Bulletin 612

BUREAU OF MINES

CARBIDES, NITRIDES, AND CARBONITRIDES OF IRON AS CATALYSTS IN THE FISCHER-TROPSCH SYNTHESIS

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U. S. DEPARTMENT OF THE INTERIOR
March 3, 1849

UNITED STATES GOVERNMENT PRINTING OFFICE : 1963

UNITED STATES DEPARTMENT OF THE INTERIOR
Stewart L. Udall, Secretary

BUREAU OF MINES
Marling J. Ankeny, Director

This publication has been cataloged as follows:

Shultz, John Floid, 1896–

Carbides, nitrides, and carbonitrides of iron as catalysts in the Fischer-Tropsch synthesis, by J. F. Shultz [and others. Washington] U.S. Govt. Print. Off., 1963.

70 p. illus., tables. 26 cm. (U.S. Bureau of Mines. Bulletin 612)
Bibliography: p. 62–64.

1. Catalysts, Iron. 2. Carbides. 3. Nitrides. 4. Carbonitrides. I. Fischer-Tropsch synthesis. (Series)

TN23.U4 no. 612 622.06173

U.S. Dept. of the Int. Library

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CARBIDES, NITRIDES, AND CARBONITRIDES OF IRON AS CATALYSTS IN THE FISCHER-TROPSCH SYNTHESIS[1]

By

J. F. Shultz,[2] L. J. E. Hofer,[2] K. C. Stein,[3] and R. B. Anderson[2]

Summary

IRON catalysts converted to carbides, nitrides, and carbonitrides have been investigated in the Fischer-Tropsch synthesis, as a part of Bureau of Mines investigations of processes for converting coal to liquid or gaseous fuels or chemicals. Three carbides of iron have been considered in this report; namely, Hägg carbide, (χ), with the approximate formula Fe_2C; hexagonal carbide, (ϵ), Fe_2C; and cementite, Fe_3C. Hägg carbide is usually formed in substantial amounts during synthesis. Hexagonal carbide is usually formed only in special catalysts operated at relatively low temperatures, and cementite is usually not produced during synthesis.

Reduced, fused-iron catalysts were converted to Hägg iron carbide by treatment with either carbon monoxide or $1H_2+4CO$ gas, and these carbided catalysts were tested in the Fischer-Tropsch synthesis with $1H_2+1CO$ gas at pressures varying from 7.8 to 21.4 atmospheres. Carbides prepared with either of the gases had essentially the same activity and selectivity.

Initial activities of catalysts converted to Hägg carbide were greater than those of corresponding reduced catalysts. At 7.8, 11.1, and 14.5 atmospheres, activity of the carbided catalysts was either constant or increased slowly with time. At 21.4 atmospheres, activity of the carbide decreased rapidly with time. Although the products from carbides had a higher average molecular weight than those from reduced catalysts, apparently these differences could be attributed largely to variations in operating temperature and not to any major change in selectivity of the catalyst. No drastic change in the selectivity was observed as occurs when reduced catalysts are converted to nitrides.

The carbides oxidized during synthesis, rate of oxidation increasing with operating pressure. In most experiments, the total carbon content increased initially and then either remained constant or decreased. The observed composition changes may be explained by two processes: (*a*) The reaction of water vapor with carbide to produce in one case magnetite and elemental carbon and in the other magnetite and methane, and (*b*) the reaction of hydrogen with carbidic or elemental carbon to form methane.

Reduced, fused-iron catalysts, converted to cementite by direct carburization or by thermal reaction of Hägg iron carbide and iron, were tested in the Fischer-Tropsch synthesis with $1H_2+1CO$ at 7.8 and 21.4 atmospheres. Catalysts containing cementite are active in the synthesis and have similar catalytic properties to Hägg carbide. At 7.8 atmospheres, cementite and Hägg carbide were usually more active and oxidized less rapidly than reduced catalysts;

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however, at 21.4 atmospheres, the activity and rate of oxidation of carbided and reduced catalysts were about the same.

Phase changes in fused-iron catalysts were determined by thermomagnetic analysis and X-ray diffraction. In the initial period of synthesis with reduced catalysts, iron is rapidly but not completely converted to Hägg carbide. Oxidation of the metallic iron and carbide proceeded at a slower rate; metallic iron oxidized more rapidly than the carbide. The carbide content increased to a maximum in the first 5 days of synthesis and then decreased slowly. The maximum quantity of iron as Hägg carbide was about 45 percent at 7.8 atmospheres and 30 percent at 21.4 atmospheres. The rate of formation of magnetite was greater at 21.4 atmospheres than at 7.8, but the rate of decrease of metallic iron was the same at both pressures.

A precipitated-iron catalyst was pretreated in a variety of ways to convert the iron to carbides. No relationship was found between the presence or absence of carbides and activity or selectivity. Activity appeared to increase with the amount of elemental carbon present in the catalyst. Catalysts that were reduced in hydrogen before further pretreatment or synthesis yielded a product of lower average molecular weight than catalysts pretreated with carbon monoxide or synthesis gas.

Synthesis tests were made on iron catalysts converted to nitrides and carbonitrides. In nitrides the following phases are known: γ,′ of approximate composition Fe_4N; ϵ, varying from Fe_3N to Fe_2N; and ζ, about Fe_2N. Carbonitrides, in general, have the same structures as nitrides, some of the nitrogen being replaced by carbon atoms. During carburization of ϵ-nitride the ϵ-carbonitride phase persists until two-thirds of the nitrogen is replaced by carbon, and beyond this point χ-Fe_2C or χ-carbonitride appears.

Changes in composition of nitrided-iron catalysts during use in the Fischer-Tropsch synthesis at 7.8 and 21.4 atmospheres operating pressure are described. The ϵ-nitrides are slowly converted to ϵ-carbonitrides, the rate of replacement of nitrogen by carbon being somewhat more rapid at 21.4 than at 7.8 atmospheres. At the lower operating pressure, oxidation and deposition of elemental carbon proceeded at a very slow rate, whereas at 21.4 atmospheres these reactions were considerably more rapid in some catalysts. At the higher pressure, the type of structural promoter appeared to be important in determining rates of oxidation and of deposition of free carbon. When used, nitrided catalysts were treated with hydrogen, the nitrogen was almost completely removed, whereas the carbon content was not greatly changed. A part of the carbon appeared either as Hägg carbide or as cementite, depending upon the temperature of hydrogenation.

Fused-iron catalysts, converted to nitrides and carbonitrides, were tested in the Fischer-Tropsch synthesis at 7.8 and 21.4 atmospheres. The activity of nitrides increased with nitrogen content up to 0.25 atom ratio of nitrogen to iron, and at this concentration of nitrogen a major change in selectivity occurred. The fraction of product in the gasoline range and the yield of alcohols increased. Nitrided catalysts oxidized more rapidly at 21.4 than at 7.8 atmospheres, but the rate of removal of nitrogen was about the same. Activities of ϵ-carponitrides prepared by treating reduced catalysts with ammonia and carbon monoxide or with monomethylamine were similar to ϵ-carbonitrides made during synthesis with nitrided catalysts.

Structural changes occurring in fused and precipitated iron catalysts during pretreatment, oxidation, and synthesis were determined. On complete reduction at 450° or 550° C., a fused-iron oxide catalyst developed an extensive pore structure, having a porosity of about 45 percent. On reoxidation with steam the volume of the individual particles remained constant, and surface area and pore volume decreased. Reoxidation with steam proceeded at a rapid rate initially, but became slow after a few hours. The reoxidized catalyst was reduced more easily than the raw catalyst. Conversion of the reduced catalyst to nitrides or carbides caused the particles to expand and the pore volume and average pore diameter to increase. The porosity, however, remained unchanged.

Structural changes in iron catalysts during synthesis are caused by a number of chemical reactions. Oxidation and carbiding take place along with the deposition of elemental carbon and waxes. Even after long periods of synthesis, most iron catalysts retain a small but significant surface area. Data are presented that show how the pore geometry of reduced iron catalysts was modified by the formation of interstitial phases and by oxidation. Structures peculiar to the interstitial compounds may be stabilized; for example, the expanded structure of iron carbide was stabilized by small quantities of carbon remaining in the lattice after most of the carbon had been removed by hydrogenation.

