In summary, then, the experimental values illustrated by the curve in Fig. 4 seem to be explainable as steady state values and not as true equilibrium values. Below 1450°, the observed methane values seem to be too high in consequence of the phenomenon of thermal diffusion (considered in a microscopic rather than a macroscopic sense) and probably of some other unexplained causes. Above 1450°, it seems likely that radicals such as CH, CH_2, or CH_3 are being formed in increasing quantities as the temperature increases and that these radicals on diffusing out away from the hot zone and into the cooler regions of the reaction vessel combine in some way to form methane. Possibly the gradual decrease in the methane content above 2000° is best explained by the preferential reactions of these radicals to form C_2H_4 rather than CH_4 at the higher temperatures. The formation of acetylene in the cool gas is probably due, in part at least, to the equilibrium formation of acetylene on the hot carbon rod and to its diffusion outward into the cooler part of the reaction system.

Conclusion.—I should still like to remark that the detailed investigation of such a system permits thermochemical estimations to be made which could not easily be reached otherwise. It is especially a useful way to demonstrate the existence of lower-valent species at high temperatures which cannot be obtained at ordinary temperatures. I believe that a more adequately worked out theory of the principle of this apparatus will lead to many practical advantages.

Summary

The reaction of carbon and hydrogen has been investigated between 1100–2600°. The concentration of methane, as a function of temperature shows a minimum at 1450° and a maximum at 2000°. Acetylene and ethylene are also obtained above 2000°. The results indicate that above 1450° some lower hydride, probably CH_3 or CH_2, is present at higher concentration on the surface of hot carbon rod than is CH_4.

SZEGED, HUNGARY RECEIVED OCTOBER 22, 1948

[CONTRIBUTION OF THE RESEARCH AND DEVELOPMENT BRANCH, OFFICE OF SYNTHETIC LIQUID FUELS, BUREAU OF MINES]

Studies of the Fischer–Tropsch Synthesis. VII. Nitrides of Iron as Catalysts[1]

BY ROBERT B. ANDERSON, J. F. SHULTZ, BERNARD SELIGMAN, W. KEITH HALL AND H. H. STORCH

The hypothesis that metal carbides are active catalysts and/or intermediates in the Fischer–Tropsch synthesis has been popular for many years.[2,3] Recent studies with cobalt[4,5] and iron[6,7] catalysts indicate that carbides of these metals are probably neither the active catalyst nor an intermediate. Nevertheless, German documents[8] as well as unpublished results of the Bureau of Mines indicate that pretreatment of iron catalysts with carbon monoxide or mixtures of carbon monoxide and hydrogen in a manner that converts the iron or iron oxide, at least partly, to Fe_2C carbides or iron (hexagonal or Hägg carbides[8,9]) increased their activity in the synthesis. From the German documents, it may be inferred that, other factors influencing activity being equal, the activity increases with the carbide content; however, the data are not as conclusive as may be desired.

The present paper describes the conversion of the reduced catalyst to nitrides of iron by treatment with ammonia, a unique departure from the usual methods of pretreating iron catalysts, and considers the effect of nitriding on activity, selectivity and life of a reduced synthetic-ammonia-type catalyst. Later papers will present studies of the influence of catalyst type and composition, operation variables (temperature, flow, and type of synthesis gas), and the amounts of nitrogen and carbon in the catalyst.

The nitrides of iron have been fairly thoroughly studied. The papers of Lehrer,[10] Brunauer, Jefferson, Emmett and Hendricks,[11] and Jack[12] describe the chemistry and structure of the iron–nitrogen system in detail. Homogeneous phases in this system are:

Phase	Nitrogen, wt. %	Atom ratio, N/Fe	Arrangement of iron atoms
α	<0.2	<0.008	Body-centered cubic
γ'	5.7–6.1	0.241–0.259	Face-centered cubic
ϵ	7.3–11.1	.314– .498	Close-packed hexagonal
ζ	11.1–11.3	.498– .508	Orthorhombic

The nitrides of iron are interstitial compounds similar to, and in some cases isomorphous with, the carbides of iron. Jack[13] showed that treat-

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[1] Article not copyrighted.

[2] Fischer and Tropsch, *Brennstoff-Chem.*, **7**, 97 (1926).

[3] Craxford and Rideal, *J. Chem. Soc.*, 1604 (1939).

[4] Weller, Hofer and Anderson, THIS JOURNAL, **70**, 799 (1948).

[5] Anderson, Hall, Krieg and Seligman, *ibid.*, **71**, 183 (1949).

[6] Kummer, Browning and Emmett, *J. Chem. Phys.*, **16**, 739 (1948).

[7] Browning, DeWitt and Emmett, *ibid.*, in press; Podgurski, Kummer, DeWitt and Emmett, THIS JOURNAL, to be published.

[8] For example, Pichler and Merkel, "Chemical and Thermomagnetic Studies on Iron Catalysts for Synthesis of Hydrocarbons," Bur. Mines Technical Paper **718** (1949).

