ε and ζ structure remaining unchanged until more than 75 percent of the nitrogen was replaced by carbon. Upon further treatment with carbon monoxide, the carbonitride changed to Hägg carbide. With massive iron nitride, no appreciable amount of oxide or elemental carbon was formed in the carburization (*53*). Apparently, the substitution reaction also occurs during the synthesis, but concomitantly with oxidation of the catalyst and deposition of elemental carbon. At synthesis temperatures (210°–250° C.), the replacement of nitrogen by carbon proceeded somewhat more rapidly at 21.4 atmospheres than at 7.8 atmospheres, but in every case, much slower than observed by Jack at 450° C. The nitrogen content of the catalyst was never decreased below atom ratios of N:Fe of 0.14, nor was Hägg carbide observed in the used, nitrided catalysts. Although all the nitrided catalysts were quite resistant to oxidation and deposition of elemental carbon at 7.8 atmospheres, these reactions proceeded much faster in some catalysts at 21.4 atmospheres. However, the stability and activity of nitrided catalysts were much greater at both pressures than those of reduced catalyst. The stability of fused catalysts at 21.4 atmospheres varied considerably with the type of structural promoter. Thus, the catalysts promoted with alumina or zirconia were much more resistant to oxidation than the magnesia-promoted catalyst.

The rate of removal of nitrogen from the catalyst was relatively independent of the composition of the synthesis gas, indicating that hydrogenation of nitrides was strongly inhibited by carbon monoxide and/or synthesis products. In pure hydrogen, iron nitrides can be completely hydrogenated in a few minutes at synthesis temperatures.

When ϵ-carbonitrides were reduced in hydrogen, most of the nitrogen was removed; however, the carbon content changed very little, and a part of the carbon appeared as carbide. That cementite was formed in X337 and Hägg carbide in X273 may be attributed to the differences in temperatures of hydrogenation; however, the differences in catalyst type and composition, especially the presence or absence of copper, may be important in determining the nature of the carbide phase. In subsequent synthesis, the hydrogenated, used catalysts behaved like reduced catalysts in regard to their selectivity and tendency to oxidize.

In the second series, the changes in catalyst composition were determined as a function of time for fused catalyst D3001 with $1H_2+1CO$ gas at 7.8 and 21.4 atmospheres (*70*). The nature and sequence of the pretreatment steps, chemical composition, and phases identified in the pretreated catalyst are given in table 16.

Figure 18 shows the composition changes that occurred in a typical completely nitrided ϵ-iron nitride catalyst (test X670, table 16), during a synthesis experiment at 21.4 atmospheres. Carbonitride was formed during synthesis by reaction of the nitride with carbon monoxide in the synthesis gas. The comparatively rapid rate of nitrogen loss during the first few days of the experiment, and the rapid carbon uptake and the persistence of the ϵ phase as determined by X-ray diffraction, are evidence of ϵ-carbonitride formation. Carbon gain, however, was considerably greater than nitrogen depletion, which is interpreted to mean deposition of free carbon during this period. With time, the rate of loss of nitrogen decreased substantially, so that at 35 days of operation the ratio N:Fe was still more than half the initial value.

TABLE 16.—*Pretreatment, composition, and activity of carbonitrides during synthesis*

(All pretreatments at atmospheric pressure. All synthesis tests at 21.4 atmospheres except where noted)

