[Contribution from Bureau of Mines, Synthetic Fuels Research Branch]

Preparation and Reactions of Carbonitrides on Iron

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Received April 14, 1952

The preparation and reactions of carbonitrides in an iron catalyst (synthetic ammonia-type) have been studied in the temperature range 250-450°. Two reactions occur when nitrides are treated with carbon monoxide, or carbides with ammonia: A rapid *completion* reaction in which carbon or nitrogen enters the lattice until the ratio of carbon plus nitrogen atoms to iron atoms increases to about 0.5, followed by a slower *substitution* reaction in which carbon replaces nitrogen or *vice versa*. When iron nitrides are treated with H_2 + CO mixtures, the rate of elimination of nitrogen from the catalyst increases with the hydrogen content of the gas, whereas the rate of incorporation of carbon exhibits a maximum at about $1H_2$ + 1CO. Nitrides are rapidly reduced by pure hydrogen; carbonitrides are reduced more slowly, the rate varying inversely with the carbon content. Nitrogen is removed more rapidly than carbon, and the residual interstitial carbon appears as carbide.

The iron-nitrogen,[2,3,4,5] iron-carbon,[6,7,8,9] and iron-carbon-nitrogen[5,8,10] systems are of considerable interest in metallurgy and in the catalytic syntheses of ammonia and hydrocarbons. The use of iron nitrides as catalysts and their transformation to carbonitrides during the Fischer-Tropsch synthesis have been studied in this Laboratory[11,12,13]

Phases Identified in the Iron-Carbon-Nitrogen System

Symbol or name	Crystal structure	Approximate composition Nitrides	Carbonitrides	Carbides
γ'	Face-centered cubic	Fe_4N	$\sim Fe_4X^a$	....
ϵ	Close-packed hexagonal	Fe_3N to Fe_2N	$\sim Fe_3X$ to Fe_2X	$\sim Fe_2C$
ζ	Orthorhombic	Fe_2N	$\sim Fe_2X$	....
χ (Hägg or percarbide)	....	.....	....	$\sim Fe_2C$
Cementite	Orthorhombic	.....	....	Fe_3C

^{a} X = carbon plus nitrogen.

Two types of reaction may occur during the formation of iron carbonitrides: A *completion* reaction in which carbon or nitrogen enters the lattice until $\bar{C} + \bar{N}$ has increased to about 0.5, the approximate upper limit of the ϵ-phase[14]; any interstitial atoms already present are retained in the lattice. The second is a *substitution* reaction in which one interstitial atom replaces the other; this reaction is slower than the first and usually proceeds only after the completion reaction is finished. Phase changes may occur in both types of reaction. For example, Jack observed that Hägg iron carbide (or "iron percarbide"[5]) appeared at 450° when $\bar{N}$ had decreased below 0.18, that is, when about 64% of the nitrogen atoms of Fe_2N had been replaced by carbon.

When metallic iron and iron nitrides are treated with carbon monoxide, the principal reaction is

$$2CO \longrightarrow CO_2 + C_{\text{(interstitial or elemental)}} \tag{1}$$

If the carbon monoxide is virtually completely consumed, for example, at high temperatures and/or at low flow rates, oxidation of the iron also occurs, regardless of the phase in which it is present

$$CO + {}^3/_4Fe \longrightarrow {}^1/_4Fe_3O_4 + C_{\text{(interstitial or elemental)}} \tag{2}$$

Jack[5,8,9] studied reactions of the Fe-C-N system using an iron powder. The data presented in this paper were obtained on an iron synthetic ammonia catalyst, and include in addition to the reactions considered by Jack, the carburization of nitrides with synthesis gas and the reduction of carbonitrides with hydrogen.

Experimental

Samples of 6- to 8-mesh, fused iron oxide, synthetic-ammonia type catalyst (Bureau of Mines number D-3001), were used for all experiments. The unreduced catalyst contained 67.4% total iron, 21.7% ferrous iron, 4.61% MgO, 0.57% K_2O, 0.71% SiO_2 and 0.65% Cr_2O_3.

The gases employed were: Electrolytic hydrogen which was further purified by passage over hot copper or through a Deoxo purifier and over Anhydrone; anhydrous ammonia, which was passed over freshly fused potassium hydroxide; cylinder carbon dioxide; and carbon monoxide prepared by the dehydration of formic acid in the presence of phosphoric acid and dried over Anhydrone. Hydrogen-carbon monoxide mixtures (Fischer-Tropsch synthesis gas) were prepared by reforming natural gas, compressed in steel cylinders at 130 atmospheres, and freed of small quantities of iron carbonyl by passage through glass beads at about 200°. As used, one-component gases were more than 99.8% pure (mass spectroscopic analyses); the synthesis gas contained less than a total of 0.5% nitrogen, methane and carbon dioxide. Gas flows, controlled by micrometric needle valves, were measured by small capillary flowmeters.

