cal mechanism of dissociation is involved. Rupture of just one of the U–H bonds would be expected to give a slightly higher value of the entropy change per mole H_2 than rupture of all three bonds. Neither assumption of partial dissociation in this sense, nor assumption of a larger molecular aggregate for UH_3 leads to improved consistency. From the small magnitude of ΔH it may be inferred that release of hydrogen from the solid phase requires relatively little energy. The rapid decrease of this energy with increasing amounts of hydrogen in the solid phase is shown in Table III.

TABLE III

PRESSURE EQUATIONS AND VALUES OF ΔH FOR $UH_{2.94}$ TO $UH_{3.0}$

Values of A and b in equation $\log P_{atm} = (-A/T) + b$; ΔH in kcal./mole H_2

s in UH_s	A	b	ΔH (apparent)
2.940	4540	6.88	20.8
2.955	4230	6.63	19.4
2.970	3820	6.24	17.5
2.985	3125	5.47	14.3
2.997	2130	4.33	9.7
3.000	1730	3.90	7.9

The apparent variation of ΔH with composition for compositions in the vicinity of UH_3 suggests a solution process in which the hydride and metal are in solid solution. Such a system would be expected to behave in the manner shown. This possibility is being explored by the senior author and C. E. Mes-

ser and preliminary results with the Pd–H system[18] seem to indicate that such solid systems as this may be treated by a classical method based on Margules' equation. According to this interpretation the logarithm of the equilibrium pressure along the ascending portions of the isotherms should be proportional to $\log (a_{UH_3}/a_U)$, where a refers to activity.[19] This permits not only a quantitative interpretation of the observed behavior of the U–H system in the regions where the isotherms are ascending but also leads to a fundamental relationship between composition, temperature and pressure which expresses the behavior of the system as a whole, plateau regions as well as ascending regions.

(18) L. J. Gillespie, *et al.*, THIS JOURNAL, **48**, 1207 (1926); **58**, 2565 (1936); (also *cf.* J. R. Lacher, *Proc. Roy. Soc. (London)*, **525**, 161 (1937)).

(19) An approximate interpretation along this line has been suggested by one of the referees, R. E. Powell, who has pointed out that the isotherms at 600, 625 and 650° when plotted with log P as abscissa and log (mole fraction UH_3/mole fraction U) as ordinate, are straight lines having a slope of 3/2 in keeping with the equation UH_3 (solid solution) $\rightleftharpoons$ U (solid solution) + 3/2 H_2. This permits calculation of the value of $\Delta H \cong 20$ for the dissociation of UH_3 which is in good agreement with the plateau value of 20.5 kcal./mole H_2. The interpretation assumes however that the mole fraction ratio is equivalent to the activity ratio and is applicable only to the ascending portions of an isotherm, whereas the rigorous treatment is applicable over the entire isotherm without commitment as to the nature of the phases present.

MEDFORD, MASS.

[CONTRIBUTION FROM THE SYNTHETIC FUELS RESEARCH BRANCH, BUREAU OF MINES, REGION VIII]

Hexagonal Iron Carbide as an Intermediate in the Carbiding of Iron Fischer–Tropsch Catalysts[1,2]

BY MILTON MANES, ARTHUR D. DAMICK, MORRIS MENTSER, ERNST M. COHN AND L. J. E. HOFER

In the course of a study of the composition of Fischer–Tropsch catalysts and of the relationships between iron carbides in catalysts and in steels, a method has been developed for the thermomagnetic analysis of mixtures containing α-iron, Hägg iron carbide (χ), and hexagonal close-packed iron carbide (ϵ). Iron catalysts have been carbided to about 25% carbide at temperatures ranging from 190 to 350°. Analyses of these catalysts by the new method demonstrate that the hexagonal close-packed carbide may be the only carbide component up to 250° and is formed at temperatures as high as 325°. The results are evidence that hexagonal close-packed carbide is the precursor of Hägg carbide. Furthermore, it appears likely that both higher carbides are precursors of cementite. The data explain why hexagonal close-packed iron carbide is rarely found in fully carburized catalysts even though it is the first-formed carbide over a relatively wide range of temperatures.

The present work was undertaken as part of a program for investigating the composition of Fischer–Tropsch catalysts and the relationships between iron carbides in catalysts and in steels.