Test X—	Reduction in hydrogen [1]			Nitriding in ammonia [2]		Composition of pretreated catalysts		Composition of used catalysts				Activity [3] per gram Fe, A_{Fe}
	Temperature, ° C.	Time, hours	Reduction, percent	Temperature, ° C.	Time, hours	N:Fe	Component phases [4]	C:Fe	N:Fe	O:Fe	Component phases	
517	550	24	96.5	None	----------	0.0	M, α	0.28	0	1.05	ϵ', χ, S, M	69
274	550	20	99.0	500	1	.07	α, γ'	.23	.02	.99	M, α, χ	63
447	550	20	98.3	250	1	.11	α, γ'	.34	.01	1.03	M, α, χ	90
766	450	40	98.4	350	0.5	.16	α, γ'	.17	.09	1.11	M, α	75
445	550	20	99.1	450	1.5	.18	γ', α	.38	.03	.95	M, χ, α	99
219	550	20	97.4	385	4	.26	γ', α	.35	.10	.63	γ', ϵ	109
617	550	20	100	250	10	.35	γ', ϵ, α	.51	.08	.80	ϵ, M	88
711	450	40	97.4	350	8	.38	ϵ, γ'	.32	.06	.94	M, ϵ	76
225	550	20	96.4	350	6	.41	ζ, ϵ	.40	.14	.56	ϵ, M	115
612	550	20	100	350	6	.45	ϵ	.36	.20	.76	ϵ, M, S	81
620	550	20	100	350	12	.46	ϵ, M	.41	.23	.62	ϵ, M, S	126
518	550	24	96.5	350	6	.46	ϵ	.35	.19	.58	ϵ, M, S	95
670	550	20	99.8	350	22	.47	ϵ	.36	.26	.36	ϵ, M, S	111
215 [5]	550	20	98.7	385	4	.46	ϵ	.36	.31	.23	ϵ	70
218 [5]	550	20	97.5	385	8	.43	ϵ	.42	.23	.15	ϵ, M	68
361	500	24	97.2	None	----------	.0	α, M	.18	.0	1.14	M. α	54
194 [5]	450	40	----------	None	----------	.0	α	[6] .31	.0	[5] 1.09	M, χ, α	27

[1] Space velocity 2,300 to 2,700 $hr.^{-1}$ in all tests.

[2] Space velocity 950 to 1,050 $hr.^{-1}$ in all tests.

[3] Activity defined in chapter on synthesis tests with carbides of iron.

[4] α=metallic iron; χ=Hägg carbide; M=magnetite; S=$MgCO_3$ or $FeCO_3$; γ'=γ'-nitride or γ'-carbonitride; ϵ=ϵ-nitride or ϵ-carbonitride, ζ=ζ- nitride, and ϵ'=hexagonal close-packed carbide. Phases tabulated in order of decreasing intensity of X-ray diffraction pattern.

[5] Tested at 7.8 atmospheres.

[6] O:Fe and C:Fe after 95 days of synthesis.

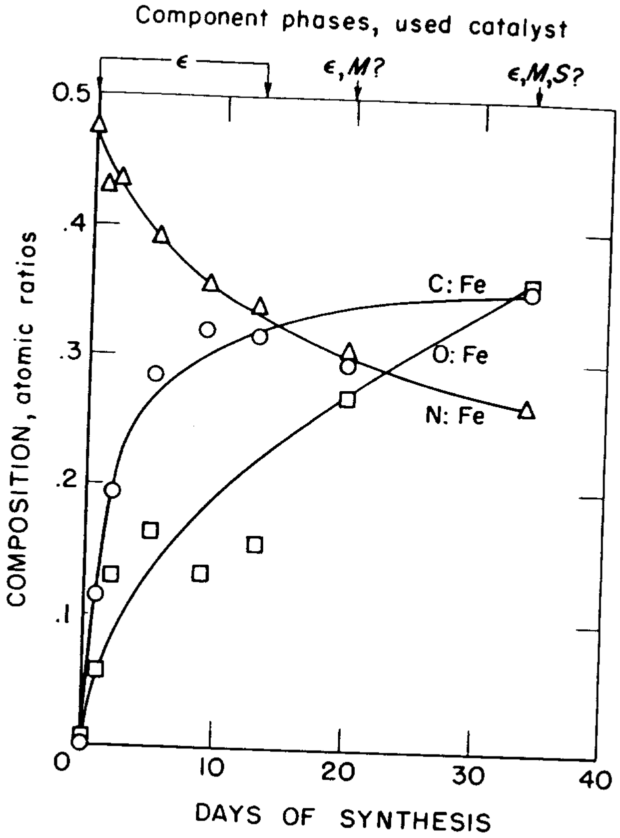

Figure 18.—Composition Changes of a Nitrided-Iron Catalyst During Synthesis With $1H_2+1CO$ at 21.4 atmospheres.

