

ACTIVITY AND SELECTIVITY IN THE FISCHER-TROPSCH SYNTHESIS

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

The following generalizations may be made:

(1) All active elements have partly filled *d* bands; (2) in the iron group active phases are ferromagnetic (this is probably a corollary of criterion 1); (3) for the iron group active phases, including metals, nitrides, carbonitrides, and oxides, can be converted to carbides by treatment with carbon monoxide at synthesis temperatures (150° to 300° C.); and (4) oxides of active elements are reducible in hydrogen at temperatures less than 500° C., and the ratio $p_{H_2O}:p_{H_2}$ required to produce bulk oxide from the metal is not lower than the value for iron, 0.013.

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

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

In the last 10 years nitrides and carbonitrides of iron have been found to be effective Fischer-

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

Phase	Formula ¹	Activity	Ferromagnetic
Metallic iron	α -Fe	High	Yes.
Magnetite	Fe ₃ O ₄	Probably high	Yes.
Ferrie oxide	α -Fe ₂ O ₃	Unknown ²	No.
Ferrous oxide	γ -Fe ₂ O ₃	do ²	Yes.
Iron carbides:	FeC	do ³	No.
Hexagonal	ϵ -Fe ₃ C	High	Yes.
Hägg	χ -Fe ₃ C	do	Yes.
Cementite	Fe ₃ C	do	Yes.
"FeC"	~"FeC" ⁴	do	Yes.
Iron nitrides	γ -Fe ₄ N	do	Yes.
	ϵ -Fe ₃ N-Fe ₂ N	do	Yes.
Iron carbonitrides	γ -Fe ₃ (N,C)	do	Yes.
	ϵ -Fe ₂ (N,C)	do	Yes.
Metallic cobalt	α -Co	do	Yes.
	β -Co	do	Yes.
Cobalt oxide	Co ₃ O ₄	Low ⁴	Yes.
Cobalt carbide	Co ₃ C	do	No.
Metallic nickel	Ni	High	No.
Nickel oxide	NiO	do	Yes.
Nickel carbide	Ni ₃ C	Low ⁴	No.
Sulfides, chlorides, sulfates of iron, cobalt, and nickel.	do	do	No.

¹ Formulas shown are only approximate. In some instances composition may vary over a range.

² These phases are probably not stable in the synthesis and revert to magnetite, iron, or iron carbide.

³ Uncertainties in the composition of the so-called "FeC" carbide are very large.

⁴ May reduce at synthesis conditions; however, initial activity is low.

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

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

¹⁴ Anderson, R. B., Shultz, J. F., Seligman, B., Hall, W. K., and Storch, H. H., Studies of the Fischer-Tropsch Synthesis. VII. Nitrides of Iron as Catalysts: Jour. Am. Chem. Soc., vol. 72, 1950, pp. 3502-3508.

¹⁵ Anderson, R. B., and Shultz, J. F., Iron Nitride Catalyst in Carbon Oxide Hydrogenation: U.S. Patent 2,629,728, Feb. 24, 1953.

¹⁶ Anderson, R. B., Iron Nitrides as Fischer-Tropsch Catalysts: Advances in Catalysis, vol. V., Academic Press, Inc., New York, N.Y., 1953, pp. 355-384.

¹⁴ For example, Baltzis, J. H., Hydrocarbon Polymers From Carbon Monoxide: U.S. Patent 2,795,561, June 11, 1957.

¹⁵ See footnote 12, p. 3.

conditions²⁰ indicate that this catalyst could contain magnetite, possibly a poorly defined form of Hägg iron carbide, and free carbon. This poorly defined Hägg iron carbide can sometimes be detected only by magnetic analysis. The diffraction analysis of the catalyst in test X341 both before and after operation is consistent with the above observation, except that reflections of metallic copper can also be detected.