Pretreated and used iron Fischer-Tropsch catalysts were studied by electron and X-ray diffraction, using powder techniques. For precipitated catalysts that had been carbided or nitrided, the same phases were identified by both electron and X-ray diffraction. Nitrided fused or sintered catalysts showed diffraction patterns of iron nitrides, but carbided samples produced only the electron-diffraction patterns of magnetite or structural promoters, although X-ray lines for the carbides were obtained. Before extraction with toluene, used catalysts gave electron-diffraction patterns only of wax. Except for some samples of extracted, used nitrided catalysts for which electron-diffraction patterns of ϵ-iron carbonitride were obtained, extracted, used catalysts showed only the electron-diffraction lines of magnetite or of the structural promoters. For all catalysts the electron-diffraction patterns of the interstitial phases were less complete than the corresponding X-ray-diffraction patterns. Implications of the diffraction data with respect to the mechanism of the synthesis are considered.

The appendix presents the composition of catalysts described in this bulletin and the experimental procedures for preparing and testing catalysts. In addition, a method for obtaining pure carbon monoxide from compressed synthesis gas and a device for feeding small quantities of liquid at a constant rate are described.

INTRODUCTION

This report describes investigations of carbides, nitrides, and carbonitrides as catalysts in the Fischer-Tropsch synthesis. In this catalytic process hydrogen and carbon monoxide, which may be obtained by gasification of coal or lignite, react to form hydrocarbons and oxygenated organic molecules. Although the Fischer-Tropsch synthesis produces a distribution of molecules varying over a wide range of carbon numbers, by proper choice of catalysts and operating conditions substantial yields of desirable products such as gasoline, wax, or gaseous hydrocarbons can be produced. To distinguish it from other hydrogenations of carbon monoxide that yield high-molecular-weight products, the Fischer-Tropsch synthesis may be defined as a hydrogenation of carbon monoxide that yields, predominantly, molecules with straight carbon chains, at least in the range C_4 to C_{10}. Iron, cobalt, nickel, and ruthenium are the only elements that are effective as catalysts in the Fischer-Tropsch synthesis.

Iron, cobalt, and nickel are members of a small group of metals that can be converted to interstitial carbides by treatment with carbon monoxide in the temperature range 150° to 350° C. This observation has led to numerous postulates that carbides are intermediates and/or the active catalytic phases in the synthesis, starting with the hypotheses of Fischer and Tropsch in 1926 (*39*)[4] (see references *6*, *15*, *73*, and *80* for reviews of the carbide "theory"). Despite the great interest in iron carbides, few synthesis tests have been reported on catalysts largely converted to these phases. Therefore, methods were developed for preparing relatively pure iron carbides in a catalytic form, and these preparations were studied in the synthesis.

Investigations of the Bureau of Mines laboratory at Bruceton, Pa., about 1950 revealed that nitrides and carbonitrides of iron were unusual Fischer-Tropsch catalysts with respect to stability, life, and selectivity (*5*, *14*, *16*). Iron nitrides and carbonitrides with compositions varying over a wide range were prepared, and their properties in the synthesis were evaluated. The last section of this bulletin reports studies of the changes in pore geometry and changes of phases and chemical composition of iron catalysts during pretreatment and synthesis.

Three reviews of the preparation of carbides and their physical and chemical properties have been published by Bureau of Mines workers (*46*, *47*, *67*), and a bulletin describing recent work is being prepared by L. J. E. Hofer.

In this bulletin the process of converting a catalyst to carbide is termed "carbiding" or "carburization." "Carbiding" is used for processes that produce principally carbide. "Carburization" is a general term denoting a treatment that adds carbon to the catalyst. "Carburization" can be used for processes that produce principally carbide, principally elemental carbon, or a mixture of both; it can be used as well in converting a nitride to a carbonitride. "Nitriding" is used as a general term describing addition of nitrogen to the catalyst.

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[4] Italicized numbers in parentheses refer to items in the bibliography at the end of this report.

PREPARATION OF CARBIDES, NITRIDES, AND CARBONITRIDES OF IRON IN CATALYTIC FORM

Experimental procedures for converting the iron in catalysts to relatively pure carbides, nitrides, or carbonitrides have been adapted from procedures evolved in small-scale experiments in glass equipment for use in metallic systems of adequate capacity for catalyst testing. All preparative steps were done at atmospheric pressure, unless specific pressures are mentioned. (Catalysts, their compositions, and methods of preparing them, together with testing procedures are given in the appendix.)

1. *Reduction in Hydrogen.*—Catalysts were reduced in hydrogen in a special metal block reactor (*16, 73*) that was rotated about a transverse axis to permit easy introduction and discharge of the catalyst. Precautions were taken to avoid oxidation of the catalyst during cooling and subsequent handling. Finally, the catalyst was transferred through rubber connections in a stream of carbon dioxide to a special weighing bottle (*16*).

2. *Nitriding in Ammonia.*—The metal block reactor was used, and the same precautions were observed as in reductions. In addition, when the catalyst was removed from the reactor, the flow of ammonia was continued at the rate used during nitriding until the catalyst temperature was less than 50° C. Before transferring the catalyst to the weighing bottle the system was flushed first with prepurified nitrogen and then with carbon dioxide (*16*).

3. *Preparation of Hägg Carbide.*—Conversion of the reduced catalyst to Hägg carbide was accomplished in the reactor as described under 1. Two procedures were used for reduced fused catalyst:

> *A.* With pure carbon monoxide at an hourly space velocity of 100, the carbiding temperature was increased progressively from 150° to 350° C. as required to maintain carbon dioxide content of the exit gas at about 20 percent (*44*). Approximately 20 hours was required to deposit carbon corresponding to the formula Fe_2C, Hägg carbide being the predominant phase detected by X-ray diffraction or thermomagnetic analysis. This carbiding procedure is particularly advantageous for preparing Hägg carbide. Because the rate of carbiding is maintained low and approximately constant, the possibility of the following two side reactions occurring is minimized: (1) Deposition of elemental carbon due to overheating, and (2) oxidation of elemental iron or carbide by excessively large concentrations of carbon dioxide, resulting from high conversion of carbon monoxide. Carbiding freshly reduced catalysts at 325° to 350° C. would produce cementite, elemental carbon, and magnetite in addition to Hägg carbide. In the carbiding schedule the catalyst was largely converted to Hägg carbide by the time that these temperatures were reached, and apparently only Hägg carbide was formed under these conditions.
>
> *B.* In carbiding reduced catalyst with $1H_2+4CO$ gas, the temperature was increased by steps—12 hours at 200° C., 12 hours at 250° C., and 12 hours at 275° C. This procedure similarly minimized possibilities of overheating and oxidation due to excessively high rates of carbiding, and usually satisfactory samples of Hägg carbide, without excessive amounts of elemental carbon or magnetite could be prepared this way.

Precipitated catalysts were converted to Hagg carbide by the following methods:

The catalysts were pretreated, without prior reduction, using $2H_2+1CO$ gas at an hourly space velocity of 2,500, 310° C., and atmospheric pressure for 6 hours in the synthesis reactors. The catalysts were not removed from the reactor before synthesis, but analyses after synthesis indicated that this activation procedure had converted a substantial portion of the catalyst to Hagg carbide and that an appreciable quantity of elemental carbon was deposited.

Other pretreatments of precipitated catalysts were made in the reactor mentioned in 1, using carbon monoxide according to procedure *A*). A reduced catalyst was largely converted to Hagg carbide in 13 hours, the temperature being increased from 185° to 300° C. as required to maintain the carbon dioxide content of the exit gas at 20 percent. In another test the raw catalyst was treated with carbon monoxide. Although the temperature required to produce 20 percent CO_2 in the exit gas did not exceed 250° C., an appreciable amount of carbides was not found in the catalyst.

4. *Preparation of Cementite.*—Three methods, all at atmospheric pressure, were employed to prepare cementite.

> *A.* Conversion of Hägg iron carbide to cementite. This method is based on the observation that Hägg carbide reacts with metallic iron to form cementite (*48, 68*). This reaction proceeds more rapidly than the decomposition of Hägg carbide into cementite and free carbon. Reduced catalysts were carburized with carbon monoxide in a metal block reactor to convert two-thirds of the iron to Hägg carbide (*16*). Helium was then passed over the catalyst; the temperature was increased to 475° C.; and it was maintained for 2 hours. The catalyst was dropped into the receiving vessel and was cooled in helium.
>
> *B.* Direct preparation with $2H_2+1CO$ gas.[5] Catalysts largely converted to cementite were prepared by carburizing the reduced sample with $2H_2+1CO$ gas at a space velocity of 2,500 $hours^{-1}$ and 310° C. for 6 hours in the reactor. The carburized sample was then dropped into the receiving vessel and cooled in $2H_2+1CO$.
>
> *C.* Direct preparation with methane. Pure methane was passed over the reduced catalyst at an hourly space velocity of 1,000 and 500° C. for 4 hours in the reactor mentioned in 1. The catalyst was dropped into the receiver in methane and cooled to room temperature.