[9] Hofer, Cohn and Peebles, THIS JOURNAL, **71**, 189 (1949).

[10] Lehrer, *Z. Elektrochem.*, **36**, 383, 460 (1930).

[11] Brunauer, Jefferson, Emmett and Hendricks, THIS JOURNAL, **53**, 1778 (1931).

[12] Jack, *Proc. Roy. Soc.* (*London*), **A195**, 56 (1948).

[13] Jack, *ibid.*, **A195**, 41, 56 (1948); Goodeve and Jack, *Trans. Faraday Soc.*, 82 (1948).

ment of iron nitrides with carbon monoxide at 450° converted them to a series of carbonitrides in which carbon merely replaced the nitrogen, the crystal structure of the ϵ- or ζ-phases remaining essentially unchanged until about 75% of the nitrogen was replaced. On further carbon monoxide treatment, the Hägg carbide Fe_2C or $Fe_{20}C_9$, was formed. Above 500°, a mixture of Hägg carbide and cementite was formed by carbon monoxide treatment. It is significant that no free carbon was formed in carbon monoxide treatments of the nitrides at temperatures as high as 600°, compared with sizable amounts of free carbon known to be deposited in similar treatments of α-iron even at considerably lower temperatures.

Experimental

All of the tests described in this paper were made with a fused synthetic-ammonia-type catalyst designated by our number D3001. The catalyst was prepared by the electrical fusion method,[14,15] and had the following composition: total iron 67.4%, ferrous iron 21.7%, MgO 4.61%, K_2O 0.57%, SiO_2 0.71%, and Cr_2O_3 0.65%.

Before testing or nitriding, the catalyst was reduced in electrolytic hydrogen at 450 or 550° and a space velocity of 2,500 in a special reduction unit shown in Fig. 1. The furnace consisted of an electrically heated aluminum-bronze block that was cast about an iron pipe. The reactor was controlled by a differential expansion regulator consisting of a quartz tube traversing the length of the furnace and the block itself.[16] With the reactor at temperature and in the position shown in Fig. 1, the catalyst was placed into the tube in a nitrogen atmosphere. When the catalyst had reached reduction temperature, hydrogen was passed over it at the desired rate. At the end of the reduction period, the reactor was rotated 180° and tapped with a hammer, causing the catalyst to fall into the cooling vessel where it was cooled in hydrogen for about thirty minutes. Carbon dioxide was then passed through the cooling vessel to protect the catalyst from any accidental oxidation in transfer. With carbon dioxide flowing, the cooling vessel was detached, and the catalyst was poured through a rubber sleeve into the glass weighing bottle which was also being flushed with carbon dioxide. This bottle was then closed with its ground-glass cap, and enough carbon dioxide was passed through the cap to remove any air. The bottle plus catalyst was weighed, and the weight was compared with that of the bottle filled with carbon dioxide. After this weighing, the catalyst was either charged into the testing units or returned to the reduction furnace for nitriding. In transferring the catalyst, the following precautions were always taken: (a) The catalyst was kept in a stream of carbon dioxide, (b) no carbon dioxide was passed over the catalyst until its temperature was lower than 50°, (c) all transfers were made through rubber or metal connections so that the catalyst was never exposed to air.

Ammonia treatments, either in the reduction unit or with the catalyst in place in the testing unit, were made in a similar manner. Anhydrous ammonia was used without further purification. At the end of the ammonia treatment, the catalyst was not permitted to remain in an inert gas or in a slow flow of ammonia, because these conditions favor the hydrogenation or decomposition of the nitride. The catalyst was either immediately dropped from the reduction unit, or the temperature of the reactor was decreased rapidly while, in either case, a high flow of ammonia was maintained until the catalyst had cooled below 250°. The catalyst was then transferred and weighed; usually, a weighed sample was removed for X-ray examination.

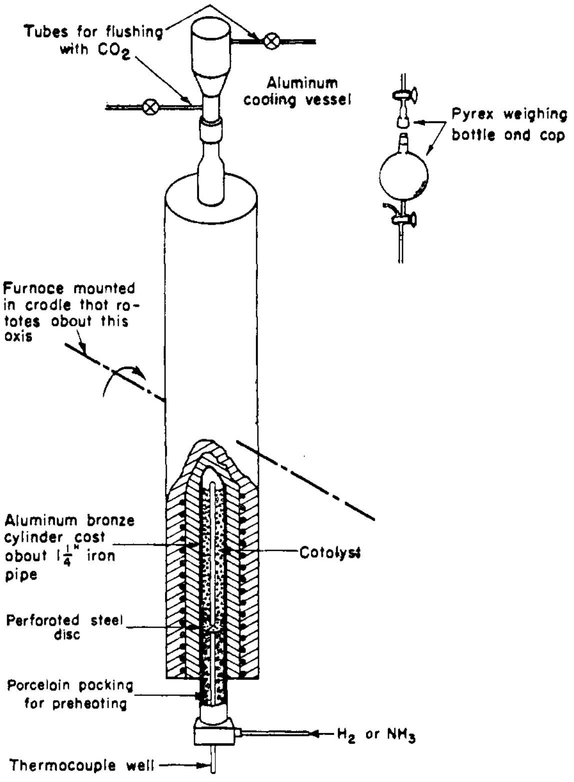

Fig. 1.—Reduction unit.