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

With fused iron oxide catalysts similar changes in selectivity can be produced by varying the pretreatment; in addition, the activity of these catalysts may be varied over a wide range by the pretreatment. The standard fused catalyst, D3001, has the following composition in the raw state: Fe 67.4, MgO 4.6, K₂O 0.6, SiO₂ 0.7, and Cr₂O₃ 0.7 weight-percent, the remainder being oxygen in this state. The catalyst has the structure of a mineral magnetite in which the nonferrous constituents are dissolved in solid solution. The surface area is also well below 0.1 m.²/g. Samples of 6- to 8-mesh catalyst D3001 were given the pretreatments shown in table 2 before being used in the synthesis with 1H₂+1CO gas at 300 p.s.i.g. pressure and an hourly space velocity of 300. Although the conditions of reduction varied

somewhat, these differences produced only small changes in activity and selectivity.

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

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

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

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

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

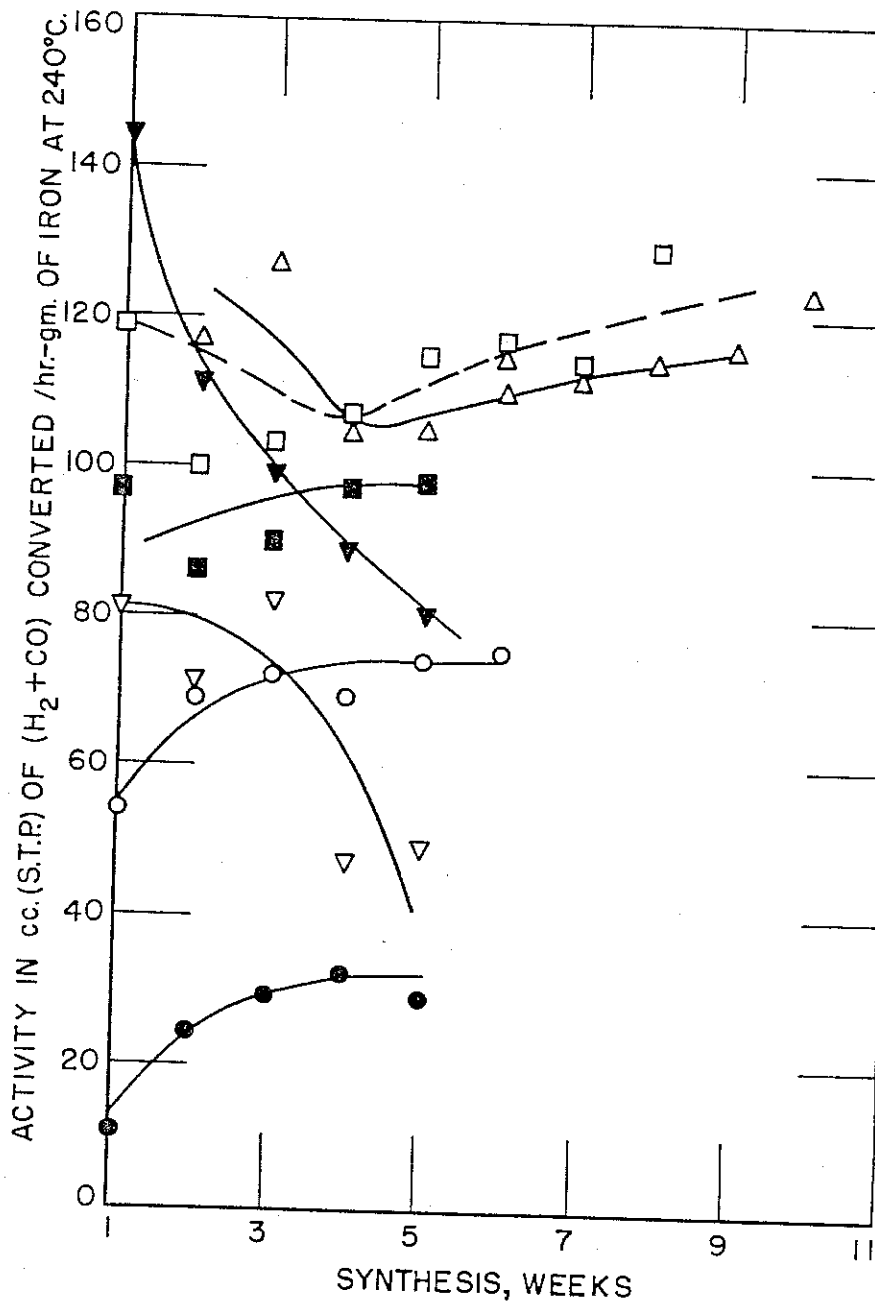
²² Shultz, J. F., Hall, W. K., Seligman, B., and Anderson, R. B., Studies of the Fischer-Tropsch Synthesis. XIV. Hägg Iron Carbide as Catalysts: Jour. Am. Chem. Soc., vol. 77, 1955, pp. 213-221.