As shown by figure 19, retention of nitrogen was not significantly affected by operating pressure during synthesis at 7.8 and 21.4 atmospheres. The data at 21.4 atmospheres are reproduced from figure 18; those at 7.8 atmospheres refer to test X218 (*75*), table 16.

Iron catalysts are gradually oxidized during Fischer-Tropsch synthesis. In figure 18, the rate of this reaction may be compared with rates of gain of carbon and loss of nitrogen. The slope of the O:Fe curve and the appearance of magnetite (*M*) and possibly siderite or magnesite (*S*) as major phases after 20 to 30 days of operation show that oxidation of iron is progressive in nitrided catalysts, as it is in reduced ones. Both nitrided (tests X218 and X670, table 16) and reduced catalysts (tests X194 and X361) showed increased rates of oxygen absorption with increasing pressure (fig. 20). Comparison of the performance of a nitrided with a reduced catalyst tested at the same operating pressure shows that nitriding substantially retarded oxidation (*10, 71, 72*).

As shown in figure 21, the nitrided catalyst at 21.4 atmospheres gained more carbon during synthesis than the reduced catalysts, while in tests at 7.8 atmospheres the carbon-gain was slightly larger for the reduced catalyst. For the nitrided catalyst the gain in carbon was almost doubled by increasing the pressure from 7.8 to 21.4 atmospheres; for the reduced catalyst the carbon content was almost the same at both pressures.

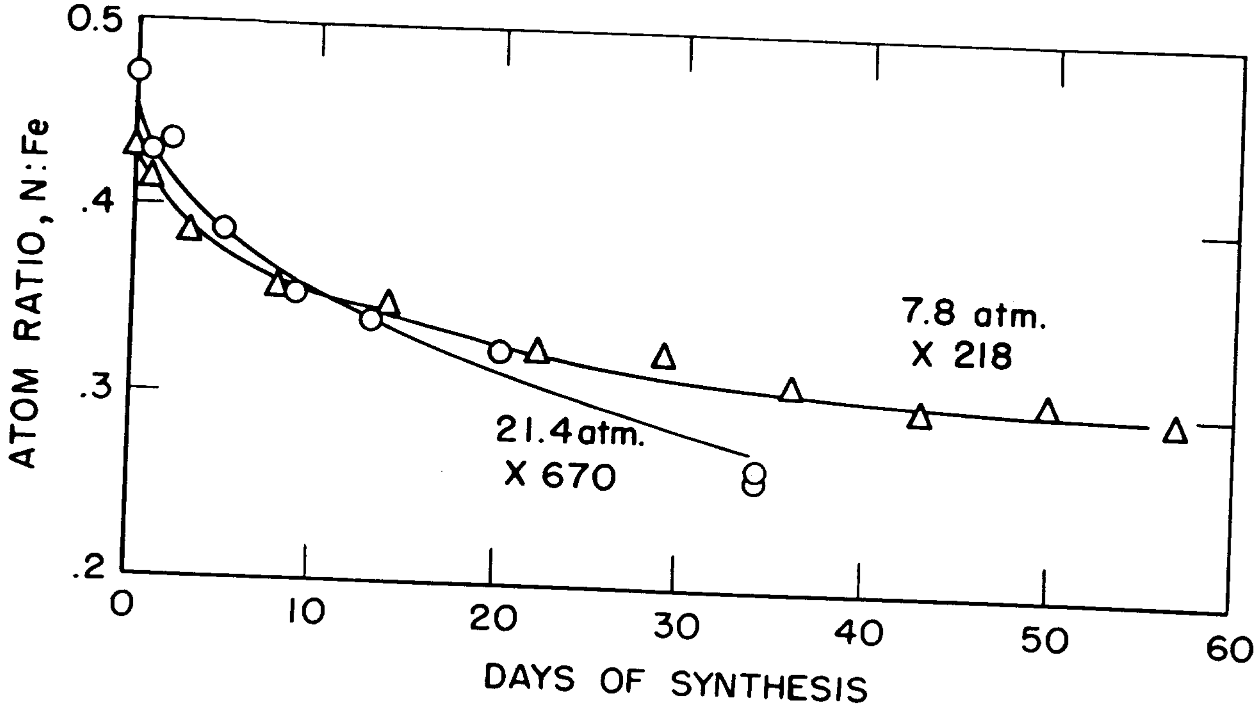

Figure 19.—Nitrogen Content During Synthesis as a Function of Time.