These methods produced catalysts containing principally cementite. Most of the samples contained metallic iron in addition to cementite, but other carbides were not found. Special care was taken in transferring catalysts to avoid oxidation (*16*).

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[5] This preparation may be regarded as an example of formation of cementite during synthesis. Small yields of higher hydrocarbons are produced; however, the activity is low, and the selectivity is poor, under these conditions.

5. *Preparation of ε-Iron Carbonitrides.*—Carbonitrides were produced from fused catalysts in four ways:

A. During synthesis nitrided catalysts were treated with $1H_2+1CO$ gas at 7.8 to 21.4 atmospheres.

B. The nitrided catalyst was treated with a stream of pure carbon monoxide at atmospheric pressure, 350° to 450° C., and an hourly space velocity of 100. The higher temperatures and longer times were required to produce a carbonitride rich in carbon and low in nitrogen.

C. Hägg iron carbide was produced according to procedure 3*A*. The carbided catalyst was then treated with ammonia at an hourly space velocity of 1,000 and 350° C. for 28 hours.

D. The reduced catalyst was treated with monomethylamine at an hourly space velocity of 1,000 and 350° C. for 28 hours.

SYNTHESIS TESTS WITH CARBIDES OF IRON

FUSED-IRON OXIDE CATALYSTS CONVERTED TO HÄGG CARBIDE

To determine the effect of method of pretreatment, synthesis pressure, and conversion, synthesis tests were made with fused-iron oxide catalysts converted to Hägg carbide, using $1H_2+1CO$ gas at pressures of 7.8, 11.1, 14.5, and 21.4 atmospheres (*72*). Conditions for reduction and carburization, and the principal phases in pretreated catalysts are given in table 1. Procedures for these pretreatments have been given. Catalysts used in these experiments were in the form of 6- to 8-mesh particles.

TABLE 1.—*Pretreatment of catalysts converted to Hägg carbide*

(Unless otherwise noted catalyst is D3001)

Test X—	Reduction in hydrogen [1]			Extent of reduction, percent	Gas	Carburization [1] [2]			Phases from X-ray diffraction [3]
	Temperature, ° C.	Space velocity, hour⁻¹	Time, hour			Temperature range, ° C.	Total time, hours	Atom ratio, C:Fe	
152	450	1,000	43	90.2	None				α
289	[4] 400–525	8,000	72	97.5	CO	[5] 227–350	18	0.56	χ, M, α
294	500	2,500	24	96.6	CO	[5] 150–350	18	.58	χ, α
320	500	2,080	24	97.7	CO	[5] 150–350	48	.56	χ, M
323	500	1,780	41	96.8	$1H_2+4CO$	[6] 200–275	48	.43	χ, α
325	500	2,330	43	97.2	$1H_2+4CO$	[6] 200–275	48	.42	χ, M
339	500	2,490	40	98.2	$1H_2+4CO$	[6] 200–275	48	.42	χ
342	500	1,990	24	97.2	CO	[5] 150–350	18	.43	χ, α
394	500	2,100	24	99.5	CO	[5] 150–350	29	.53	χ
399	500	2,860	40	97.9	CO	[5] 150–350	18	.46	χ, α
408	500	2,370	24	98.6	CO	[5] 150–350	20	.50	χ
417	500	2,450	24	98.7	CO	[5] 150–350	18	.46	χ
428	500	2,240	26	97.9	CO	[5] 160–320	19	.52	χ
515	500	1,180	24	97.8	None				α
380 [7]	[4] 400–525	6,950	48	100	None				α
416 [7]	[4] 400–525	2,450	56	100	CO	[5] 150–350	13	.42	χ, α

[1] Both pretreatment steps at atmospheric pressure.
[2] Space velocity of CO or $1H_2+4CO$ about 100 hour⁻¹.
[3] Phases from X-ray diffraction in order of decreasing intensity of pattern: χ=Hägg carbide; α=metallic iron; M=magnetite.
[4] Twenty-four hours at 400° C., 24 hours at 450° C., 12 hours at 500° C., and 12 hours at 525° C.
[5] Temperature increased as required to maintain CO_2 content of exit gas at about 20 percent.
[6] Twelve hours at 200° C., 12 hours at 250° C., and 24 hours at 275° C.
[7] Catalyst D3008 employed in these tests.

Data for the activity of reduced and reduced and carbided fused-iron catalyst as a function of time are presented in figures 1 to 4. Figures 1 and 2 compare activities of catalysts at operating pressures of 7.8 and 21.4 atmospheres (absolute), respectively. Figure 3 shows the activities as a function of operating pressure, and figure 4 compares activities of catalysts under different conditions of operation. In tests at 7.8 atmospheres the CO_2-free contraction was maintained constant at 65 and 80 percent, and in tests at 21.4 atmospheres the contraction was held at 22 and 63 percent. The CO_2-free contraction is defined as $1\text{-}E/I$, where I is the volumes (S.T.P.) of feed gas per hour and E is the volume (S.T.P.) of exit gas per hour after removal of CO_2. The CO_2-free contraction is an easily obtained measure of conversion of H_2+CO and is usually only a few percent lower than the value for conversion. In these figures the activity was corrected to a standard synthesis condition (240° C. and 65 percent conversion) by use of an empirical rate equation (*13*). Activities were computed from average weekly synthesis conditions. The activity designated by A_{Fe} is defined as cubic centimeters (S.T.P.) of H_2+CO reacted per hour per gram of iron at 240° C. when the conversion of H_2+CO is 65 percent. The logarithmic time scale was employed to include data of experiments of long duration without excessively compressing initial periods of synthesis.

Figure 5 compares product distribution data from tests of both reduced and reduced and carbided catalysts at 7.8 and 21.4 atmospheres corresponding to activity data in figures 1 and 2. Figure 6 demonstrates the effect of operating pressure on selectivity of carbided catalysts (activities in fig. 3).

The selectivity plots present distribution of total hydrocarbons in weight-percent, including oxygenated molecules dissolved in the condensed hydrocarbon phases—water-soluble oxygenated molecules being excluded. Gaseous hydrocarbons and distillation fractions of condensed hydrocarbons are shown. Numbers designated with (=) in gaseous hydrocarbons blocks indicate percentages of olefins. For the