²³ See footnote 16, p. 4.

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

TABLE 2.—Pretreatment of catalyst D3001

Test	Reduction temperature, ° C.	Subsequent treatment		Initial catalyst composition, atom ratios			Phases present
		Gas	Temperature, ° C.	C:Fe	N:Fe	O:Fe	
X282	400-525	None	None	0	0	0	α-Fe.
X397	450	H ₂ O in N ₂	325	0	0	.73	α-Fe, Fe ₃ O ₄ .
X343	500	CO	250	.37	0	-----	Fe ₃ C, α-Fe.
X342	500	He	475	.44	0	-----	Fe ₃ C(Hägg), α-Fe.
X407	550	CO	150-350	.32	.20	-----	ε-Fe ₂ (N,C).
X279	550	CO	150-250	.30	.23	-----	ε-Fe ₂ (N,C).
X225A	550	NH ₃	350	0	.44	-----	ε-Fe ₂ N.
		NH ₃	400				
		CO	350				
		NH ₃	350				



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|---|---|
| ○ X282 Reduced | ● X397 Reduced & oxidized |
| ▽ X343 Cementite | ▼ X342 Hägg carbide |
| ■ X407 Carbonitride
(carb. & nitrided) | □ X279 Carbonitride
(nitrided & carb.) |
| △ X225A Nitrided | |