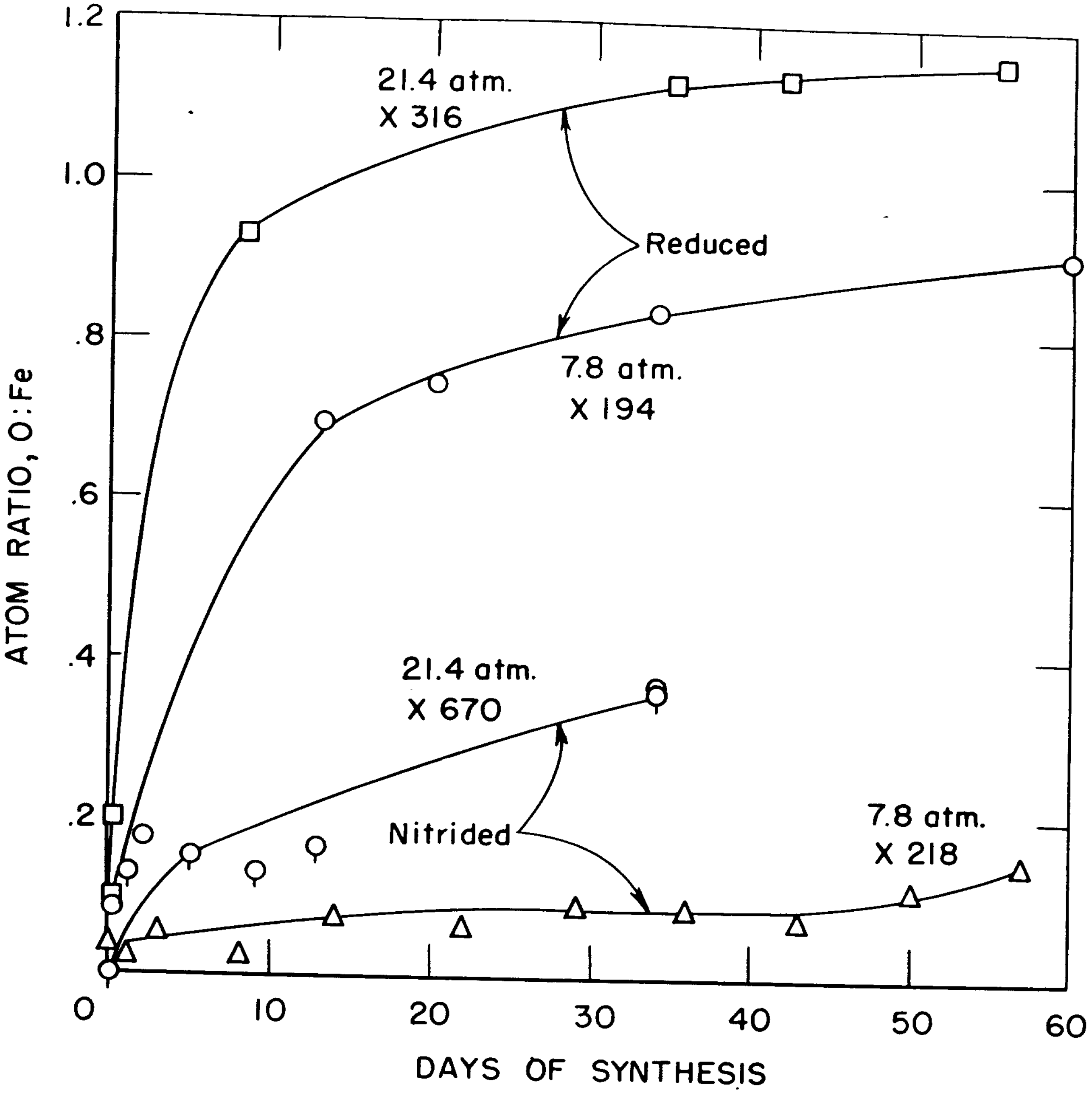

FIGURE 20.—Oxygen Content During Synthesis as a Function of Time.