The catalyst testing apparatus has been described previously.[17,18,19] In the testing of iron catalysts, carbon dioxide was removed by both wet[20] and dry caustic scrubbers placed immediately before the charcoal traps. The catalyst was charged in a stream of carbon dioxide with the reactor at room temperature. For reduced catalysts, the carbon dioxide was swept out of the reactor with synthesis gas, the pressure was increased to the desired value, and the reactor was heated rapidly to 220°. With nitrided catalysts, the carbon dioxide was purged with helium, and the catalyst was heated rapidly to 200° in helium. Then, synthesis gas was introduced, and the pressure was increased slowly to the desired value.

Testing was continuous, except for a two-hour period per week when the products were recovered. In all experiments, the flow of synthesis gas was maintained constant, and the temperature was adjusted to give apparent contractions of 63–65%. The synthesis-gas composition was very nearly 50% hydrogen and 50% carbon monoxide, the only appreciable impurities, nitrogen and methane, being less than 0.3% each. The total sulfur content of the gas was less than 0.5 grain per 1000 cubic feet.

Gas analyses were made with a Consolidated mass spectrometer. Liquid and solid hydrocarbons were separated into four fractions by a simple 1-plate distillation over the ranges: (a) To 185° at atmospheric pressure; (b) To 225° at 10 mm. (atmospheric equivalent 185 to 352°); (c) To 225° at 1 mm. (atmospheric equivalent 352 to 464°). The two lower-boiling fractions (a and b) were analyzed for functional groups by the infrared method

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[14] Larson and Richardson, *Ind. Eng. Chem.*, **17**, 971 (1925).

[15] Bridges, Pole, Beinlich and Thompson, *Chem. Eng. Progress*, **43**, 291 (1947).

[16] N. K. Anderson and Rowe, *Ind. Eng. Chem.*, **35**, 554 (1943).

[17] Anderson, Krieg, Seligman and O'Neill, *ibid.*, **39**, 1548 (1947).

[18] Anderson, Krieg, Seligman and Tarn, *ibid.*, **40**, 2347 (1948).

[19] Storch, *et al.*, Bur. Mines Tech. Paper **709**, 77 (1948).

[20] Krieg, Dudash and Anderson, *Ind. Eng. Chem.*, **41**, 1508 (1949).

of Anderson and Seyfried.[21] Catalysts were analyzed by conventional methods. Total carbon was determined by a combustion technique and nitrogen by the Kjeldahl method. X-Ray diffraction patterns were made by the usual powder method with suitable precautions employed to prevent oxidation of reduced, nitrided and used samples.[22]

Experimental Results

A. Preparation of Nitrides.—The work of Brunauer, Jefferson, Emmett and Hendricks[11] indicates that high concentrations of ammonia in ammonia–hydrogen mixtures are necessary to form nitrides of iron and that the minimum ammonia-to-hydrogen ratio required to form nitrides decreases with increasing temperature. Thus, at 400 and 450°, 40 and 27% of ammonia are necessary to form Fe_4N; while at the same temperatures 80 and 68% of ammonia are required for the formation of an ϵ-phase nitride of composition Fe_3N. Higher fractions of ammonia are necessary to form the ϵ-phase of higher nitrogen content. Although the percentage of ammonia required for nitriding decreases with increasing temperature, this fact is of little advantage, because the rate of catalytic decomposition of ammonia to nitrogen and hydrogen increases greatly with temperature.

Superimposed on these thermodynamic restrictions is the rate of nitriding, which presumably increases with temperature. The thermodynamics of the reaction, as well as the tendency of ammonia toward catalytic decomposition, require moderately high flows of ammonia for any large extent of nitriding. As shown in Fig. 2, the rate of nitriding of catalyst D3001 at ammonia space velocities of 750 and temperatures below 350° increased with temperature, and complete nitriding was possible. At 400 and 450°, the initial rate of nitriding was rapid, but the catalytic decomposition of ammonia formed sufficient hydrogen to prevent complete nitriding. The rate and extent of nitriding at 450° was increased by doubling the flow of ammonia. At 350° and a space velocity of 750, the catalyst could be quite completely nitrided (atom ratio N/Fe > 0.45) in six hours.