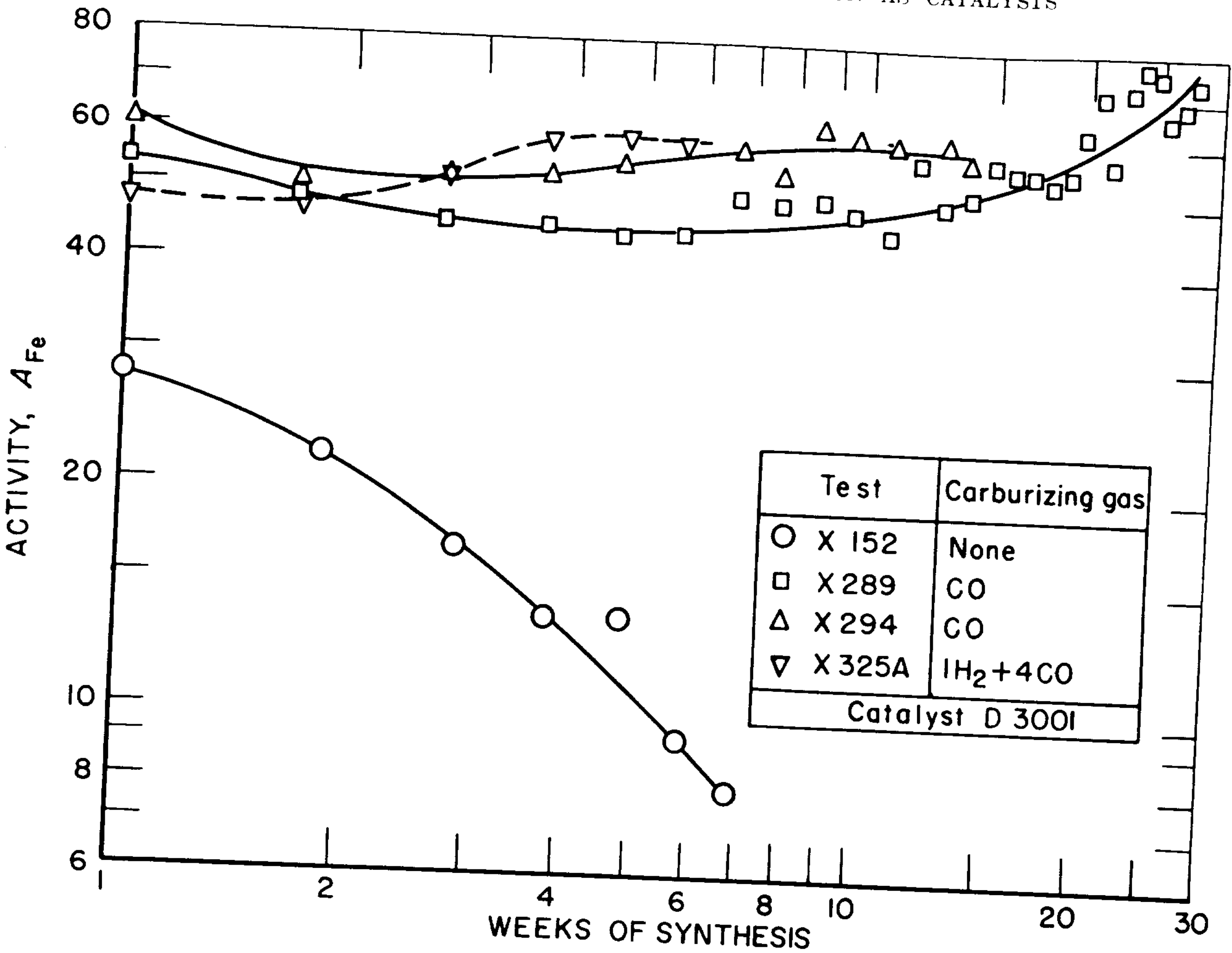

FIGURE 1.—Activity of Reduced and Carbided Catalysts as a Function of Time for Synthesis With $1H_2+1CO$ gas at 7.8 Atmospheres.

TABLE 2.—*Usage ratios* (H_2:CO) *for tests of fused catalysts with* $1H_2+1CO$ *gas*

Test X[1]—	Carbiding gas	Pressure, atmospheres, absolute	Average	
			Contraction, percent	Usage ratio, H_2:CO
152	None	7.8	65	0.72
289	CO	7.8	64	.81
294	CO	7.8	64	.75
399	CO	7.8	80	.75
325A	$1H_2+4CO$	7.8	65	.87
325B		21.4	64	.88
408	CO	11.1	63	.83
417	CO	11.1	62	.78
394	CO	14.5	64	.84
342	CO	21.4	63	.79
323	$1H_2+4CO$	21.4	64	.85
339	$1H_2+4CO$	21.4	64	.83
428	CO	21.4	22	1.46
515	None	21.4	65	.76
380	None	21.4	65	.67
416	CO	21.4	62	.80

[1] All tests with catalyst D3001 except X380 and X416, in which D3008 was used.

distillation fractions, Br is bromine number; OH weight-percent hydroxyl group; and CO, weight-percent carbonyl group as aldehyde, ketones, and acids. The relative usage[6] of H_2 and CO is given in table 2. Selectivity data are averages of the 2d through 5th week of synthesis.

Catalysts containing principally Hägg carbide have greater initial activities than do reduced catalysts. At 7.8 atmospheres the activity of the carbides remained essentially constant or increased slowly, whereas the activity of the reduced catalysts[7] decreased to one-third of its initial value in 7 weeks of synthesis (fig. 1). At 21.4 atmospheres the activity of carbides decreased rapidly with time, but the activity of reduced catalysts remained fairly constant

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[6] In the literature of the Fischer-Tropsch synthesis the relative consumption of H_2 : CO is termed "usage ratio," which is defined as moles of H_2 consumed divided by moles of CO consumed.

[7] In test X194, described in references *10* and *80*, the activity remained essentially constant in the synthesis at 7.8 atmospheres. However, in a similar test (X168 in reference *80*) the activity decreased in the same manner as shown in figure 1. In both tests, Hägg carbide was produced to some extent in the synthesis. The higher content of Hägg carbide in X194, resulting from a variation in the induction procedure, may possibly explain the constant activity observed in this test.

(fig. 2). At both synthesis pressures, activity was essentially the same for samples prepared by carbiding with either carbon monoxide or $1H_2+4CO$ gas. The great differences in activity-time trends for reduced and carbided catalysts at 7.8 and 21.4 atmospheres led to tests of carbides at intermediate pressures. At 7.8, 11.1, and 14.5 atmospheres, the activity of carbides was constant or increased slowly with time (fig. 3). Initial activities increased approximately linearly with operating pressure. In test X325 the catalyst was tested at 7.8 atmospheres for 6 weeks (figs. 1 and 3), and the activity increased slightly with time. In the 7th week the operating pressure was increased to 21.4 atmospheres. The activity was greater at the higher pressure, but it later decreased in a manner typical of catalysts tested entirely at 21.4 atmospheres.

At a given pressure the distribution of products from catalysts converted to Hägg carbide by treatment with either carbon monoxide or $1H_2+4CO$ gas was about the same as shown in figure 5. The average molecular weight of products from carbided catalysts was slightly higher than molecular weights from corresponding reduced catalysts; however, the difference in product distribution can be largely attributed to the differences in operating temperature. The average molecular weight increased with increasing synthesis pressure in the range from 7.8 to 21.4 atmospheres, shown

