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 $p_{\text{H}_{20}}$: $p_{\text{H}_{2}}$ 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 molyb-denum 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

		J 1	- S
Phase	Formula 1	Activity	Ferro- magneti
Ferrico oxide Ferrous oxide Iron carbides: Hexagonal Hägg Cementite "FeC" Iron nitrides Iron carbonitrides Metallic cobalt Cobalt oxide Ochalt carbide Metallic nickel Nickel oxide	(ε-Fe ₂ (N,C) (α-Co (β-Co 	Probably high Unknown 2do 2do 3do 3do 3do 3do dodododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododododo	No. Yes. No. Yes. Yes. Yes. Yes. Yes. Yes. Yes. Yes

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

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

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

very large.

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

Tropsch catalysts. 15-18 Nitrides can be prepared by treating reduced iron catalysts with ammonia at 300° to 350° C. Although these nitrides are hydrogenated very rapidly in pure hydrogen, in synthesis gas at 5 to 30 atmospheres and at temperatures lower than 270° C. a large fraction of the nitrogen remains for long periods; most of the nitrogen eliminated is replaced by carbon to form carbonitrides.

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

For example, Balthis, J. H., Hydrocarbon Polymers From Carbon Monoxide: U.S. Patent 2,795,561, June 11, 1957.
 See footnote 12, p. 3.

¹⁸ 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. If Anderson, R. B., and Shultz, J. F., Iron Nitride Catalyst in Carbon Oxide Hydrogenation: U.S. Patent 2,629,728, Feb. 24, 1953. If Anderson, R. B., Iron Nitrides as Fischer-Tropsch Catalysts: Advances in Catalysis, vol. V, Academic Press, Inc., New York, N.Y., 1953, pp. 355-384.

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

Figure 1 shows changes in selectivity produced by various pretreatments for a precipitated Fe₂O₃-CuO-K₂CO₃ catalyst used in synthesis with 1H₂+1CO gas at 7.8 atmospheres. ¹⁹ The distribution of hydrocarbons plus oxygenated organic molecules is shown as gaseous hydrocarbons and distillation cuts of condensed fractions. The symbols and numbers have the following meaning: (=) Volume-percent olefins in gaseous fractions; (Br) bromine number of liquid fractions; and (OH) and (CO), the weight-percent of hydroxyl and carbonyl groups, respectively.

Despite different pretreatments, the average activity was essentially constant. In test X149 the catalyst was pretreated with synthesis gas at atmospheric pressure and 230° C. In tests

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

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

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

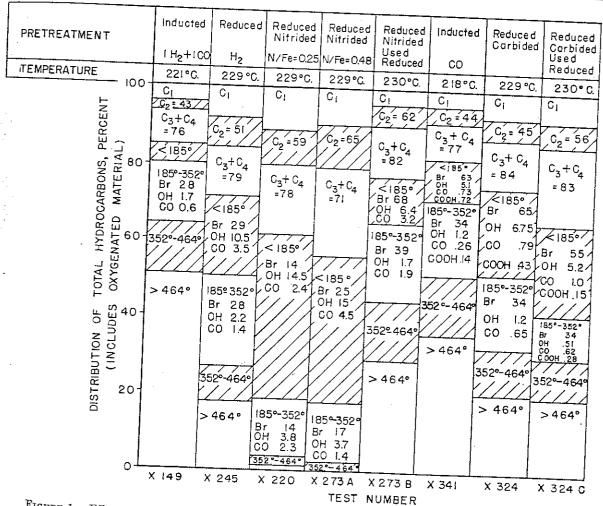


Figure 1.—Effect of Pretreatment of Precipitated Catalyst P3003.24 on Composition of Products.

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

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

With fused iron oxide catalysts similar changes in selectivity can be produced by varying the pretreatment; in addition, the activity of these catalysts may be varied over a wide range by the pretreatment. The standard fused catalyst, D3001, has the following composition in the raw state: Fe 67.4, MgO 4.6, 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

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.

somewhat, these differences produced onl_{V} small changes in activity and selectivity.