Two distinct iron carbides of approximate composition Fe_2C, namely, hexagonal carbide (ϵ) and Hägg carbide (χ), have been identified as products of the reaction of carbon monoxide with reduced iron Fischer–Tropsch catalysts. ϵ-Carbide tends to predominate at low reaction temperatures and in copper-containing catalysts, χ-carbide at higher temperatures. For example, Hofer, Cohn and Peebles[3] found χ- but not ϵ-carbide when a fused,

synthetic ammonia-type catalyst was fully carbided at 240°. They found ϵ-carbide as the principal product when a precipitated, copper-promoted catalyst was fully carbided at 190°. More recently, however, Podgurski, Kummer, DeWitt and Emmett[4] found only ϵ-carbide in a copper-free fused catalyst partly carbided at 215°. Moreover, (unpublished) experiments in this Laboratory on the carbiding with carbon monoxide of copper-free sintered and fused catalysts to about 50% carbide at 220° have yielded mixtures of ϵ- and χ-carbides.

These observations are consistent with the hypothesis that ϵ- is a precursor of χ-carbide. Since ϵ-carbide is metastable and is converted to χ-carbide by heating,[3] the presence of ϵ-carbide in partly car-

(3) L. J. E. Hofer, E. M. Cohn and W. C. Peebles, THIS JOURNAL, **71**, 189 (1949).

(4) H. H. Podgurski, J. T. Kummer, T. W. DeWitt and P. H. Emmett, *ibid.*, **72**, 5382 (1950).

bided catalysts, and its absence in catalysts fully carbided under otherwise identical conditions might simply be the result of thermal conversion of ε- to χ-carbide during the relatively long time required to carbide the catalyst fully. This hypothesis implies that carbiding for very short times should result in formation of ε-carbide at much higher temperatures than those at which it has hitherto been known to exist. One would further expect that the ε-carbide in such a sample should be converted to χ-carbide by heat treatment in vacuum at the temperature of the experiment, and at a rate that would account for the ratios of ε- to χ-carbide that have been previously observed. The experimental results reported here agree with the hypothesis and constitute reasonable evidence that ε-carbide is indeed a precursor of χ-carbide. Similar, though less complete, data indicate that both ε- and χ-carbide may be precursors of cementite.

Experimental

Two iron catalysts were used, having the following designations and compositions: A1008 (a sintered catalyst), containing 68.2% Fe, 0.12% K_2CO_3, 0.75% SiO_2, 0.58% Al_2O_3, 0.15% MgO and an estimated 0.1% Mn; and D3001 (a synthetic ammonia-type catalyst), containing 66.8% Fe, 0.6% SiO_2, 0.8% Cr_2O_3, 4.6% MgO and 0.6% K_2O. The catalysts were ground to 100–200 mesh and reduced for 70 hours in pure hydrogen (electrolytic hydrogen passed through palladized asbestos at 350–400°, soda lime and magnesium perchlorate) at hourly space velocities exceeding 10,000 and at 400° (A1008) or 450° (D3001). By the application of glass breakseal techniques and by manipulating the ferromagnetic catalysts with a magnet,[5] the reduced batches were divided into individual weighed samples and stored in glass ampoules under vacuum.

The carbiding apparatus was essentially the one described by Weller.[6] Carbon monoxide was recirculated over the heated samples at constant pressure, and the resulting carbon dioxide was continuously removed in a trap immersed in liquid nitrogen. The loss of volume served as an approximate measure of the extent of carbiding. After consumption of a predetermined amount of carbon monoxide, the reaction was terminated by rapidly pumping off the remaining gas. In the experiments at the highest temperatures, the sample tubes were quenched in petroleum ether to minimize conversion of ε- to χ-carbide. The evacuated sample tubes were filled with petroleum ether, and the partly carbided samples were analyzed.