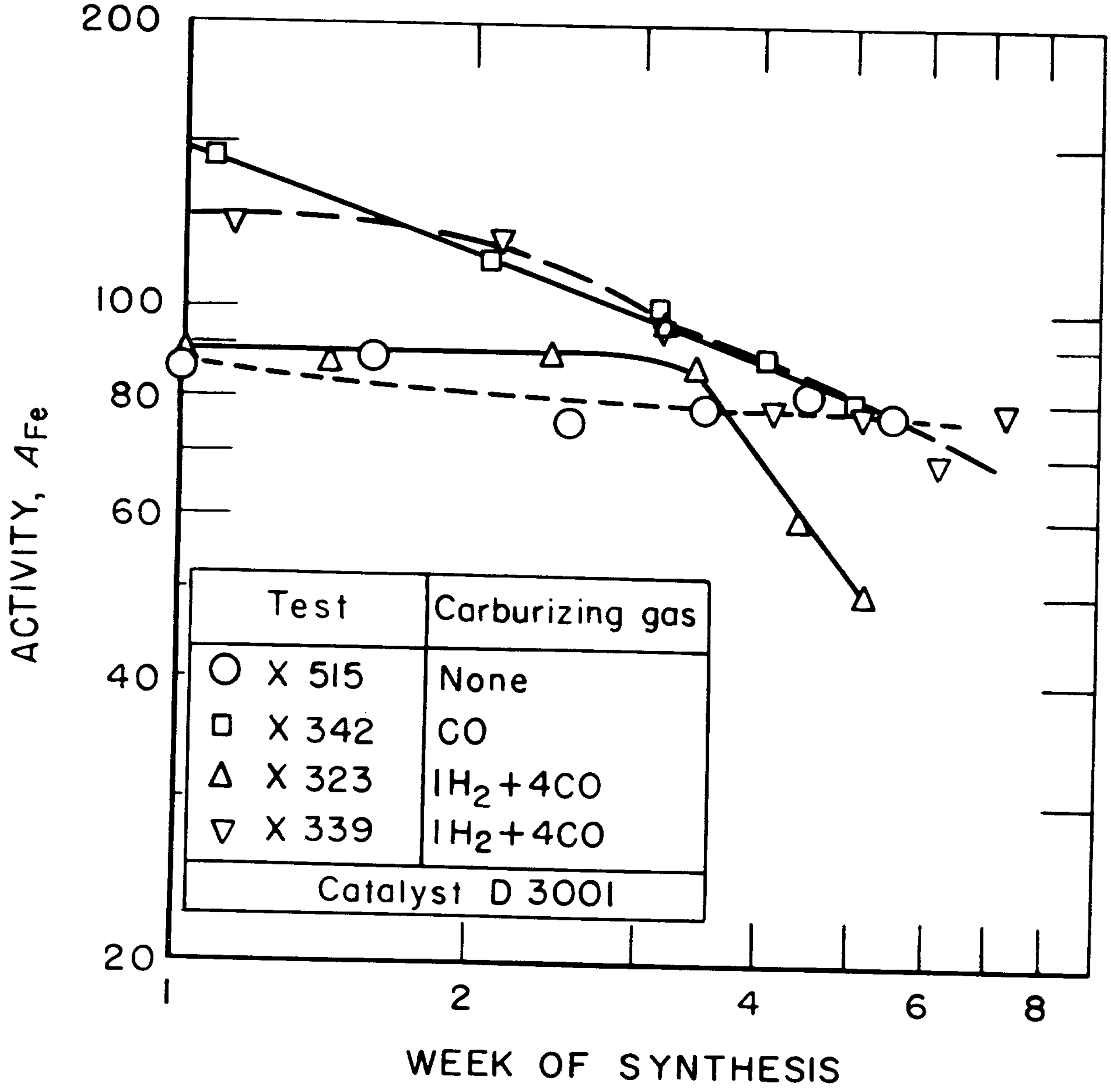

FIGURE 2.—Activity of Reduced and Carbided Catalysts as a Function of Time for Synthesis at 21.4 Atmospheres.

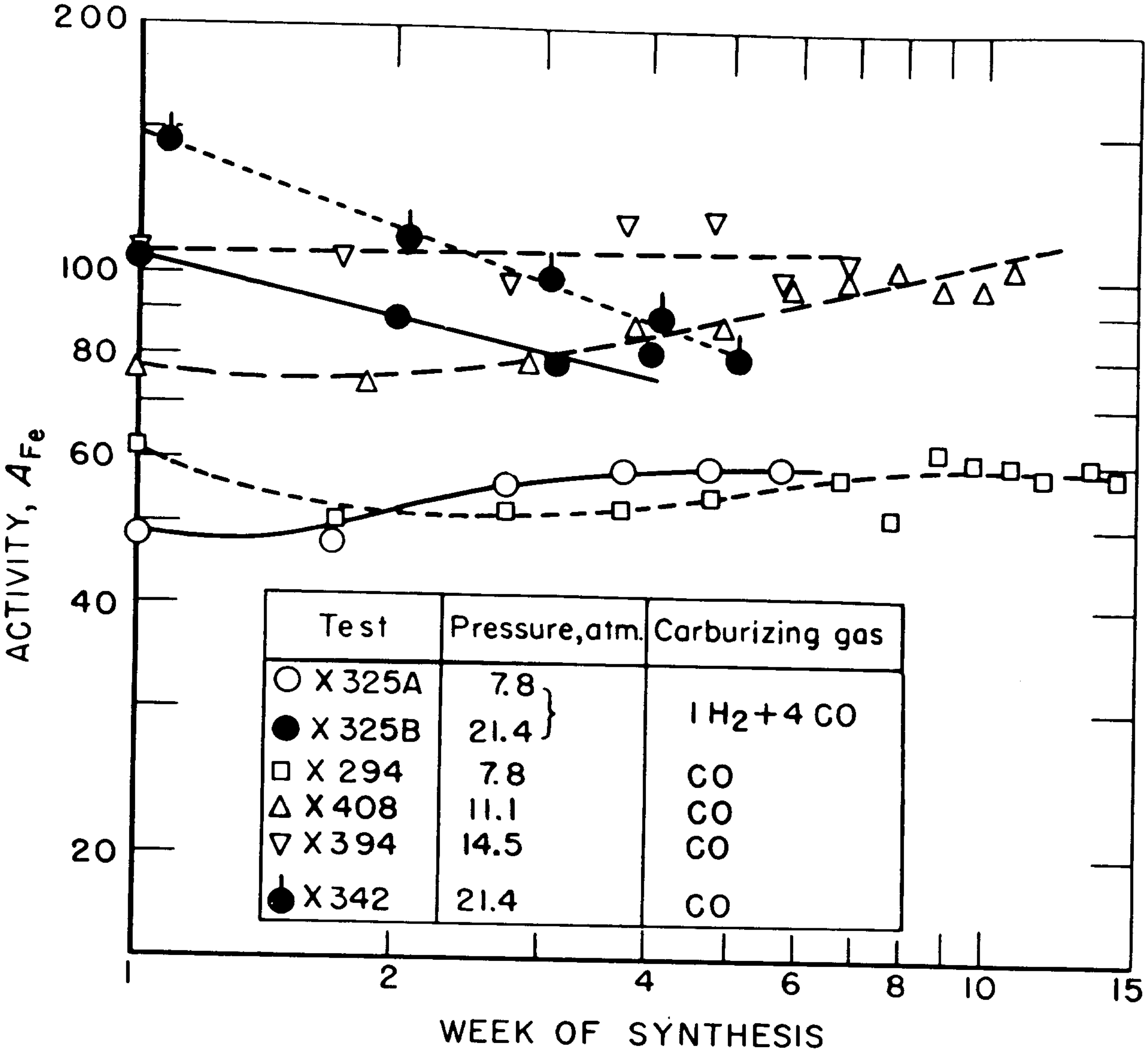

FIGURE 3.—Activity-Time Plots for Carbided Catalyst, D3001, at Various Operating Pressures.

in figures 5 and 6. In all cases the amount of oxygenated molecules in the oil phase from carbided catalysts was low and was not significantly different from products from reduced catalysts. The carbided catalysts had somewhat higher usage ratios (H_2:CO) than corresponding reduced preparations (table 2). The high usage ratio in test X428 resulted chiefly from operation at low conversion. The selectivity of carbided catalysts with respect to the production of hydrocarbons and oxygenated molecules was about the same as the selectivity of reduced catalysts.

In tests at 7.8, 11.1, and 14.5 atmospheres the activity remained essentially constant, and tests continuing as long as 25 weeks were possible, since catalyst disintegration was not severe. At 21.4 atmospheres, however, the activity of carbided catalysts decreased rapidly, and catalyst deterioration caused plugging of the reactor and related difficulties after only a few weeks of synthesis.

Figure 4 demonstrates the influence of conversion on activity of carbides at 21.4 atmospheres. In contrast to the rapid decline of activity and catalyst disintegration at 65 percent contraction, the activity of a carbide at low conversions, 22 percent (test X428), increased more than threefold in the first 12 weeks, and then decreased to about the initial value by the 16th week. Apparently the improved operability in test X428 results from the lower concentration of reaction products, especially water, in the gas stream. Figure 4 also compares tests at 7.8 atmospheres in which the apparent contraction was maintained at 65 percent (text X294) and 80 percent (X399). With time, the activity of the catalyst operated at the higher conversion decreased, while at the lower conversion the activity increased.

Another fused-iron catalyst (D3008, promoted with alumina and alkali) was tested with $1H_2+1CO$ gas at 21.4 atmospheres in both the reduced and carbided states. The initial activity of the carbide was higher than that of the reduced catalyst, but the activity of carbided catalyst decreased rapidly with time, as observed for catalyst D3001. Activities of the reduced and carbided samples were:

	Activity, A_{Fe}	
Duration of synthesis, weeks:	*Reduced* (*X380*)	*Hägg carbide* (*X416*)
1	108	157
2	95	110
3	85	---------
4	73	---------
5	67	---------
6	59	---------

The particles of the sample converted to Hägg carbide deteriorated so rapidly that the converter tube plugged during the 3d week of synthesis.