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

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

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

Table 2.—Pretreatment of catalyst D3001

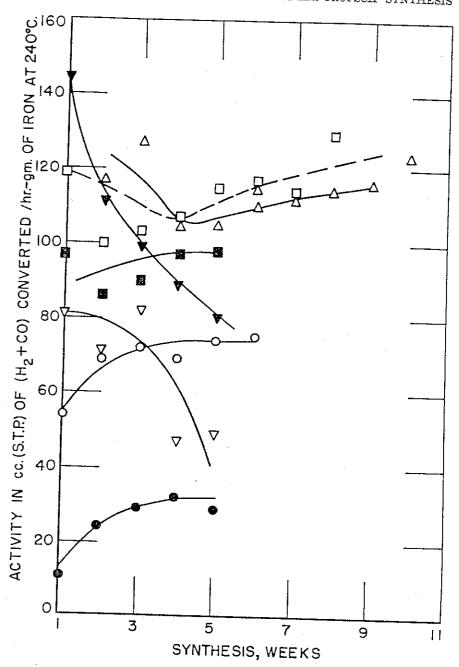
${f Test}$	Reduction tempera- ture, ° C.	Subsequent treatment		Initial catalyst composition, atom ratios				
		Gas	Tempera- ture, ° C.	C:Fe	N:Fe	O:Fe	Phases present	
282	400-525 450 500 500 550 550	None H ₂ O in N ₂ CO He CO NH ₃ CO NH ₃ CO	None 325 250 475 150-350 150-250 350 400 350 350	$\left.\begin{array}{c} 0\\0\\0\\3\\37\\.44\\3\\.32\\\end{array}\right\} \\ \left.\begin{array}{c} 32\\0\\0\\\end{array}\right\}$	0 0 0 0 . 20 . 23	0 . 73	α -Fe. α -Fe, Fe ₃ O ₄ . Fe ₃ C, α -Fe. Fe ₂ C(Hägg), α -Fe. ϵ -Fe ₂ (N,C).	

²¹ Shultz, J. F., Hall, W. K., Dubs, T. A., and Anderson, R. B., Studies of the Fischer-Tropsch, Synthesis. XV. Cementite as Catalysis: 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 Mitrided Iron Catalysts During the Synthesis: Jour. Am. Chem. Soc., vol. 74, 1952, pp. 637–640.



- O X282 Reduced
- ∇. X343 Cementite
- X407 Carbonitride (carburized, nitrided)
- Δ X225A Nitrided
- X397 Reduced & oxidized
- ▼ X342 Hägg carbide
- ☐ X279 Carbonitride (nitrided, carburized)

Figure 2.—Effect of Pretreatment on Activity of Catalyst D3001 (1H₂+1CO Gas at 300 p.s.i.g.)