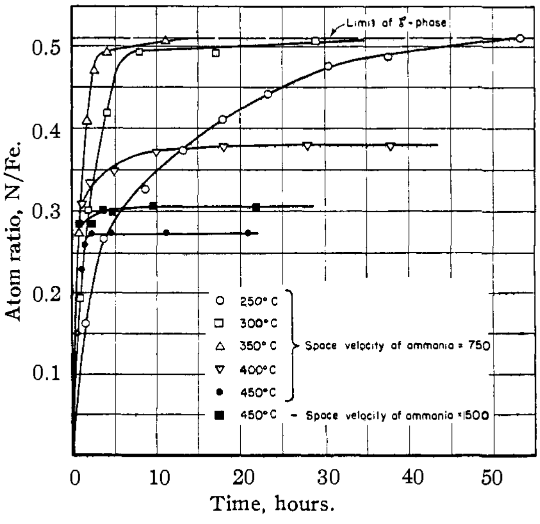

Fig. 2.—Rate of nitriding of catalyst D-3001 in ammonia at various temperatures.

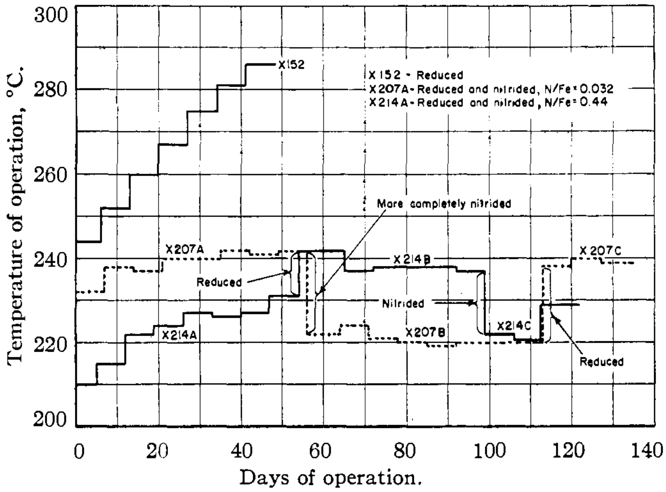

Fig. 3.—Temperatures of operation required to maintain constant conversions on reduced and nitrided samples of catalyst D3001 at 7.8 atmospheres.

B. Activity and Selectivity of Nitrided Iron Catalysts.—Figures 3 to 5 and Table I compare activity and selectivity data obtained from tests of reduced and nitrided iron synthetic-ammonia-type catalyst D3001 at 7.8 and 21.4 atmospheres (absolute) with $1H_2$-to-1CO gas. In these figures, averages of the temperatures during seven-day periods of testing are plotted against time in days. The actual temperature usually did not deviate more than 4° from this average. The space velocity of synthesis gas was maintained approximately constant at 100 and 300 for tests at 7.8 and 21.4 atmospheres, respectively, and the temperature was varied to maintain apparent contractions of about 65%. Thus, the temperature of operation is a measure of catalytic activity, the activity varying in an inverse manner with the temperature of operation. In Fig. 3, for tests at 7.8 atmospheres, the operating temperature of the reduced catalyst in Test X152 increased steadily from 250 to 286° in about forty days. In Test X207A, a catalyst that was nitrided only partially to the γ'-phase (N/Fe = 0.032) operated at 240°, a temperature significantly lower than that of X152. After fifty-six days of testing, the catalyst was treated with ammonia under conditions that should convert the iron to an ϵ-phase nitride. In subsequent testing (X207B), this catalyst

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[21] J. A. Anderson and Seyfried, *Anal. Chem.*, **20**, 998 (1948).

[22] Hofer and Peebles, THIS JOURNAL, **69**, 893 (1947).

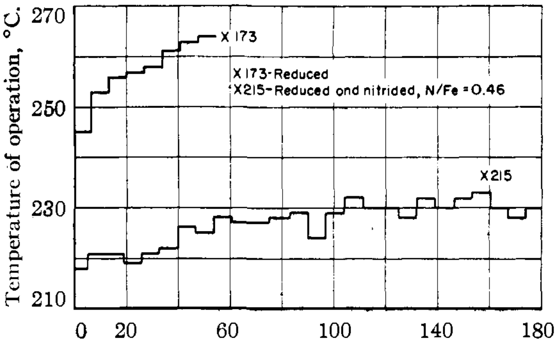

Fig. 4.—Temperatures of operation required to maintain constant conversions on samples of reduced and nitrided catalyst D3001 at 7.8 atmospheres.