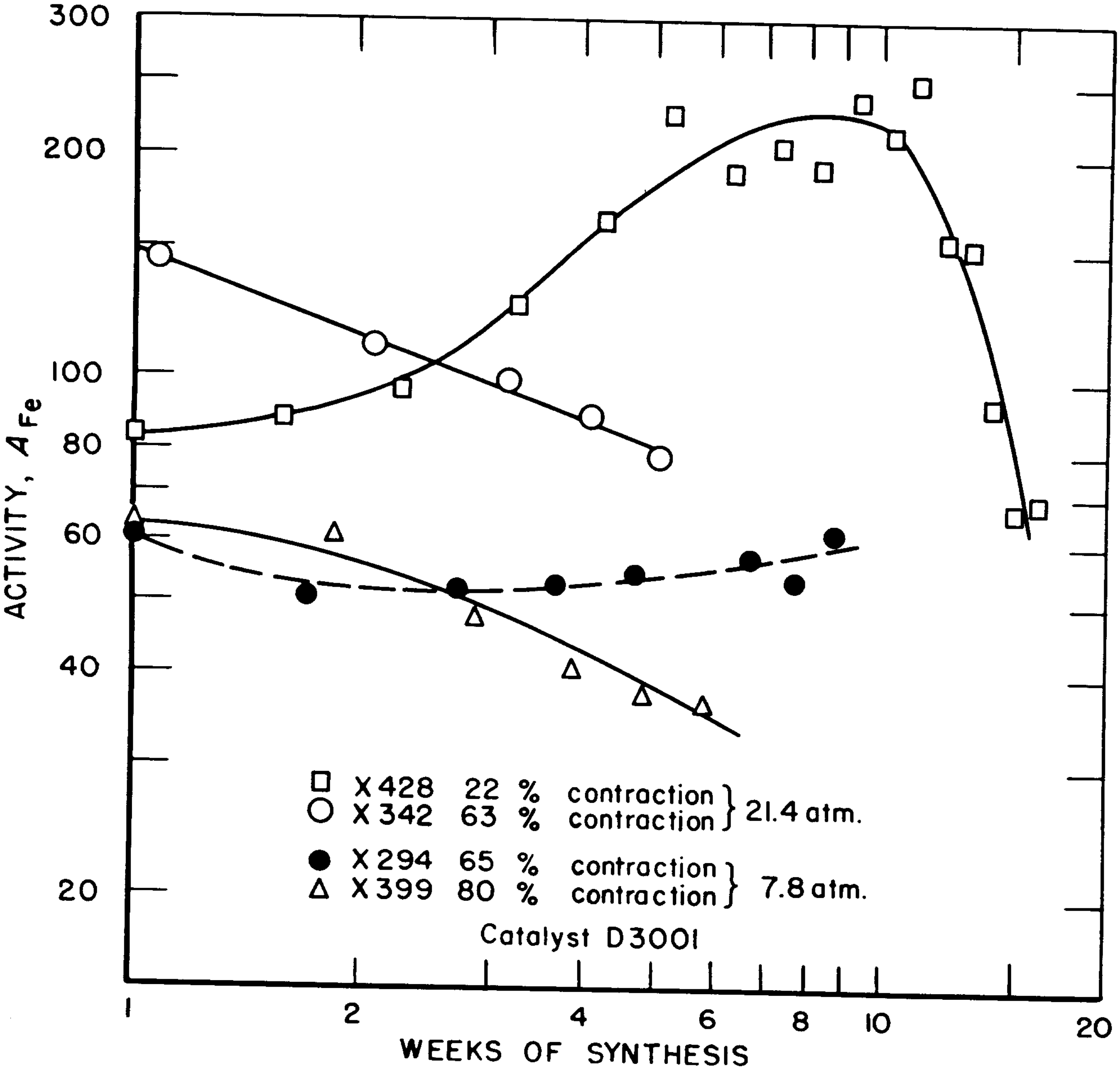

FIGURE 4.—Variation of Activity With Time.

	7.8 atm.				21.4 atm.		
Test number	X152	X289	X294	X325A	X339	X342	X515
Carbiding gas	None	CO	CO	$1H_2+4CO$	$1H_2+4CO$	CO	None
Phases present	α	χ,M,α	χ,α	χ	χ	χ,α	α
Temperature, °C.	270	229	229	230	250	243	248
Space velocity, hr.$^{-1}$	97	103	106	101	292	334	303
Contraction, percent	65.2	64.3	63.7	65.3	64.4	63.2	64.6
Activity, A_{Fe}	14	46	53	55	78	104	80

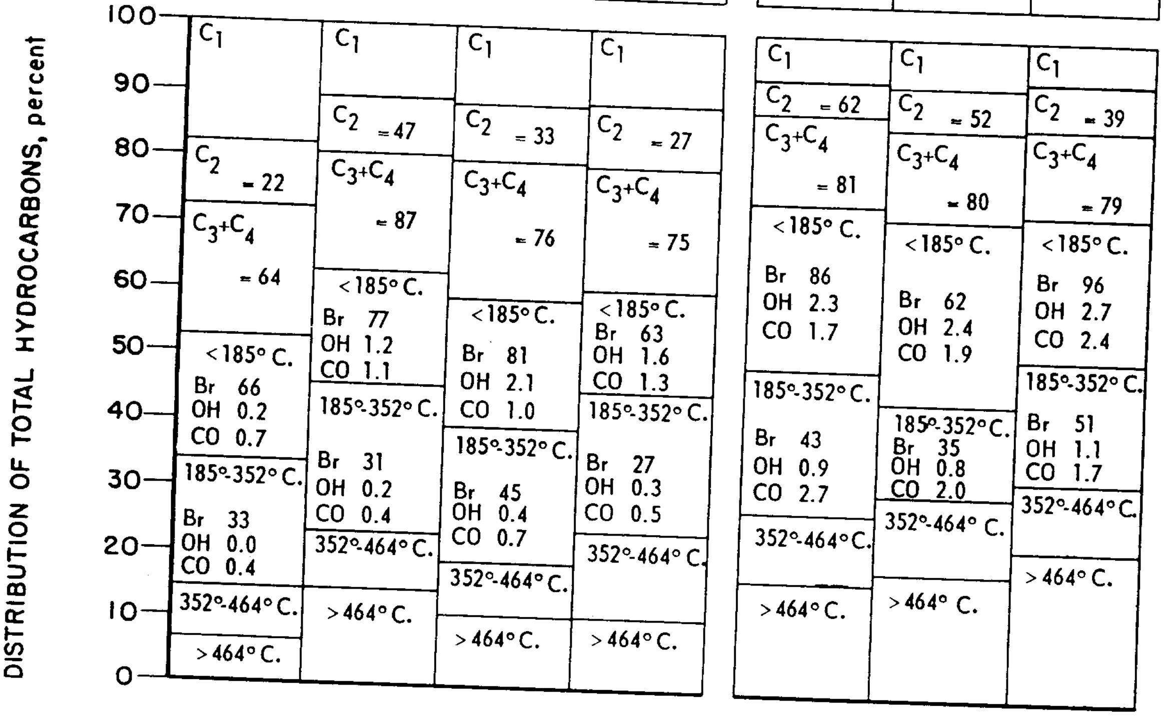

FIGURE 5.—Product composition of Reduced and Carbided Catalyst, D3001, With $1H_2+1CO$ Gas at 7.8 and 21.4 Atmospheres. Symbols representing phases are defined in tables 1 and 3. Total hydrocarbons includes oxygenated material dissolved in liquid phase.

Changes in composition of catalysts in the tests described in the previous section were followed as a function of time. Figures 7 to 11 present phases identified by X-ray diffraction and changes in carbon and oxygen contents from chemical analyses for tests at 7.8 to 21.4 atmospheres. Data from chemical analyses are presented as atom ratios C:Fe and O:Fe. Since X-ray analyses indicated that α-iron was present in only minor amounts, an estimate of the content of Hägg carbide was made, assuming that the iron of the catalyst was present as either Fe_3O_4 or Fe_2C. This value, expressed as atom ratio C:Fe, represents the maximum amount of carbide. A further complication of this simple approximation is the presence of carbonates in the samples. Analyses for carbon dioxide and iron were made on the final samples of each series. These data and the corrections to the atom ratios of total carbon, carbidic carbon, and oxygen to iron, assuming that carbon dioxide was present as magnesium carbonate, are given in table 3. Corrected values were used for only the data of tests X320 and X342 in figure 10. Uncorrected data used in other figures show the trend of composition changes satisfactorily.

The data of Figures 7 to 11 may be summarized as follows:

1. The atom ratio O:Fe increased during synthesis, approaching the value for magnetite, namely, 1.3 in tests at 14.5 and 21.4 atmospheres. The rate of oxidation increased with operating pressure.

2. The atom ratio total C:Fe increased rapidly in the first 5 days of synthesis and then either remained constant or decreased. At 7.8 atmospheres the total C:Fe remained essentially constant after the initial increase, but from 11.1 to 21.4 atmospheres the atom ratio total C:Fe decreased with time. In the initial period the total C:Fe increased from about 0.5–0.6 to 0.7.