The experiments were made in glass systems. Two types of reaction tubes, both equipped with special four-way stopcocks,[15] were used. During reactions, their temperatures were controlled to ±3°. After treatment in the first type tube[16] and subsequent cooling to room temperature, the entire charge was transferred in a stream of carbon dioxide to a glass tube attached to the filling arm by a ground joint, and the portion of the tube containing the sample was sealed at both ends. In this and other transfers, due precautions were taken to preclude atmospheric oxidation as well as heating of the sample during sealing off. The second type reaction tube was similar to the first, but it contained a larger charge (about 50 cc. as compared with 10 cc.

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(5) K. H. Jack, *Proc. Roy. Soc.* (*London*), **A195**, 34 (1948).

(6) L. J. E. Hofer, E. M. Cohn and W. C. Peebles, This Journal, **71**, 189 (1949).

(7) The early studies of higher iron carbides by Hägg, Halle and Herbst, and Pichler and Merkel have been reviewed in reference 6.

(8) K. H. Jack, *Proc. Roy. Soc.* (*London*), **A195**, 56 (1948).

(9) K. H. Jack, *ibid.*, **A195**, 41 (1948).

(10) The reader is referred to an informative review of nitrides, carbonitrides, and carbides by H. L. Riley, *Quart. Rev.* (*London*), **3**, 160 (1949).

(11) R. B. Anderson, J. F. Shultz, B. Seligman, W. K. Hall and H. H. Storch, This Journal, **72**, 3502 (1950).

(12) J. F. Shultz, B. Seligman, J. Lecky and R. B. Anderson, *ibid.*, **74**, 637 (1952).

(13) J. F. Shultz, B. Seligman, L. Shaw and R. B. Anderson, *Ind. Eng. Chem.*, **44**, 397 (1952).

(14) Throughout this paper, the carbon and nitrogen contents are expressed as the ratios of these atoms to iron atoms: $\bar{C}$ = atom ratio of carbon to iron, $\bar{N}$ = atom ratio of nitrogen to iron.

(15) R. B. Anderson, *Ind. Eng. Chem.*, *Anal. Ed.*, **18**, 156 (1946).

(16) R. B. Anderson, W. K. Hall and L. J. E. Hofer, This Journal, **70**, 2465 (1948).

in the other reaction vessel) and was provided with a helix of glass tubing which extended out of the furnace zone. A representative portion of the catalyst was transferred into the helix by proper manipulation, and the section of the helix containing this sample was sealed off. From the known weight of catalyst plus glass removed, weight of glass, and weight changes during reaction, the weight change per gram of charge was calculated. Both types of reaction tube were weighed on an analytical balance.

Composition data for reduction of raw catalysts or nitrides and for nitriding of reduced catalysts were obtained from weight changes only. For carburization of reduced and nitrided samples, ammonia treatment of carbides and hydrogenation of carbonitrides, chemical analyses for iron, carbon and nitrogen were obtained in addition to weight changes.

When the sample had not been treated with synthesis gas, the glass ampoules containing the catalyst were scratched with a file and introduced through an "air lock" into a dry-box filled with carbon dioxide at a slight positive pressure. The ampoules were broken, and the samples were ground to finer than 80 mesh, quartered, and placed in small tared vials with screw caps equipped with neoprene gaskets for weighing and transferring to apparatus for analysis. Before this dry-box procedure, samples treated with synthesis gas were freed of wax by continuous extraction with boiling toluene in an A.S.T.M. extraction apparatus for rubber products. The toluene was removed by evacuation at 100°. The method of transferring and extracting the samples was usually satisfactory as indicated by low oxygen values calculated by difference.

Nitrogen was determined by a modification of the standard Kjeldahl method, and the carbon by a method similar to the gravimetric determination of carbon in steel. Iron was determined by a standard dichromate titration method.

Raw catalyst samples were essentially completely reduced with hydrogen at a space velocity[17] of 1,000 in 20 hours at 550°. For use in the reaction tube in which only one sample was obtained per experiment, a relatively large quantity of catalyst (150 cc.) was converted to the desired initial phase—nitride, carbonitride or carbide—in an aluminum block reactor and transferred in carbon dioxide to a special glass storage bulb[11]; portions of this material were transferred in carbon dioxide to the reaction tubes. With the other type of tube, the initial phases were prepared *in situ*. At the end of a period of treatment, the gas flow was stopped by closing the four-way stopcock on the reaction tube, the furnace was removed, and the sample was cooled rapidly in the presence of the residual gas. Evacuation at reaction temperatures was avoided to prevent the possible loss of nitrogen. The methods of preparing iron nitrides,[11] Hägg carbide,[18] and cementite[19] have been described previously.