maintained the required conversion at about 220°. In the 18th week of the test, the catalyst was hydrogenated at 385° under conditions that should remove all of the nitrogen. The temperature of operation (X207C) was increased to about 240°; however, it was still more active than the reduced catalyst in X152. The catalyst in Test X214A was nitrided to the ε-phase (N/Fe = 0.44). It operated initially at 210°, and the temperature had to be increased to about 230° over a period of fifty-five days. At this point the catalyst was hydrogenated to remove the nitrogen, and the temperature (X214B) increased to about 240°. After the 15th week, the catalyst was treated with ammonia under conditions that should convert the iron to an ε-phase nitride, and the temperature of operation decreased to 224°. Test X215 (Fig. 4) was a life test of an ε-phase (N/Fe = 0.46) catalyst. The catalyst in X215 was reduced at 550° before nitriding, and its activity may be compared with that of Test X173 for an unnitrided catalyst also reduced at 550°. In six months of testing in X215, the temperature required to maintain constant conversions increased from 218 to 230°. When the catalyst was removed from the reactor after 190 days of operation, the entire charge dropped freely, and the particles had the same appearance as when initially charged. This is a marked contrast to tests of reduced catalysts at 7.8 atmospheres (*e. g.*, X152 and X173), which were usually terminated in less than eight weeks by plugging of the catalyst bed by carbon deposition and related processes.

Experiments at 7.8 atmospheres indicate that nitriding only slightly into the γ′-phase lowered the operating temperatures significantly and that more complete nitriding (to the ε-phase) decreased the temperature still further. Nitrided catalysts, hydrogenated after several weeks of testing, operated at significantly lower temperatures than reduced catalysts. Nitrided catalysts operated at nearly constant temperatures compared with steadily increasing temperatures for reduced catalysts.

Operation of reduced catalysts at 21.4 atmospheres was characterized by nearly constant temperatures of operation as indicated by Test X200A (Fig. 5). After eighty-eight days of testing, this catalyst was nitrided and the temperature of operation was decreased from 260 to 245°. The catalyst in X219 was nitrided to a mixture of γ′- and ε-phases (N/Fe = 0.262), and that in X225 was converted to the ε-phase (N/Fe = 0.444). Both of these catalysts operated at constant temperatures of about 240°. Thus, at 21.4 atmospheres the increase in activity of the nitrided catalysts over the reduced was not as great as at 7.8 atmospheres.

Table I presents the conditions of pretreatment and operation of the various catalyst tests and a simple characterization of their gaseous and liquid products. The yields of C_1-to-C_4 hydrocarbons and liquid-plus-solid hydrocarbons are expressed as weight per cent. of the total.[23] In all experiments, the total of gaseous and liquid-plus-solid hydrocarbons varied from 100–120 g./cu. m. of synthesis gas. Acid numbers were determined on the total oil phase. The oil phase was separated into four fractions by a simple 1-plate distillation at atmospheric and reduced pressures. The products of the two lowest fractions were analyzed by infrared methods,[21] and the data are reported as weight per cent. of functional groups present; *i. e.*, weight per cent. of OH group or weight per cent. of α- or internal double-bond-olefins as C=C. Thus, pure ethyl alcohol has 100 × 17/46 = 37% of OH group, and pure 2-pentene has 100 × 24/70 = 34.3% internal double bond C=C group.

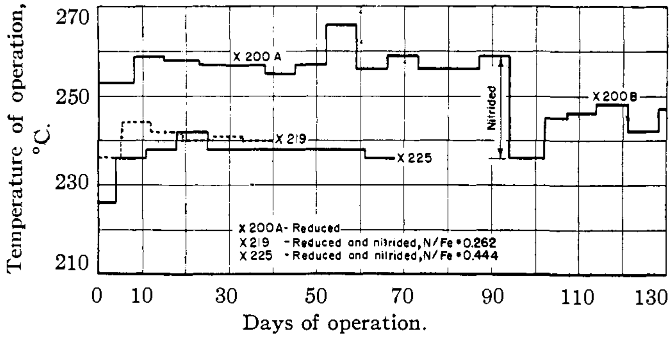

Fig. 5.—Temperatures of operation required to maintain constant conversions on samples of reduced and nitrided catalyst D3001 at 21.4 atmospheres.

At operating pressures of 7.8 atmospheres, the catalyst nitrided to only N/Fe of 0.032 in X207A, produced smaller yields of gaseous hydrocarbons, and the average molecular weight of the products was greater than that of products from the reduced

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(23) Liquids plus solids include oxygenated compounds dissolved in the hydrocarbon phases.

TABLE I

TESTS OF REDUCED AND NITRIDED CATALYST D3001 (Fe_3O_4–MgO–K_2O)