3. Although only approximations, the values for

maximum carbidic carbon showed the same trends as the phases from X-ray diffraction. As the synthesis proceeded, X-ray-diffraction lines of magnetite appeared. The lines of magnetite increased in intensity, and those of Hägg carbide decreased. In tests at 14.5 and 21.4 atmospheres, the magnetite lines eventually became the prominent pattern, and in some experiments at 21.4 atmospheres the lines of Hägg carbide disappeared. In tests at 21.4 atmospheres, lines of metallic iron were found in the used catalysts. In a subsequent section magnetic analyses of two of these carbided catalysts are shown to agree reasonably well with the estimates from chemical analyses.

4. At 21.4 atmospheres the rate of oxidation and the rate of removal of carbon were greatly decreased by operation at low conversions—about 25 percent in test X428, compared with 65 percent in X320 and X342. It should be noted that the amount of synthesis gas

Test number	X294	X408	X394	X342
Phases present	χ, α	χ	χ	χ, α
Pressure, atm.	7.8	11.1	14.5	21.4
Temperature, °C.	229	239	235	243
Space velocity, hr.$^{-1}$	106	245	247	334
Contraction, percent	63.7	63.6	64.3	63.2
Activity, A_{Fe}	53	87	106	104

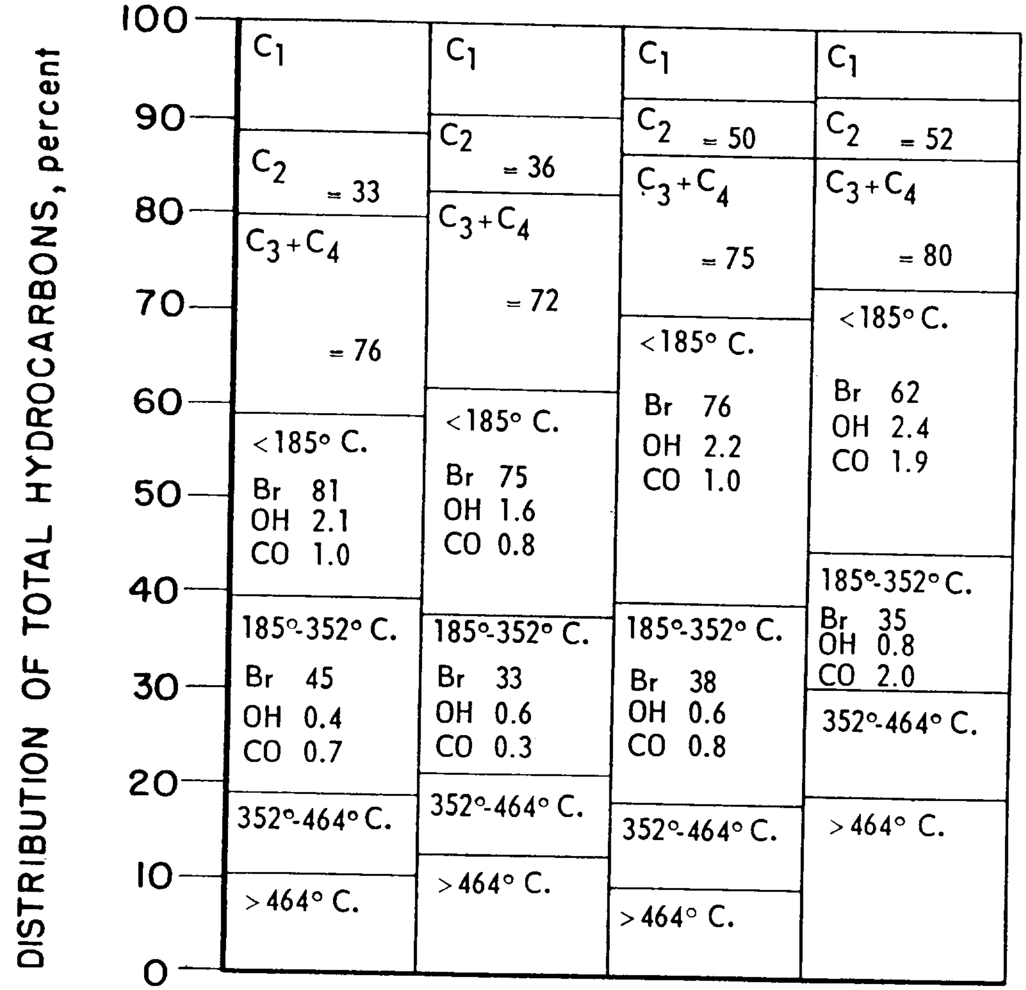

FIGURE 6.—Product Composition of Carbided Catalyst, D3001, as a Function of Operating Pressure. Symbols representing phases are defined in tables 1 and 3. Total hydrocarbons includes oxygenated material dissolved in liquid phases.

TABLE 3.—*Composition changes of catalysts showing carbonate content*

Test X—	Operating pressure, atmosphere	Time, days	CO_2,[1] percent	Total C:Fe	Atom or mole ratios [2]			Phases from X-ray analysis [3]
					Maximum carbidic C:Fe	O:Fe	CO_2:Fe	
289	7.8	194	3.52	0.673 (.610)	0.289 (.336)	0.564 (.438)	0.063	χ, *M*
408	11.1	76	4.15	.546 (.469)	.185 (.243)	.840 (.686)	.077	*M*, χ
394	14.5	20		.630	.191	.824		*M*, χ, *S*
		48	5.27	.536 (.431)	.036 (.119)	1.235 (1.023)	.105	*M*, χ, *S*
320	21.4	21	6.32	.493 (.368)	.030 (.123)	1.254 (1.004)	.125	*M*, α
323	21.4	39	5.45	.504 (.409)	.284 (.356)	0.574 (.384)	.095	*M*, α
325	7.8, 21.4	70	5.66	.392 (.255)	.055 (.137)	1.186 (0.968)	.109	*M*, α
339	21.4	57	7.70	.347 (.188)	0 (.026)	1.58 (1.26)	.159	*M*, *S*
342	21.4	37	5.31	.487 (.377)	0 (.029)	1.47 (1.26)	.110	*M*, α, *S*
416	21.4	16	0.46	.265	.134	.975	.008	*M*, α

[1] Weight-percent CO_2 on extracted sample; iron was also determined on this sample.

[2] Values in parentheses are corrected for carbon and oxygen as carbon dioxide, assuming that it is present as $MgCO_3$.

[3] Phase presented in order of decreasing intensity of diffraction pattern: χ=Hägg carbide; *M*=magnetite; α=metallic iron; *S*=carbonate as $MgCO_3$ or $FeCO_3$.

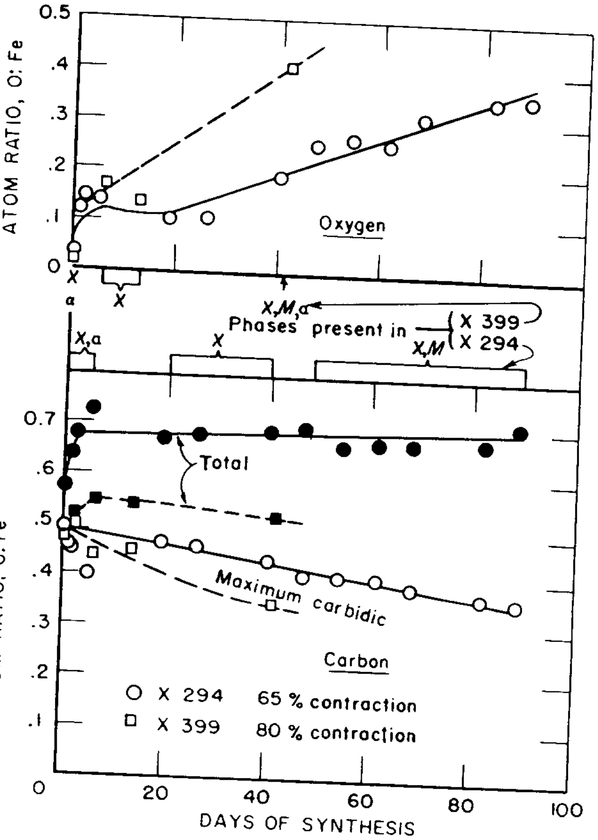

FIGURE 7.—Composition Changes of Carbided Catalyst, D3001, in Synthesis With $1H_2+1CO$ Gas at 7.8 Atmospheres. Symbols representing phases are defined in tables 1 and 3.

converted per unit time was greater in test X428 at the lower conversion. Similarly, in tests at 7.8 atmospheres, a catalyst operated at about 80-percent conversion (X399) oxidized more rapidly than the sample tested at 65-percent conversion (X294).