Results

Carburization of ϵ-Iron Nitride with Carbon Monoxide.—Table I presents the composition and phase changes during treatment of an ϵ-nitride ($\bar{N} = 0.46$) with carbon monoxide at 250 to 450°. At a space velocity of 80 and at temperatures below 400°, carbon entered the catalyst without replacing nitrogen until $\bar{C} + \bar{N}$ had increased to about 0.5. At 350° and 400°, following the completion reaction, carbon replaced nitrogen, with $\bar{C} + \bar{N}$ remaining about 0.5. At 450° the carbon content increased more rapidly in the first hour than possible by reaction 1, based on the flow of carbon monoxide, and the presence of magnetite confirmed that reaction 2 had occurred. Under these conditions the catalyst lost nitrogen more rapidly than it gained carbon, and Hägg carbide was the principal phase after 5 hours. At the same temperature but at a space velocity of carbon monoxide of 2500, carbon was deposited at a somewhat greater rate than at the lower flow; the rate was not sufficient, however, to lead to oxidation according to equation 2. In the first hour $\bar{C} + \bar{N}$ increased to 0.59 and then remained about constant. Although carbon deposition was more rapid, the nitrogen content decreased at a slower rate. The principal phase was ϵ-carbonitride, with Hägg carbide appearing only after the nitrogen content had decreased below $\bar{N} = 0.16$.

TABLE I

CARBURIZATION OF ϵ-IRON NITRIDE WITH CARBON MONOXIDE

Temperature, °C.	Time, hours	$\bar{C}$	$\bar{N}$	$\bar{C} + \bar{N}$	Phases[a]
A. Space velocity = 80 hr.$^{-1}$					
Original nitride, A	0	0.00	0.46	0.46	ϵ
250	1	.02	.47	.49	ϵ
	5	.02	.46	.48	ϵ
	10	.03	.45	.48	ϵ
300	1	.02	.46	.48	ϵ
	5	.04	.45	.49	ϵ
	10	.04	.47	.51	ϵ
350	1	.04	.45	.49	ϵ
	5	.06	.44	.50	ϵ
	10	.08	.43	.51	ϵ
400	1	.03	.46	.49	ϵ
	5	.14	.36	.50	ϵ
	10	.30	.18	.48	ζ
450	1	.18	.20	.38	ϵ, M
	5	.41	.02	.43	χ, M, α(?)
	10	.46	.01	.47	χ, α(?), M(?)
B. Space velocity 2500 hr.$^{-1}$					
450	1	0.32	0.27	0.59	ϵ
	5	.42	.16	.58	ϵ
	10	.53	.08	.61	ϵ, χ

[a] ϵ = ϵ-nitride or carbonitride, ζ = ζ-carbonitride, α = α-iron, M = magnetite and χ = Hägg carbide. Phases in order of decreasing intensities of X-ray diffraction patterns.

Carburization of ϵ-Iron Nitride with Synthesis Gas.—With low space velocities of $1H_2 + 4CO$ gas at 300°, carbon replaced nitrogen with $\bar{C} + \bar{N}$ remaining at 0.45 (Table II). At 350°, substitution and completion reactions occurred simultaneously. At 400 and 450°, carbon was deposited at a greater rate than possible for reactions 1 and 3

$$H_2 + CO \longrightarrow H_2O + C_{(\text{interstitial or elemental})} \qquad (3)$$

and the diffraction pattern of magnetite was observed in addition to Hägg carbide and α-iron. At 350° and a space velocity of 1000, both carbon deposition and nitrogen elimination were more rapid than at the lower flow, and magnetite was not found. Although $\bar{C}$ increased to very high values, Hägg carbide did not appear until $\bar{N}$ was less than 0.18. Similar results were obtained with $0.7H_2 + 1CO$ gas (Table III), except that some magnetite was formed upon carburization at 350° and low space velocity. At a space velocity of 1000, no oxidation occurred at 350°, but the carbon content increased greatly ($\bar{C} = 1.52$ in 11 hours). Again, Hägg carbide appeared only when $\bar{N}$ was less than 0.18. With $2H_2 + 1CO$ gas at 350°, carbon was

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(17) Space velocity is defined as volumes of gas (S.P.T.) per volume of catalyst space per hour.

(18) W. K. Hall, W. E. Tarn and R. B. Anderson, *J. Phys. Chem.*, **56**, 688 (1952).

(19) E. M. Cohn and L. J. E. Hofer, THIS JOURNAL, **72**, 4662 (1950); *J. Chem. Phys.*, **18**, 766 (1950).

deposited at a greater initial rate than possible for a combination of equations 1 and 3; nitrogen was removed faster than it was replaced by carbon, so that $\bar{C} + \bar{N}$ decreased from 0.45 to 0.37. At a given temperature the rate of removal of nitrogen increased with the hydrogen content of the synthesis gas; the rate of deposition of carbon showed a maximum at about $1H_2 + 1CO$.