6–8 Mesh catalyst and $1H_2$ to 1CO gas

Test no.		X152	X173	X201[a]	X207A	X207B	X207C	X214A	X214B	X214C	X215	X200A	X200B	X219	X225
Reduction in H_2															
Temp., °C.		450	550	450	450	......	385	450	385	......	550	450	......	550	550
Hours		43	40	40	40	......	4	40	4	......	20	40	......	20	20
Space vel.[b]		2500	2500	2500	2500	......	1000	2500	5000	......	2500	2500	......	2500	2500
% redn.		91.8	98.2	100	96.1	......	?	100.8	?	......	100.4	92.6	......	99.0	98.1
Nitriding in NH_3															
Temp., °C.		......	......	.....	450	385	......	385	......	385	385	......	385	385	350
Hours		......	......	......	5	4	......	4	......	4	4	......	4	4	6
Space vel.[b]		......	......	......	5000	5000	......	5000	......	1000	5000	......	5000	5000	1000
Atom ratio, N/Fe		0	0	0	0.032	?	?	0.44	?	?	0.46	0	?	0.262	0.444
Fe phases present		α-Fe	α-Fe	α-Fe	α-Fe + γ′-phase	?	?	ε-phase	?	?	ε-phase	α-Fe	?	γ′ + ε-phases	ε and ζ(?) phases
Testing data															
Weeks av.		2–5	2–8	2–8	2–8	10–17	18–20	2–8	10–15	16–18	2–18	2–8	13–18	2–5	3–10
Space vel.[b]		98	97	99	97	98	108	98	101	99	100	306	295	296	293
Temp., °C.		263	259	227	240	222	239	225	238	224	226	257	243	242	238
Operating press. atm.		7.8	7.8	7.8	7.8	7.8	7.8	7.8	7.8	7.8	7.8	21.4	21.4	21.4	21.4
Contraction, %		65.0	63.0	64.8	65.3	69.5	70.8	64.1	63.6	62.6	62.8	65.5	63.0	64.0	65.2
Usage ratio, H_2/CO		0.72	0.72	0.78	0.75	0.80	0.77	0.75	0.75	0.79	0.74	0.72	0.80	0.77	0.79
Hydrocarbon prod., wt. %[c]															
C_1		17.8	16.0	7.2	12.4	32.8	14.6	20.9	11.9	26.8	21.6	12.3	16.6	17.6	16.2
C_2		9.6	11.3	5.9	6.8	19.2	8.9	10.1	9.0	6.5	12.2	7.9	11.7	11.2	9.7
C_3		13.8	11.5	8.8	10.9	20.5	16.1	15.4	12.8	17.6	14.6	9.5	15.3	14.2	11.5
C_4		6.1	6.6	5.3	7.4	9.3	10.0	9.2	8.3	11.3	8.8	6.1	5.6	5.6	6.6
C_1–C_4		47.3	45.4	27.2	37.5	81.8	49.6	55.6	42.0	62.2	57.2	35.8	49.2	48.6	44.0
Liquids plus solids[d]		52.7	54.6	72.8	62.5	18.2	50.4	44.4	58.0	37.8	42.8	64.2	50.8	51.4	56.0
Distilln. of liq. plus sol.[d] wt. %															
<185°		38.1	31.2	19.8	26.7	58.4	33.3	64.0	39.7	56.5	61.9	37.6	64.3	57.4	67.3
185–352°		35.5	38.4	24.3	38.1	35.0	37.4	32.0	31.3	32.9	34.5	27.9	24.6	31.7	25.0
352–464°		14.9	14.4	15.9	16.5	5.1	12.6	3.3	11.8	10.6	2.9	11.9	5.8	6.8	5.2
>464°		11.5	16.0	40.0	17.7	1.5	16.7	0.7	17.2	0.0	0.7	18.9	4.2	4.1	2.5
Acid no.		0.76	1.20	2.08	0.78	2.4	1.0	1.03	0.96	2.91	1.26	7.72	1.86	0.80	3.0
Infrared anal. of fract. wt. % of group															
<185°	OH	0.2	0.6	2.1	1.3	9.1	1.5	7.8	1.1	14.6	12.2	3.4	12.0	7.2	11.7
	α-olefins	4.9	2.6	7.4	4.8	2.0	5.5	5.2	4.3	1.5	1.3	7.0	1.6	2.6	1.9
	other olefins	5.1	6.3	1.6	4.5	1.2	2.7	0.7	4.6	0.0	0.4	0.9	0.0	1.9	0.0
	CO (ketones, acids)	0.6	0.7	1.1	0.5	1.4	0.5	1.4	0.5	0.9	1.5	1.7	1.4	1.2	1.4
	COO (esters)	0.1	0.1	0.2	0.1	0.6	0.2	0.5	0.2	0.1	0.2	0.5	0.5	0.5	0.3
	Bromine no.	66	59	60	62	21	55	39	59	10	11	53	11	30	11
185–352°	OH	0.0	0.1	0.7	0.0	0.8	0.1	1.0	0.1	1.4	1.6	0.7	2.5	0.8	2.7
	α-olefins	1.1	0.6	3.4	0.9	0.8	1.6	1.0	0.8	1.0	0.4	4.0	0.6	0.6	0.6
	other olefins	3.9	3.6	1.9	3.5	1.5	2.6	1.2	3.4	0.8	1.4	1.3	0.8	2.1	0.5
	CO (ketones, acids)	0.3	0.3	0.4	0.2	0.7	0.3	0.6	0.2	0.6	0.8	0.8	1.2	0.6	1.3
	COO (esters)	0.6	0.1	0.3	0.0	0.7	0.1	0.3	0.1	0.5	0.6	0.9	0.8	0.4	1.0
	Bromine no.	33	28	35	29	16	28	15	28	12	12	35	9	18	8