TEMPERATURE,°C.	252	279	257	040	045	07.0	
ACTIVITY	72	28	62	242 95	245 93	238 .128	238
· · · · · · · · · · · · · · · · · · ·	REDUCED	REDUCED	REDUCED	REDUCED	REDUCED	REDUCED	115 PED:105
PRETREATMENT		OXIDIZED		CARBURIZED	CARBURIZED		REDUCED NITRIDED
			HEATED		NITRIDED	CARBURIZED	ייייויוטבּט
		α-Fe,	Fe ₃ C,	Fe _p C	€- CARBO-	€-CARBO-	
PHASES	α-Fe	Fe ₃ O ₄	α-Fe	(Hägg),	NITRIDE		€-NITRIDE
		1 3 4	α-, ε	α-Fe	HILL	Fe ₃ O ₄	
100							
	C ₁	C _I	C ₁	Cl	Cl	Cı	C
			C ₂₌₆₀				
90	C2 = 64	G2 = 70/	V / / /	C2 = 51			
	C ₃ + C ₄	///	C ₃ + C ₄	////	, , , . ,		
	= 80	C ₃ +C ₄	• .	C ₃ +C ₄	C ₂ = 19		
80		±82	=82	±8I		C2 =19	$C_2 = 23$
2	/< I85°c/		<185°C	_	2///	02///	
TOTAL PRODUCTION	Br 85	< 185°C.	r ,		C ₃ +C ₄		
을 70	он 3.3/		Br 83 OH 2.6	<í85°C.1	= 72	C ₃ +C ₄	C ₃ +C ₄
Ō	kan'i	OH 2.51	(a) 1	Br 621	- 12	3, 4	3
Ř	COOH 2.3	100 1 2	COOH 1.5	OH 2.4		= 67	= 68
¹¹ , 60	1///	COOH 2.6	777/	CO 1	· · · · · · · · · · · · · · · · · · ·		
ÄL	Y////			[соон] /"[Ĺ<185°¢.∕		
OT	105° 750° 0		185°-352°C,		Br 661	, , , , , , , , , , , , , , , , , ,	. <185°C.′
<u></u> 50.——	185°-352° G. Br 37	185 ² -352°C,	Br 43		OH 7.91	. <185°C.1	Z 1
FO 30	Br 37 OH .51	Br 52 OH .77	OH .76	////	.97 .97	0- 001	Br 141
	СО СООН .52		.81	185°-352°C.	COOH] .9	04 115	OH 12.4
- 40 		COOH) .85	COOH) 'BI	Br 35		COOH LB	COOH 1.7
ŞC	352°-464°C			он .в.		COOH ,	11/
PERCENT 0 04		352°-464° C.	352°-464° C.	COOH .5			
^L 30		352-464 C.			185°-352° C.		
	> 464°C.				Br 27	////	
	}			////	OH 1.6		
20	· •		>464°C.		CO _{OH} .55	/ 185°-352°C.	
		>464°C.		>464°C.	352°-464°C.	Br 14	85°-352°C.
			İ	-404°C.	////	OH 1.9	Br 8
10 —	ľ	[ļ	j	>464° C.	COOH LI	
						00011	COOH LI
	ļ				Ł	/ / / / L	552°-464° G.1
0				l		>464°C.	, TO T. VI
•	X 282	X 397	X343	X342	X 407	X279	X225

Figure 3.—Selectivity of Catalyst D3001 After Various Pretreatments.

Synthesis with 1H₂+1CO₂ 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 statistics. 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 1H₂+1CO gas statistics. 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.

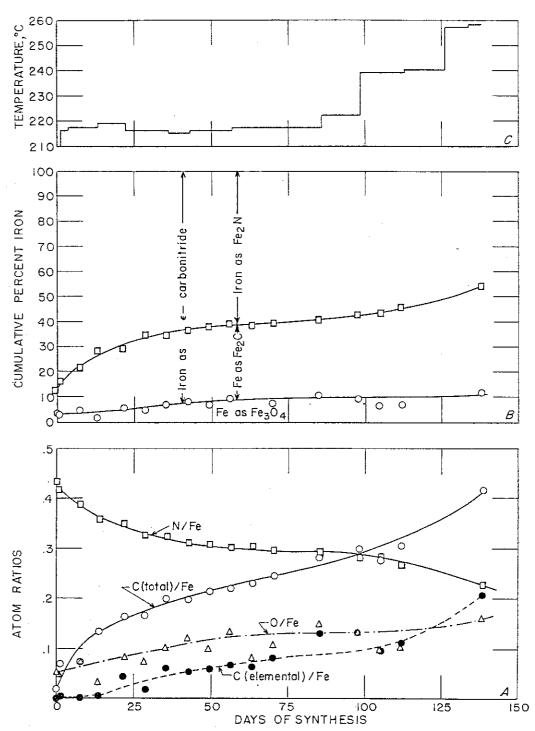


FIGURE 4.—Changes in Composition of Catalyst D3001 During Synthesis With 1H₂+1CO Gas at 100 p.s.i.g. in Test X218: A, Atom ratios of nitrogen, total carbon, elemental carbon, and oxygen to iron; B, distribution of iron as carbonitride and magnetite; C, temperature.

1.7 C. 8.5. L. C. 5 OH,

oxidaws the atalyst re. In gas at of the educed ride, 9.