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

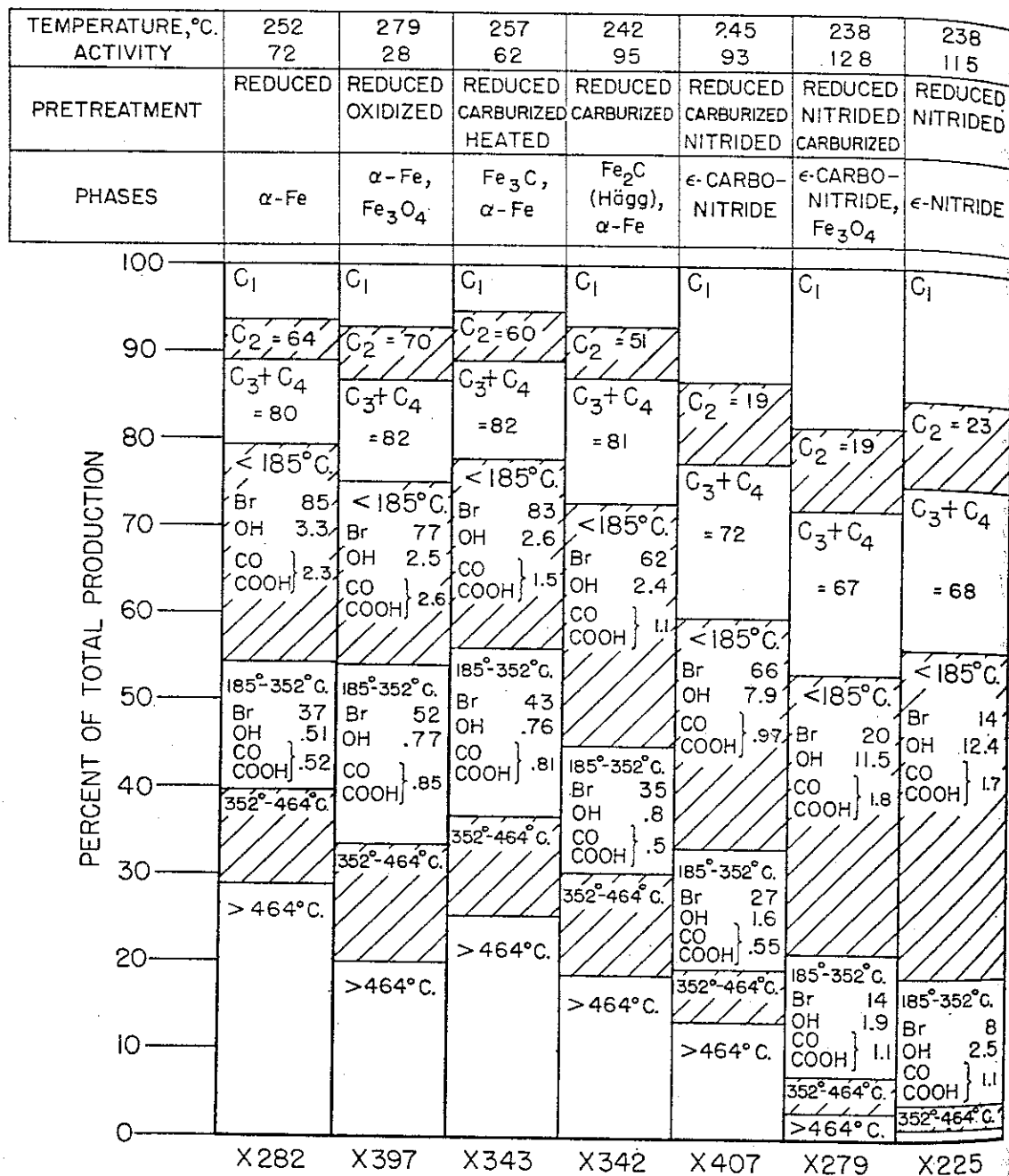


FIGURE 3.—Selectivity of Catalyst D3001 After Various Pretreatments. Synthesis with $1\text{H}_2+1\text{CO}_2$ Gas at 300 p.s.i.g. Notations in blocks: Br, Bromine number of fraction; OH, CO, and COOH, weight-percentages of these groups.

iron catalysts converted to interstitial phases (carbides, nitrides, or carbonitrides) are higher than the initial activities of reduced catalysts; however, this advantage may be lost owing to chemical changes. Reduced catalysts oxidize rapidly at both 100 and 300 p.s.i.g. Carbides (Hägg and cementite) resist oxidation at 100 p.s.i.g. but oxidize as rapidly as reduced catalysts at 300 p.s.i.g.; this reaction may

account for their rapidly decreasing activity at this pressure. Nitrides, however, resist oxidation at both pressures. Figure 4 shows the chemical changes occurring in a nitrided catalyst during synthesis at 100 p.s.i.g. pressure. In 75 days of synthesis with $1\text{H}_2+1\text{CO}$ gas at 100 p.s.i.g. the following percentages of the iron were converted to magnetite: Reduced catalyst, 38; Hägg carbide, 20; and ϵ -nitride, 9.

The unusual properties of nitrides and carbonitrides of iron suggest studies of other interstitial phases of iron-group metals, such as borides, borocarbides, boronitrides, etc.

Unfortunately, these phases, as well as nitrides of cobalt and nickel, are very difficult to prepare in the finely divided state essential for catalysis.