TABLE II

CARBURIZATION OF ϵ-IRON NITRIDE WITH $1H_2 + 4CO$ GAS

Temperature, °C.	Time, hours	$\bar{C}$	$\bar{N}$	$\bar{C} + \bar{N}$	Phases[a]
A. Space velocity = 80 hr.$^{-1}$					
Original nitride, B	0	0.02	0.43	0.45	ϵ
250	1	.03	.41	.44	ϵ
	5	.04	.40	.44	ϵ
	10	.04	.42	.46	ϵ
300	1	.05	.41	.46	ϵ
	5	.10	.35	.45	ϵ
	12.2	.15	.31	.46	ϵ
350	1	.05	.41	.46	ϵ
	5	.13	.37	.50	ϵ
	10	.26	.26	.52	ϵ
400	1	.08	.35	.43	ϵ, M, χ
	5	.31	.22	.53	ϵ, M
	10	.56	.14	.70	ϵ, χ
450	1	.23	.14	.38	ϵ, M, χ
	5	.45	.004(?)	.45	χ, M, α
	10	.50	.07	.57	χ, M, α
B. Space velocity = 1000 hr.$^{-1}$					
350	1	0.18	0.28	0.46	ϵ
	5	0.89	.18	1.07	ϵ
	10	1.47	.14	1.61	ϵ, χ
	24.6	1.66	.13	1.79	ϵ, χ

[a] See footnote of Table I.

TABLE III

CARBURIZATION OF ϵ-IRON NITRIDE WITH $0.7H_2 + 1CO$ AND $2H_2 + 1CO$ GASES

Temperature, °C.	Time, hours	$\bar{C}$	$\bar{N}$	$\bar{C} + \bar{N}$	Phases[a]
A. $0.7H_2 + 1CO$ gas at space velocity = 100 hr.$^{-1}$					
Original nitride, C	0	0.02	0.43	0.45	ϵ
255	1	.03	.40	.43	ϵ
	5	.04	.38	.42	ϵ, χ(??)
	10	.05	.37	.42	ϵ, χ(??)
300	1	.04	.39	.43	ϵ, χ(??)
	5	.12	.31	.43	ϵ
	7.8	.14	.30	.44	ϵ
	10	.16	.28	.44	ϵ
350	1	.06	.39	.44	ϵ, M
	5	.27	.23	.50	ϵ, α, M
	10	.45	.19	.64	ϵ
B. $0.7H_2 + 1CO$ gas at space velocity = 1000 hr.$^{-1}$					
350	1	0.22	0.26	0.48	ϵ
	5.7	0.87	.18	1.05	ϵ
	11	1.52	.08	1.60	χ, ϵ
C. $2H_2 + 1CO$ gas at space velocity = 100 hr.$^{-1}$					
350	1	0.06	0.37	0.43	ϵ, M
	5	.18	.19	.37	ϵ, M
	10	.19	.18	.37	ϵ, M

[a] See footnote of Table I.

Carburization of α-Iron, γ'-, and γ'- + ϵ-Nitrides with Carbon Monoxide and $0.7H_2 + 1CO$.—Tables IV and V present data for the carburization of α-iron and γ'- and γ'- + ϵ-nitrides. At all temperatures studied, only the completion reaction

TABLE IV

CARBURIZATION OF α-IRON AND γ'-NITRIDES WITH CARBON MONOXIDE

Temperature, °C.	Time, hours	$\bar{C}$	$\bar{N}$	$\bar{C} + \bar{N}$	Phases[a]
(Space velocity = 80 hr.$^{-1}$)					
Reduced catalyst, D	0	0	0	0	α
250	2	0.11	0	0.11	
	6	.24	0	.24	
	12	.28	0	.28	χ,α
Original nitride, E	0	..	0.08	..	α, γ'
250	1	0.07	.06	0.13	α, γ'
	4	.19	.06	.25	α, γ'
	10	.25	.04	.29	α, γ'
300	1	.11	.07	.18	α, γ'
	5	.27	.05	.32	α, γ'
	10	.29	.08	.37	γ', α
350	1	.24	.07	.31	α, γ', M
	5	.33	.07	.40	ϵ, χ, M, α
	10	.36	.08	.44	χ, α
400	1	.10	.05	.15	α, γ', M
	5	.32	.04	.36	χ, M
	10	.53	.02	.55	χ
Original nitride, F	0	0	0.21	0.21	γ', α, ϵ(??)
350	1	0.17	.21	.38	γ', ϵ, M
	5	.26	.21	.47	ϵ, χ

[a] α = α-iron, M = magnetite, γ' = γ'-nitride or carbonitride, ϵ = ϵ-carbide or carbonitride, and χ = Hägg carbide. Phases in order of decreasing intensities of X-ray diffraction patterns.