5. In tests at 7.8 to 14.5 atmospheres the catalyst retained sufficient mechanical stability to permit long periods of synthesis without plugging the reactor tube even in experiments in which the catalyst was repeatedly removed from the reactor for sampling. The stability of the sample in the test at 14.5 atmospheres was very good in view of the high degree of oxidation in this test. With Hägg carbide at 21.4 atmospheres and high conversions, particle deterioration and plugging of the reactor terminated most of the tests in 2 to 4 weeks. Sampling was difficult because the catalyst was caked in the reactor; therefore, the analytical data shown in figure 10 are from two separate tests that were terminated after 3 and 6 weeks of synthesis.

6. With catalyst D3001 the carbon dioxide content of the used catalyst increased with operating pressure. In a few experiments at 14.5 and 21.4 atmospheres diffraction lines corresponding to $MgCO_3$ or $FeCO_3$ were found. These phases are isomorphous and cannot be distinguished by X-ray diffraction. However, it seems likely that most of the carbon dioxide is present as magnesium carbonate, since sizable amounts of carbon dioxide were found in catalysts containing magnesia as promoter, and only small amounts were found in preparations promoted with alumina or zirconia (*75*). Furthermore, the ratio CO_2:Fe exceeded the value of 0.10, corresponding to complete conversion of magnesia and potassium oxide to carbonates by significant amounts in only two samples.

7. In a 21.4-atmosphere test of fused catalyst D3008 (Fe_3O_4-Al_2O_3-K_2O) converted to Hägg carbide (fig. 11), both oxidation and particle deterioration proceeded rapidly, and the reactor plugged during the 3d week of synthesis. The X-ray-diffraction pattern of metallic iron was found in all samples.

8. The carbide of Eckstrom and Adcock (*30*), the

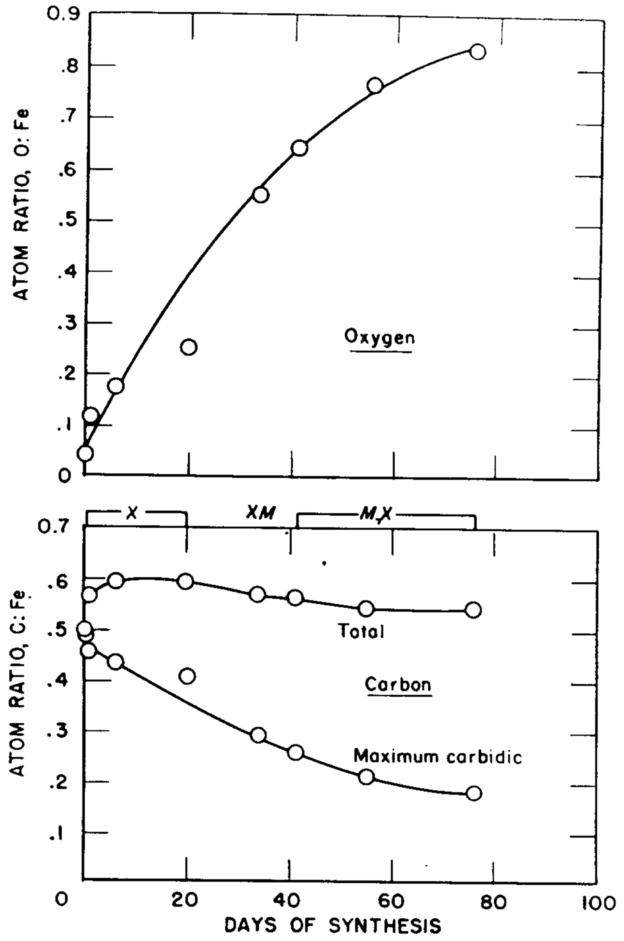

FIGURE 8.—Composition Changes of Carbided Catalyst, D3001, in Synthesis With $1H_2+1CO$ Gas at 11.1 Atmospheres, Test X408. Symbols representing phases are defined in tables 1 and 3.

hexagonal carbide, and cementite were not found in any of the catalysts after pretreatment or use in synthesis.

Fused catalysts converted to Hägg carbide have about the same selectivity as the corresponding reduced samples. The only significant difference was the higher usage ratios, $H_2:CO$, observed for the carbided samples. Available data (*13*) indicate that the principal primary synthesis reaction has a usage ratio of about 2, and this value is decreased by the water-gas shift reaction. Thus, the magnitude of usage ratio may largely depend upon the rate of the water-gas reaction, and if this reaction scheme is correct, it may be inferred that carbides are somewhat less active catalysts for this step. Data of Kölbel (*56*) showing that the water-gas shift reaction ($1H_2O+1CO$ at 240° C. and 1 atmosphere) proceeds more slowly on carbided than on reduced catalysts are consistent with these results.

In the synthesis with catalysts converted to Hägg carbide, the total carbon content increased in the first few days of testing. The initial increase in carbon content may result from two processes: (*a*) The formation of magnesium carbonate in catalyst D3001, and (*b*) con-

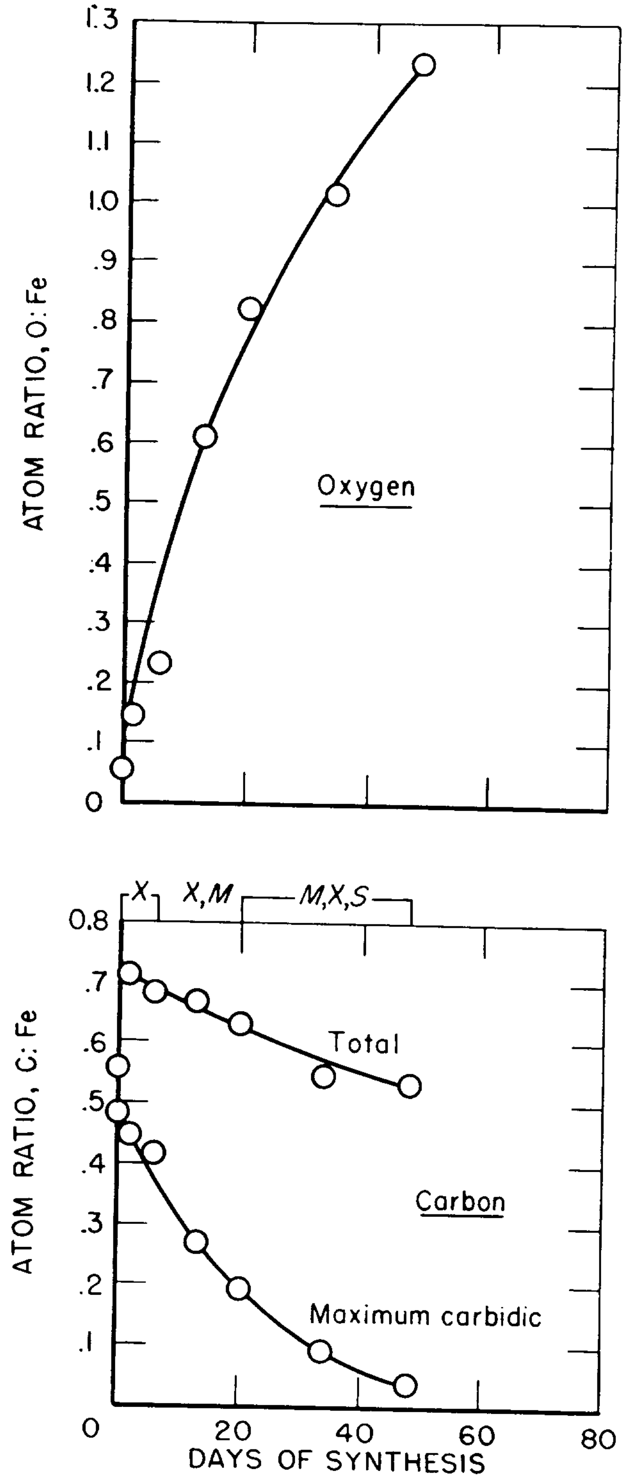

FIGURE 9.—Composition Changes of Carbided Catalyst, D3001, in Synthesis With $1H_2+1CO$ Gas at 14.5 Atmospheres (Test X394). Symbols representing phases are defined in tables 1 and 3.