[a] 40–60 mesh catalyst used in this test. [b] Volumes of feed gas (S. T. P.) per volume of catalyst space per hour. [c] Total hydrocarbon includes oxygenated compounds dissolved in the hydrocarbon phases. [d] Liquids plus solids include oxygenated compounds dissolved in the hydrocarbon phases.

catalyst in X152. The infrared analyses of the liquid fractions were about the same. With more completely nitrided catalysts in Tests X207B, X214A, X214C and X215, the fraction of gaseous hydrocarbons produced was greater and the average molecular weight of products was lower than the corresponding values obtained with the reduced catalyst in Tests X152 and X173. The infrared analyses indicate that these fairly completely nitrided catalysts produce greater yields of alcohols as indicated by 7.8 to 15.6% of OH group compared with 0.2% for the reduced catalyst. Products from nitrided catalysts that were hydrogenated after several weeks of testing (X207C and X214B) were similar to those of reduced catalyst in X152 except that the yields of methane from Tests X207C and X214B were somewhat lower. At 21.4 atmospheres, the products of nitrided catalysts in X200B, X219 and X225 compared with those of reduced catalyst in X200A showed approximately the same differences as observed in tests at 7.8 atmospheres. Preliminary mass spectrometric analyses indicate that 25–48 weight % of the aqueous phase produced by nitrided catalysts was oxygenated organic molecules, chiefly alcohols. Since the weight of the aqueous phase was 30–40 % of the weight of the hydrocarbon phases, the yields of liquids plus solids from nitrided catalysts would be increased about 10% if the water-soluble organic molecules were included.

Because the tests of nitrided catalysts were made at significantly lower temperatures than those of reduced catalysts, the effect of this temperature difference on product distribution must be considered. Usually, lowering the operating temperature decreases the percentage of gaseous hydrocarbons and increases the average molecular weight and the amount of OH group. The extent of the temperature effect may be illustrated by Test X201 with reduced 40–60 mesh catalyst. Because of the smaller particle size, this catalyst could be operated at about the same temperature as the rather completely nitrided catalyst (X207B, X214A, X215); it was found, however, that the difference between the production of gaseous hydrocarbons and the average molecular weight of products obtained from this catalyst and those values from reduced and nitrided catalysts was even more pronounced than in comparisons with X152 and X173. The total olefin content was about the same for the reduced catalysts in X201 and X152 and X173. The products from X201 contained more alcohols than those from X152 and X173 but considerably less than those from completely nitrided catalysts. Thus, the high yields of gaseous hydrocarbons and the products of lower average molecular weight formed by the nitrided catalysts cannot be attributed to the lower temperature of operation. Alcohol formation is favored by the lower temperatures at which nitrided catalysts operate; however, these catalysts produce about three to four times as much alcohol as the reduced catalyst in X201.

Table I shows the product distribution data calculated as averages of several weeks of operation. In tests at 100 p. s. i. g., the distribution of products from fairly completely nitrided catalysts changed considerably with time of operation as illustrated by data of Test X215 in Fig. 6.

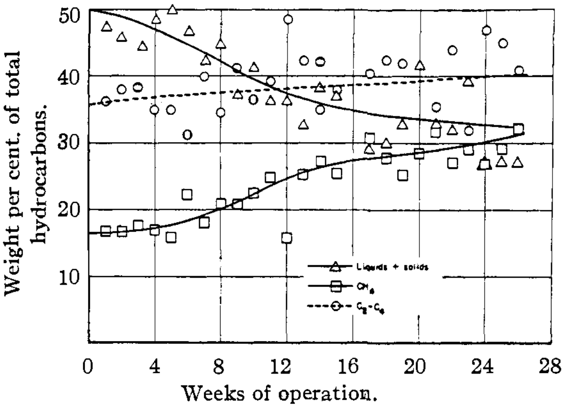

Fig. 6.—Variation of products from nitrided iron catalyst D3001 with time. Test X215 with 1 H_2 to 1 CO gas at 7.8 atmospheres.

The yield of liquids-plus-solids decreased from 50 to 34% in twenty-three weeks of operation while the methane increased from 17 to 29%. The yield of C_2–C_4 hydrocarbons increased only slightly during the experiment. At 300 p. s. i. g., the product distribution remained more nearly constant as shown in Fig. 7. The yield of methane remained constant, but the C_2–C_4 hydrocarbons increased somewhat at the expense of the liquids-plus-solids.