ACITIVITY, SELECTIVITY, AND COMPOSITION CHANGES OF PARTLY NITRIDED CATALYSTS

The influence of initial nitrogen content of catalysts on their performance in the synthesis was studied at 21.4 atmospheres operating pressure with $1H_2+1CO$ synthesis gas (*70*). Fused catalyst D3001 was used in all of these tests. Time and temperature of nitriding were varied over wide limits to attain the desired range of nitrogen content (table 16). It is doubtful if this temperature variation in itself influenced the behavior of the catalysts, as reduction in any given instance was effected at a higher temperature than was nitriding.

At the lower nitrogen to iron ratios, to 0.26, nitriding produced γ'-iron nitride and metallic iron as the major components (table 16, control test X517 and tests X274, X447, X766, X445, and X219). In the synthesis, the γ' phase proved unstable; in every experiment except X219, it disappeared completely and is assumed to have been transformed to magnetite, χ-iron carbide, and metallic iron.

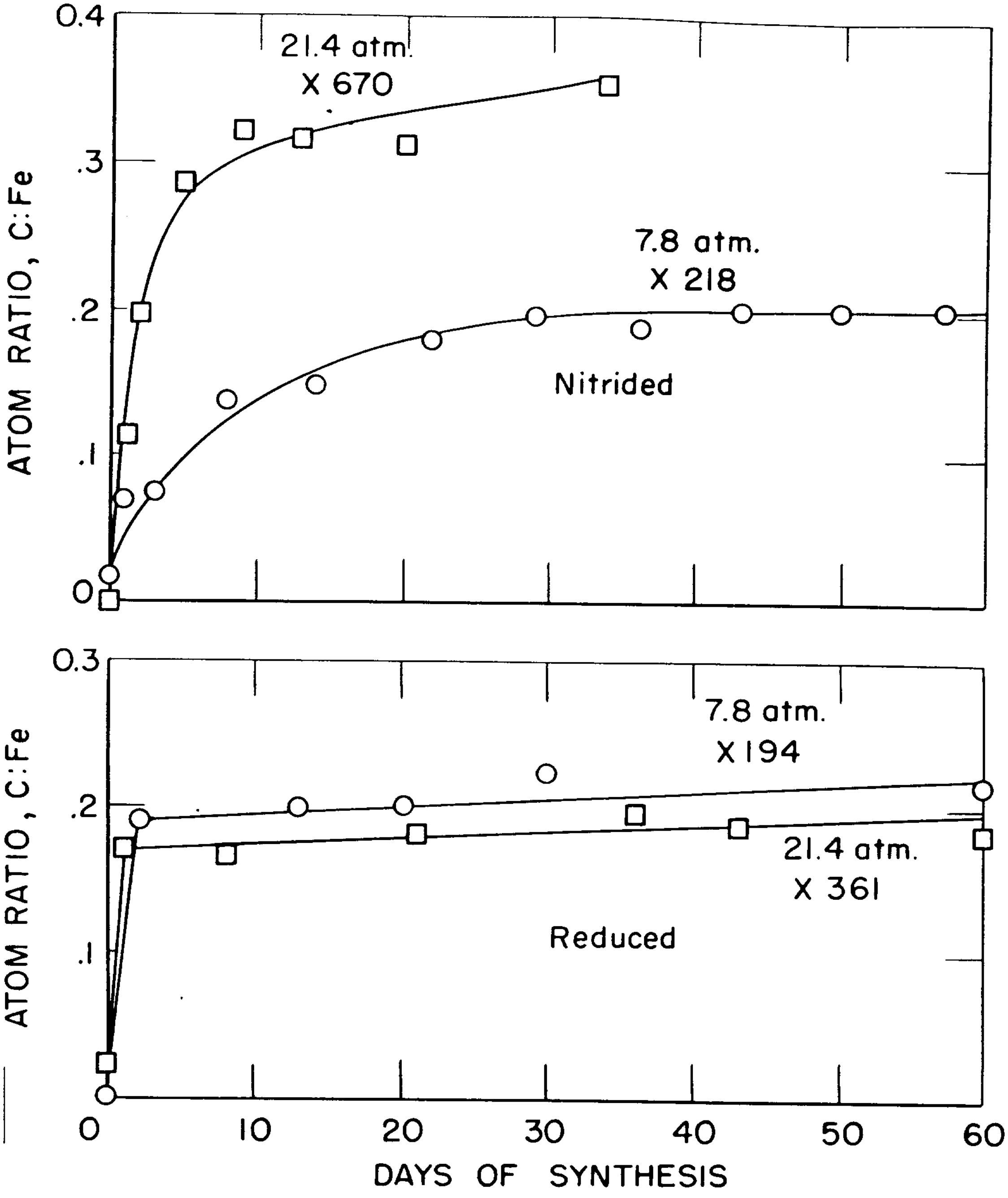

FIGURE 21.—Carbon Content During Synthesis as a Function of Time

In tests X617 and X711 with N:Fe of 0.35 and 0.38, respectively, the pretreated catalyst contained both the γ' and ϵ-phases, but after synthesis the catalyst contained ϵ-carbonitride and magnetite.

Upon nitriding to N:Fe values above 0.40, ϵ-nitride was the principal phase formed (table 16, tests X612, X620, X518, and X670). The ζ phase was also found in test X225. During synthesis, these phases were converted to ϵ-iron carbonitride, which persisted as a major component through the experiments. Despite the fact that the nitrogen content of the catalysts decreased with time, the ϵ-iron carbonitride structure was maintained, and the products of synthesis retained the characteristics associated with nitrided catalysts, even at N:Fe values as low as 0.14.

In figure 22, activity is plotted as a function of the initial nitrogen to iron ratio.