TABLE V

CARBURIZATION OF γ' + ϵ-NITRIDES WITH CARBON MONOXIDE AND $0.7H_2 + 1CO$ GAS

Temperature, °C.	Time, hours	$\bar{C}$	$\bar{N}$	$\bar{C} + \bar{N}$	Phases[a]
A. Carbon monoxide at space velocity = 100 hr.$^{-1}$					
Original nitride, G	0	0.0	0.29	0.29	γ', ϵ
350	1	.11	.29	.40	ϵ, γ'
	5	.21	.29	.50	ϵ
	10	.25	.26	.51	ϵ
	16	.25	.27	.52	ϵ
	24	.26	.27	.53	ϵ
	48	.29	.26	.55	ϵ
400	1	.14	.27	.41	ϵ, γ', M
	5	.27	.26	.53	ϵ
	10	.30	.24	.54	ϵ
	16	.35	.21	.56	ϵ
	24.3	.35	.20	.55	ϵ
	48	.39	.18	.57	
B. $0.7H_2 + 1CO$ gas at space velocity = 100 hr.$^{-1}$					
300	1	.05	.27	.32	
	5	.17	.22	.39	ϵ, γ'
	10	.28	.20	.48	ϵ, γ'
	16	.29	.17	.46	ϵ, γ'
	24	.43	.16	.59	ϵ, γ'
	48	.74	.15	.89	ϵ, γ', χ

[a] See footnote of Table IV.

was observed until $\bar{C} + \bar{N}$ equaled or exceeded 0.5. In series E ($\bar{N} = 0.08$), α-iron was the most prominent phase indicated by X-ray diffraction until $\bar{C}$ exceeded 0.27, and the γ′-phase was the only interstitial phase observed at $\bar{C}$ less than 0.32. Hägg carbide was the major phase produced upon extended carburization at 350 and 400°. In series F ($\bar{N} = 0.21$), the γ′-phase was the principal component after one hour of carburization although $\bar{C} = 0.17$ and $\bar{C} + \bar{N} = 0.38$. After 5 hours, the X-ray patterns of ε-carbonitride and Hägg carbide were found. The carburization with carbon monoxide of series G (Table V) containing the γ′- and ε-phases ($\bar{N} = 0.29$) produced ε-carbonitrides. Treatment of this sample with $0.7H_2 + 1CO$ gas at 300° yielded a mixture of ε- and γ′-carbonitrides with the former predominant, and nitrogen was removed more rapidly than with carbon monoxide at 400°.

In Fig. 1 the rate of carburization with carbon monoxide at 350° is related to the initial nitrogen content of the catalyst. The initial rate of carburization varied inversely with the initial nitrogen content. This result was also observed in carburizations with carbon monoxide at 250° and with $0.7H_2 + 1CO$ gas at 300°. Carburization with carbon monoxide at 350° of samples containing the α- and γ′-phases usually yielded the χ- and ε-phases together with magnetite and iron.

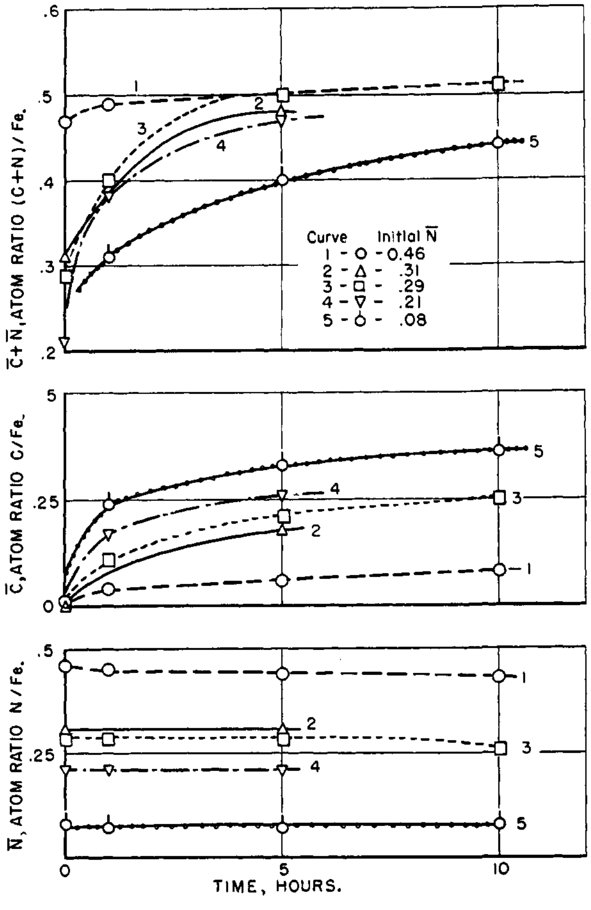

Fig. 1.—Variation of the rate of carburization of iron nitrides with carbon monoxide at 350° and space velocities of 80 and 100 hr.$^{-1}$ as a function of initial nitrogen content.