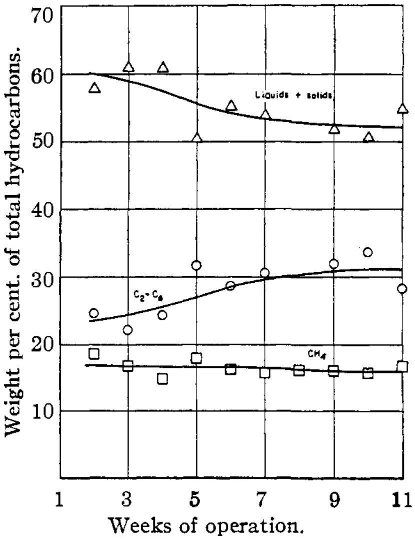

Fig. 7.—Variation of products from nitrided iron catalyst D3001 with time; test X225 with 1 H_2 to 1 CO gas at 21.4 atmospheres.

In the synthesis, nitrogen was only very slowly removed from the catalyst, even though the nitride is very rapidly hydrogenated with pure hydrogen at synthesis temperatures. Presumably the rate of hydrogenation of the nitride is very strongly inhibited by the carbon monoxide in the synthesis gas. Analyses of used catalysts in several of the tests in Table I, as well as experiments in progress, indicate that: (a) carbon slowly replaces nitrogen to form a carbonitride, (b) the atom ratio, (C + N)/Fe, remains essentially constant, and (c) the catalyst appears to resist oxidation and free carbon deposition. This is shown by analyses of used catalysts in Table II. For the last two used catalysts, the ratio (C + N)/Fe exceeds the value of 0.508 which Jack[12,13] has taken as the upper limit of the ζ-phase. Thus, it appears that at least in the catalysts in X215 and X225 some free carbon is present.

Table II

Carbon and Nitrogen Content of Used Catalysts

Test	Total weeks of testing	Atom ratios		
		N/Fe	C[a]/Fe	(C + N)[a]/Fe
X214A	8	0.149	0.260	0.409
X214C	3	.160	.333	.493
X215	28	.194	.325	.519
X225	15	.139	.395	.534

[a] Total carbon used in computation of these ratios.

The data in Table I indicate that the usage ratios of nitrided and reduced catalysts were about the same; hence, the relative consumption of hydrogen and carbon monoxide is independent of the phases present in the catalyst even though the activity and selectivity are significantly different.

Discussion

The differences in selectivity of nitrided and reduced catalysts are not a result of the differences in temperature of operation and must be related to some specific change of the catalytic surface. The enhanced activity of nitrided catalysts may also result from a greater intrinsic activity; however, their increased activity may, at least in part, result from the lower-molecular-weight products. These products may be expected to desorb more readily, thus increasing the effectiveness of the surface However, a catalyst partially converted to γ'-phase nitride had a greater activity than a similar reduced catalyst, although the products are essentially the same. In this case, at least, the enhanced activity is not due to the nature of the products.

Catalysts converted to ϵ-phase nitride show the greatest increase in activity. The ϵ-phase nitrides have the same crystal structure as hexagonal Fe_2C carbide which Herbst[24] found in his most active iron Fischer–Tropsch catalysts. Possibly the arrangement and spacing of iron atoms in the hexagonal carbide and the ϵ-phase nitrides cause the high activity of catalysts containing these bulk phases. In the synthesis nitrides are gradually converted to carbonitrides with the atom ratio of total-carbon-plus-nitrogen to iron remaining approximately constant, and it is possible that the active surface is actually carbide. Nitrided catalysts appear to resist oxidation and deposition of free carbon, and these factors may also contribute to the increased activity and longer life of nitrided catalysts. Jack[12] suggested that the increased activity of γ'- and ϵ-nitrides in carburization reactions was due to the change from body-centered cubic α-iron to the more expanded face-centered cubic and hexagonal lattices.

Although studies of Emmett and co-workers[6,7] indicate that carbides of iron are neither active catalysts nor intermediates in the synthesis, German work, as well as unpublished results from our laboratory, show that iron catalysts containing sizable amounts of carbides are usually more active than similar raw or reduced catalysts. Nitrides enhance the activity in a similar manner. The way that interstitial compounds of carbon and nitrogen act as substrates for catalysts of high activity is not understood, but it may possibly be related to differences in the geometry of the resulting catalytic surfaces.

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Summary

The conversion of iron in reduced synthetic-ammonia-type catalysts to nitrides by ammonia treatment greatly increased their activity in the Fischer–Tropsch synthesis. Catalysts converted to ϵ-phase nitrides yielded a product of lower average molecular weight containing greater yields of gaseous hydrocarbons and oxygenated molecules than those products obtained from corresponding reduced catalysts. In the synthesis, nitrided iron catalysts appear to resist oxidation and deposition of free carbon, and have a greater stability and life.

Bruceton, Penna. Received December 27, 1949

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(24) Herbst, Group leader conference, Ludwigshafen, T. O. M. Reel 26, Bag 2634; Report Dr. Wenzel, T. O. M. Reel 134, Item II/10. See also refence 5, p. 15.