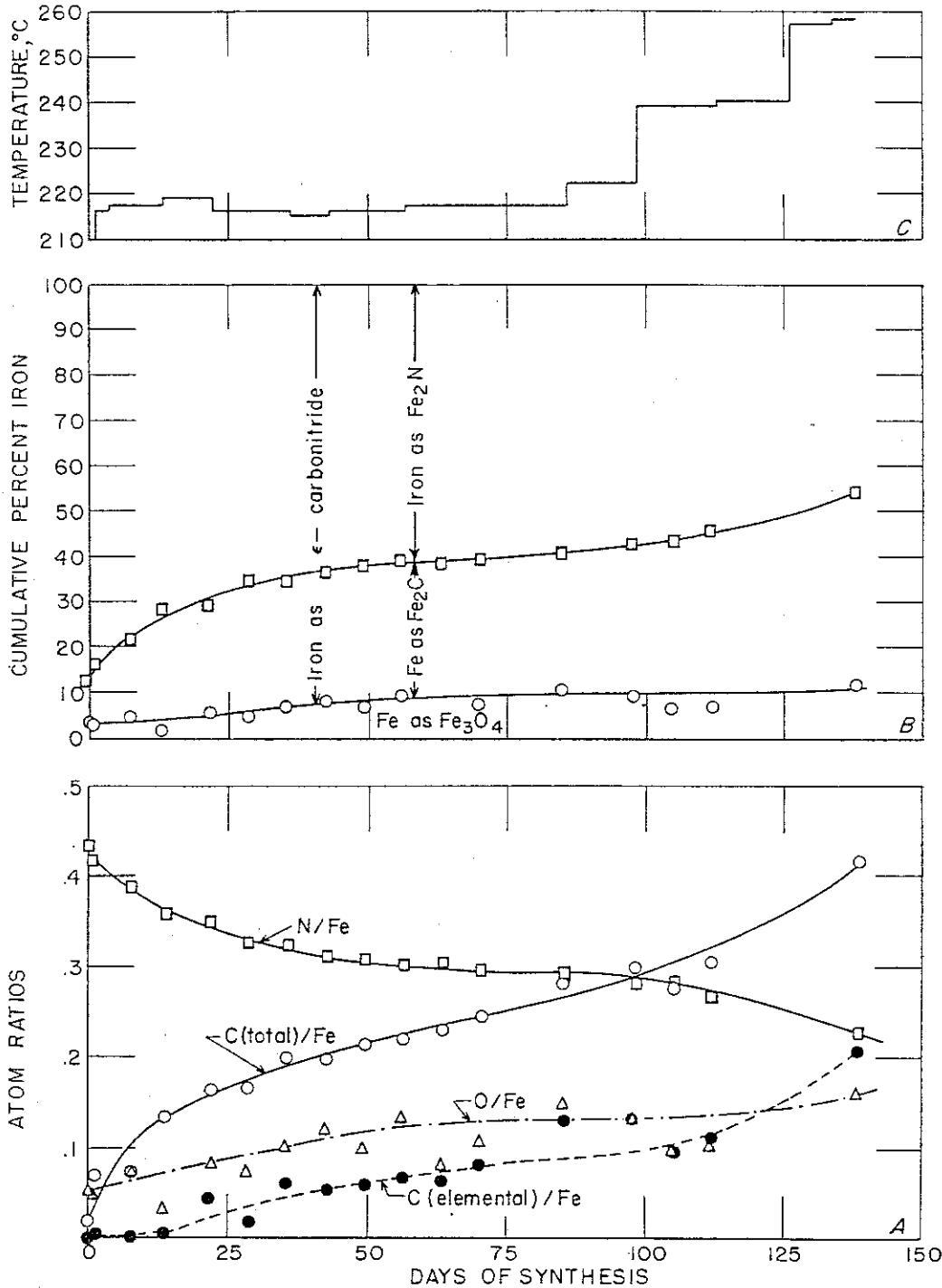


FIGURE 4.—Changes in Composition of Catalyst D3001 During Synthesis With $1\text{H}_2 + 1\text{CO}$ Gas at 100 p.s.i.g. in Test X218: A, Atom ratios of nitrogen, total carbon, elemental carbon, and oxygen to iron; B, distribution of iron as carbonitride and magnetite; C, temperature.

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