TABLE VI

AMMONIA TREATMENT OF CEMENTITE AND HÄGG CARBIDE

Temperature, °C.	Time, hours	$\bar{C}$	$\bar{N}$	$\bar{C} + \bar{N}$	Phases[a]
(Space velocity = 1000 hr.$^{-1}$)					
Cementite, H		0.35	0	0.35	C
300	1	.30	0.07	.37	C, ε
	6.25	.31	.09	.40	C, ε
	9	.30	.10	.40	C, ε
350	15	.27	.20	.47	ε
Mixture of α-iron and Hägg carbide, I		0.29	0	0.29	α, χ
345	4	.29	0.18	.47	ε, χ
350	12	.26	.24	.50	ε, χ
345	28	.19	.33	.52	ε, χ(??)
350	52	.14	.38	.52	ε
345	117	.07	.43	.50	ε
Mixture of α-iron and Hägg carbide, J		0.48	0	0.48	χ, α
350	8	.46	.06	.52	χ, ε
	24.2	.44	.12	.56	χ, ε
	48.2	.37	.21	.58	χ, ε
	72.2	.33	.25	.58	χ, ε
	120.2	.26	.34	.60	χ, ε
	158.2	.18	.42	.60	ε

[a] α = α-iron, ε = ε-nitride or carbonitride, χ = Hägg carbide, and C = cementite. Phases in order of decreasing intensities of X-ray diffraction patterns.

Ammonia Treatment of Cementite and Hägg Carbide.—When Hägg carbide and cementite were

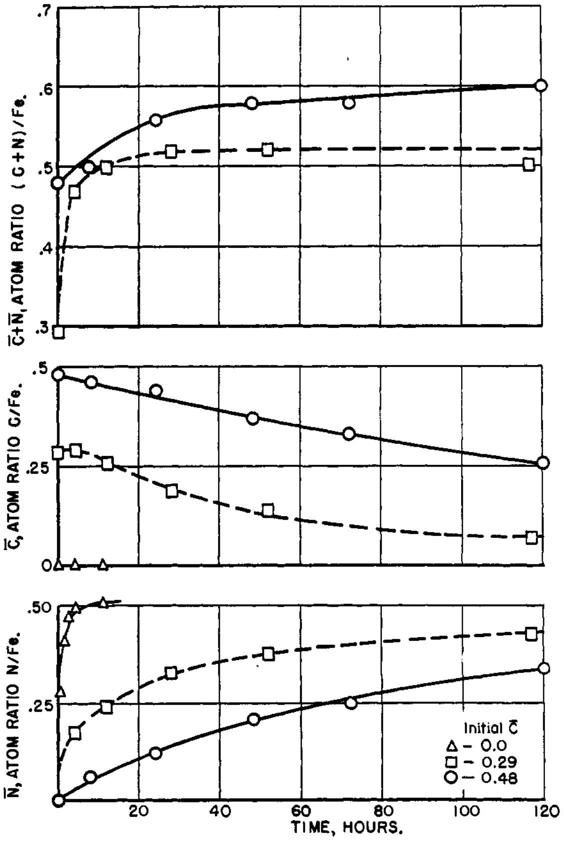

Fig. 2.—Variation of the rate of nitriding of α-iron and Hägg carbide at 350° and a space velocity of ammonia of 1000 hr.$^{-1}$ as a function of initial carbon content.

treated with ammonia at 300° or 350°, ε-carbonitride was produced. At 300° $\bar{C}$ remained essentially constant in cementite (Table VI), and the X-ray pattern of ε-carbonitride was observed in addition to that of cementite. In subsequent treatment at 350° the cementite pattern disappeared ($\bar{N} + \bar{C} = 0.47$). In the ammonia treatment at 350° of a catalyst containing about half Hägg carbide and half α-iron, nitrogen was rapidly added to the catalyst, and the substitution reaction took place only after the first 4 hours. ε-Carbonitride was the major phase when $\bar{N}$ exceeded 0.18, but Hägg carbide persisted until $\bar{N}$ increased to 0.38. With the more complete carburized sample of Hägg carbide, the nitrogen content increased more slowly, and prolonged ammonia treatment was required to cause the carbide phase to disappear. Figure 2 compares the rates of nitriding of samples containing Hägg carbide and α-iron at 350°. The rate of nitriding varied inversely with the initial carbon content of the catalyst.

Hydrogenation of ε-Nitrides and ε-Carbonitrides.—The reduction of ε-nitrides in pure hydrogen is much more rapid than that of ε-carbonitrides. The rate of reduction of carbonitrides depends to a large extent upon the manner in which they are formed.

Figure 3 shows the decrease in nitrogen content of nitrided catalysts ($\bar{N} = 0.49$–0.51) during reduction with hydrogen. At and above 200°, nitrogen was completely removed in 3 hours or less. The rate was considerably slower at 150°, and the process appeared to be autocatalytic.[20]

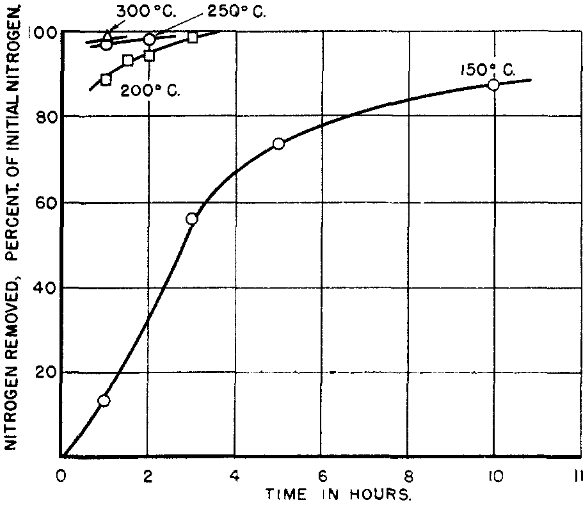

Fig. 3.—Rate of reduction of ε-nitride with hydrogen at various temperatures.