In a number of tests with nitrided-iron catalysts, more variability in activity was observed than in other synthesis tests. Examination of the catalyst after reducing and nitriding indicated that some particles had disintegrated to a fine powder, and because activity increases with decreasing particle size, marked deviations of this function from normal values were observed. Fines are also formed in the reduction of catalysts, but to a smaller extent, and reproducibility of activity is not seriously affected. Particle disintegration during pretreatment was fully appreciated only after the first part of the data for figure 22 had been obtained. Subsequently, several tests were made with catalysts that had been sieved under heptane to remove fines produced in the pretreatment. In both sets of data, activity increased with nitrogen content to N:Fe values ranging from 0.20 to 0.25 and then remained substantially constant. Examination of catalysts after synthesis by X-ray diffraction showed that those in which the initial N:Fe was 0.25 or greater generally contained the ε-phase as the major component, whereas in those containing smaller amounts of nitrogen χ-iron carbide and magnetite predominated.

Product distribution or selectivity as a function of initial N:Fe is shown in figures 23 and 24. In these curves, the term "total hydrocarbons" includes oxygenated organic compounds dissolved in the oil phase. Figure 23 is a plot of synthesis products exclusive of carbon dioxide, water, and water-soluble chemicals. The curves are based on mass spectrometric analysis of product gases and a simple distillation of liquid fractions. Figure 24 shows the weight-percent of C=C in the α and β positions and of total alcoholic hydroxyl in the fraction boiling from room temperature to 185° C. These determinations were made by the infrared spectrometer. Figure 25 shows the oxygen to iron atom ratio of the catalyst after 6 weeks of synthesis as a function of initial nitrogen content.