Data for the reduction of ε-carbonitrides in hydrogen are given in Table VII. In series K and L the reduced catalyst was nitrided and then carburized by carbon monoxide, and in series M the reduced sample was first carburized and nitrided. Sample L contained Hägg carbide in addition to ε-carbonitride, the nitrogen content having been decreased below the lower limit for the ε-carbonitride phase ($\bar{N} = 0.18$). In all cases nitrogen was removed more rapidly than carbon. During the hydrogenation of samples K and L, the carbon content remained unchanged up to about 350°, while the nitrogen was removed at an appreciable rate at and above 300°. Both carbon and nitrogen of sample M were removed at 250°. Metallic iron and in some cases Hägg carbide and cementite were produced as the nitrogen was preferentially removed from the ε-carbonitrides.

Table VII

Hydrogenation of ε-Carbonitrides

Temperature, °C.	Time, hours	$\bar{C}$	N	$\bar{C} + \bar{N}$	Phases[a]
(Space velocity = 250 hr.$^{-1}$)					
Orig. carbonitride, K (nitrided, then carburized)	0	0.23	0.27	0.50	ε
250	1	.23	.26	.49	ε, M(?)
	5	.22	.25	.47	ε, M(?)
	10	.23	.25	.47	ε, M(?)
	16	.22	.23	.45	...
	24	.22	.23	.45	ε, M(?)
	48	.23	.22	.45	...
350	54	.22	.07	.29	α, C, ε
Orig. carbonitride, L (nitrided, then carburized)	0	.36	.14	.50	ε, χ
250	1	.35	.15	.50	ε, χ
	10	.36	.13	.49	ε, χ
300	1	.35	.14	.49	
	5	.34	.07	.41	α, χ, C, M(?)
	10	.35	.02	.37	α, C, χ
350	1	.36	.07	.43	χ, ε
	5.3	.35	.02	.37	α, χ, C(?)
	10	.28	.004	.28	α, χ, C(?)
400	1	.36	.01	.37	χ, α, C(?)
Orig. carbonitride, M (carburized, then nitrided)	0	.17	.31	.48	ε
250	1	.14	.14	.28	α, ε
	5	.14	.08	.22	α, ε
	10	.10	.04	.14	α, ε, χ
	26	.13	.04	.17	α, χ
	50	.09	.03	.12	α, (?)
300	53	.06	.00	.06	α, (?)

[a] α = α-iron, M = magnetite, ε = ε-phase, χ = Hägg carbide, and C = cementite. Phases in order of decreasing intensities of X-ray diffraction patterns.

Discussion

The results of the present paper are in general agreement with those obtained by Jack,[9] and the few differences between the two studies may be explained by differences in the physical state of the iron. Jack employed a fine-mesh, pure iron powder, presumably with virtually no internal surface, whereas a reduced catalyst with relatively large internal surface and high porosity[18,21] was employed in the present experiments. Such catalysts have the advantage of being more reactive than massive iron so that, for example, relatively pure Hägg carbide, without appreciable amounts of elemental carbon, can be prepared by carburization with carbon monoxide at low temperatures (225° to 275°).

The crystallites of the phases in the catalyst are much smaller than those in massive iron, and the resulting X-ray diffraction patterns are weak and diffuse compared with those obtained from iron powders. With catalysts the ε-nitride or carbonitride phases were obtained under conditions under which Jack obtained ζ-phases.[9] The ε- to ζ-trans-

(20) P. H. Emmett and K. Love, This Journal, **55**, 4043 (1933).

(21) W. K. Hall, W. E. Tarn and R. B. Anderson, *ibid.*, **72**, 5426 (1950).

formation involves only slight changes in the positions of the iron atoms, causing some of the lines in the diffraction pattern to split into two lines. Either the ζ-phase was not formed in the poorly crystallized catalyst or, if present, its X-ray pattern could not be distinguished from that of the ϵ-phase due to the diffuseness of the diffraction lines.

The carburization of nitrided iron catalysts with carbon monoxide proceeded by a relatively rapid completion reaction followed by a slower substitution reaction. In agreement with Jack's results[9] Hägg carbide appeared when $\bar{N}$ became less than about 0.16–0.18, that is, when more than 64–68% of the nitrogen corresponding to the upper limit of the ϵ-nitride phase had been replaced by carbon. The rate of carburization of the catalysts varied inversely with the nitrogen content. Thus, a reduced catalyst was partly converted to Hägg carbide ($\bar{C} = 0.26$) in ten hours at 250°, whereas an ϵ-nitride was virtually unchanged under similar conditions. At higher temperatures the same dependence of rate on $\bar{N}$ was observed; the reaction, however, does not proceed as cleanly with catalysts containing the α- or γ'-phases. Jack[9] stated that the formation of γ'- or ϵ-nitrides expands the lattice and changes the arrangement of iron atoms thus permitting carbon to penetrate nitride more rapidly than α-iron. This conclusion is not valid for the carburization of catalysts with large surface areas.

In the carburization of ϵ-nitrides with low space velocities of carbon monoxide, small amounts of magnetite were found whenever the rate of incorporation of carbon was greater than that possible for complete consumption of carbon monoxide by reaction 1. This magnetite presumably was formed by the over-all reaction 2. Although magnetite was not formed at higher space velocities of carbon monoxide, some free carbon was probably deposited since $\bar{C} + \bar{N}$ exceeded 0.5 and approached 0.6 in some cases. For this as well as previous work, no accurate limits of composition can be given for the interstitial phases containing carbon, because of the lack of a method for distinguishing unambiguously between elemental and interstitial carbon. In the present study of carburization with carbon monoxide at temperatures not exceeding 400°, the upper limit of $\bar{C} + \bar{N}$ of the ϵ-carbonitride phase was about 0.5. At 450° Jack found values of $\bar{C} + \bar{N}$ as high as 0.56 for the upper limit of the ζ-carbonitride phase.[8]

In the treatment of nitrides with H_2 + CO mixtures magnetite was produced under conditions under which the carbon monoxide was rather completely consumed. At low conversions of carbon monoxide (high space velocity of synthesis gas) magnetite formation did not occur, but very sizable quantities of elemental carbon were produced. Carbon deposition also occurs in the range of synthesis temperatures, 225–275°, but at a slower rate. In contrast to these experiments at atmospheric pressure, elemental carbon deposition is trivial in the Fischer–Tropsch synthesis at 7 to 21 atmospheres[12] where the production of hydrocarbons and alcohols predominates.

The reaction of ϵ-nitrides with carbon monoxide was accelerated by the presence of hydrogen. The rate of removal of nitrogen increased with increasing hydrogen content, whereas the rate of deposition of carbon was greatest at about 50% hydrogen. Jack and Goodeve[9,22] demonstrated that the removal of nitrogen was the slow step in the carburization of ϵ- or ζ-nitrides with carbon monoxide, and this concept can be extended to explain the present data as follows: (a) The rate of elimination of nitrogen (the slow step according to Jack) increased with the hydrogen content of the synthesis gas. (b) With gas containing more than 50% carbon monoxide, incorporation of carbon in the catalyst was sufficiently rapid so that each eliminated nitrogen atom was replaced at once by a carbon atom, the number of nitrogen plus carbon atoms remaining constant. (c) With less than 50% carbon monoxide, the incorporation of carbon was slower than the elimination of nitrogen, and the number of nitrogen plus carbon atoms decreased. (d) The rate of reduction of nitride by pure hydrogen was very rapid; relatively small amounts of carbon monoxide strongly inhibit the reduction of iron nitride.

Both Hägg carbide and cementite were converted to ϵ-carbonitride by treatment with ammonia. The rate of nitriding of the catalysts decreased with their initial carbon content. Cementite was nitrided at about the same rate as a sample containing $^2/_3$ Hägg carbide and $^1/_3$ α-iron. At low temperatures, that is, less than 600°, cementite cannot be converted to Hägg carbide by thermal treatment[23] or carburization. This transformation can be accomplished, however, by converting cementite to ϵ-carbonitride and carburizing the product to Hägg carbide.

The rate of reduction of carbonitrides by hydrogen was considerably slower than that of the reduction of nitrides. Carbon was removed more slowly than nitrogen, whether the carbonitride was prepared by carbiding of nitride or by nitriding of carbide. This was not unexpected since Hägg carbide prepared from this catalyst was hydrogenated much more slowly than ϵ-carbonitride or ϵ-nitride. The carbide phases appeared upon removal of the nitrogen.

Carbonitrides prepared from nitride were hydrogenated more slowly than those made from carbide. This suggests that the interstitial component (carbon or nitrogen) which entered the lattice last was present in greater concentrations near the surface.

Acknowledgment.—The authors are pleased to acknowledge the assistance of Mrs. W. C. Peebles in making the X-ray diffraction analyses.

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[22] C. Goodeve and K. H. Jack, *Disc. Faraday Soc.*, **4**, 82 (1948).

[23] L. C. Browning, T. W. DeWitt and P. H. Emmett, THIS JOURNAL, **72**, 4211 (1950).