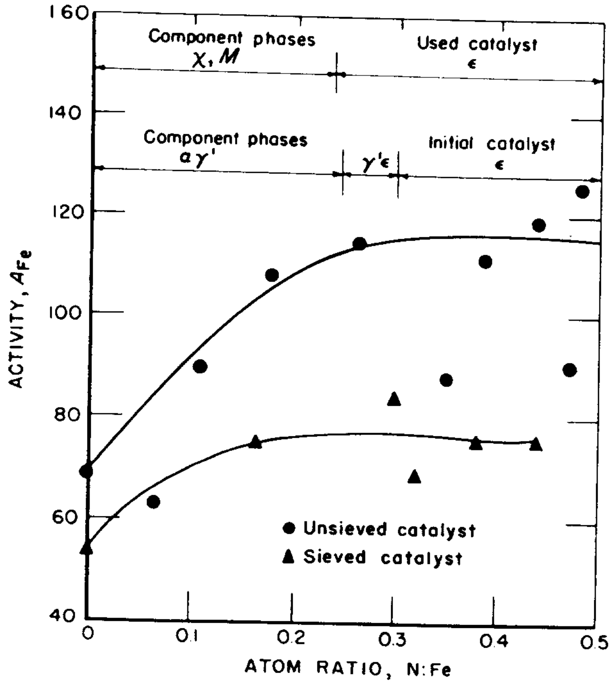

FIGURE 22.—Variation of Activity With Initial Nitrogen Content.

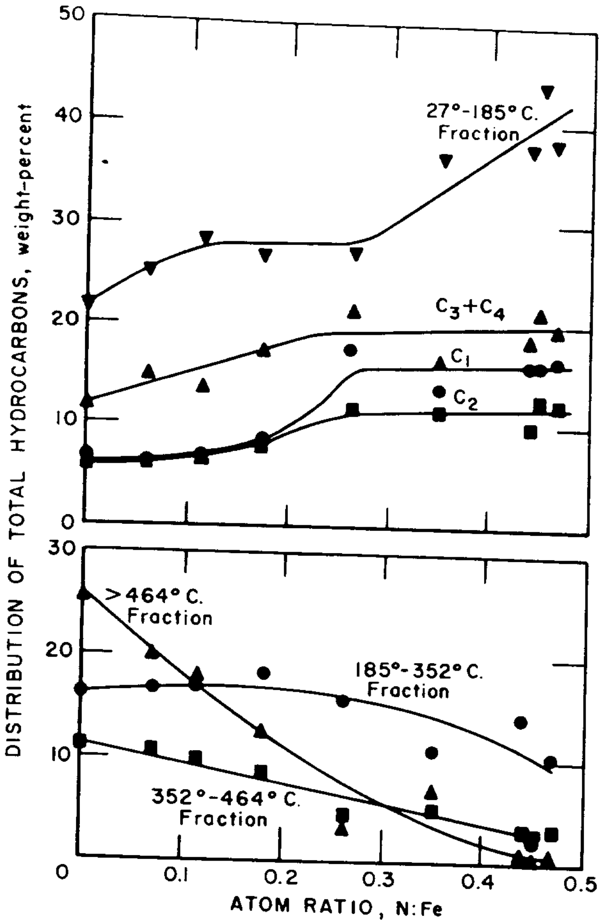

FIGURE 23.—Effect of Initial Nitrogen Content of Catalysts on Distribution of Products. Total hydrocarbons includes oxygenated material dissolved in liquid phase.

As the initial nitrogen content of the catalyst was increased the activity increased to about N:Fe=0.25 and then remained relatively constant. Also, at about this position, a major change in selectivity occurred. Specifically, increased production of alcohols and products of lower molecular weight associated with nitrides and carbonitrides was observed. At N:Fe ratios less than 0.25, the products were characteristic of reduced or carbided catalysts.

Phase changes during synthesis (table 16) indicate that the principal phases present in used catalysts with initial N:Fe less than 0.25 were magnetite and Hägg carbide, whereas for initial values greater than 0.25 ε-carbonitride