The analysis was performed on the magnetic balance by a modification of the procedure of Hofer and Cohn.[7] After measurement of the magnetic moments at room temperature, the samples were heated rapidly to 300° in the balance, and the magnetic moments were measured as soon as this temperature was attained. The samples were then annealed at 300°. At that temperature the transition from ε- (Curie point 380°) to χ-carbide (Curie p. 247°) took place, resulting in a loss of magnetic moment. The final, constant magnetic moment at 300° was measured after the transition was completed. The total amount of χ-carbide in the annealed samples was calculated from this measurement and from a subsequent one at room temperature. A thermomagnetic analysis was then made to check for the presence of cementite. This precaution is important, because a sample containing higher iron carbide and free iron could conceivably lose magnetic moment at 300° by the synthesis of cementite.[8] The absence of cementite proved that this reaction was not significant in the analysis of samples carbided up to 325°. In several samples, the carbides were tentatively identified by X-ray diffraction analysis. (Because of the short duration of carbiding, the carbides were present in small amounts and were poorly crystallized. This

(5) G. Braude, N. Shurmovskaya and B. Bruns, J. Phys. Chem. (U.S.S.R.), 22, 483 (1948).

(6) S. Weller, This Journal, 69, 2432 (1947).

(7) L. J. E. Hofer and E. M. Cohn, Anal. Chem., 22, 907 (1950).

(8) L. J. E. Hofer and E. M. Cohn, J. Chem. Phys., 18, 766 (1950).

fact and the use of filtered, rather than monochromatic, X-radiation resulted in very weak carbide patterns from which many lines were missing.) Moreover, in one sample the presence of ε-carbide was confirmed by its Curie point, obtained on rapid heating. As an additional check on the analytical method, the samples were heated at 450° to convert all of the carbide to cementite, and the amount of cementite thus formed agreed well with the sum of ε- and χ-carbide found by the initial analysis. A comparison of the absolute amounts of total carbide with the approximate values calculated from the consumption of carbon monoxide during carbiding indicates that the magnetic analyses for total carbide may be somewhat high. This, however, does not alter the conclusions which are drawn from the data. Although no magnetite was found by X-ray analyses of the reduced and the carbided catalysts, its presence (up to 5%) would not have affected the magnetic analyses significantly.

Results and Discussion

The experimental results are summarized in Tables I and II. At 250°, ε-carbide appeared as the

TABLE I

HIGHER IRON CARBIDES IN CARBIDED IRON CATALYSTS

Carbiding		Subsequent tempering		Magnetic analysis[a]	
Temperature, °C.	Duration, min.	Temperature, °C.	Duration, min.	ε, %	χ, %
Catalyst A-1008					
250	15			25	0
		250	300	16	11
275	6			21	7
		275	30	12	14
300	3			9	9
325	1³/₄			8	13
350	¹/₂			b	b
Catalyst D-3001					
190	60			25	0
250	3			34	0
275	1			26	6

[a] Carbide + iron = 100%. [b] Hägg carbide and cementite present.

TABLE II

X-RAY DIFFRACTION ANALYSES

Catalysts		A-1008				D-3001		
Carbiding temperature, °C.		250	275	300	325	275		
χ-Carbide							ε-Carbide	
Intensity[a]	d/n						Intensity[a]	d/n
vW	2.62							
W	2.48							
W	2.39						W	2.38
M	2.26							
M	2.18						M	2.16
vS	2.06	2.07	2.07	2.07	2.07	2.07	vS	2.08
vS	2.03					2.04		
W(br)	1.98							
M	1.91							
S	1.81		1.80	1.80?	1.80			
vW	1.76							
vW	1.72							
vW	1.67							
vW	1.62							
S	1.57	1.59				1.59	S	1.60
vW	1.50		1.48	1.48	1.48			
vW	1.37	1.36	1.36	1.36	1.36	1.36	M	1.37
vW	1.34							
vW	1.32				1.32			
W	1.27							
W	1.25							
M	1.21	1.23	1.23	1.23	1.23	1.23	M	1.21
W	1.17		1.20					
W	1.16						M	1.16

[a] W = weak, M = medium, S = strong, v = very, br = broad.

sole product, and its presence was demonstrated up to 325°. It is conceivable that more refined experimental methods would detect it at even higher temperatures. The annealing experiments show that the transition from ε- to χ-carbide *in vacuo* is sufficiently rapid to account for the absence of ε-carbide from most fully carbided iron catalysts, especially since the rate of carbiding decreases rapidly with the extent of carbiding. Moreover, the decreasing ratio of ε- to χ-carbide with increasing temperature may be accounted for on the basis that much, if not all, of the χ-carbide found at higher temperatures was originally ε-carbide.

Merkel and Weinrotter[9] found ε-carbide as the initial carbide in copper-containing iron catalysts that had been used in synthesis at 220°. They also observed that the ε-carbide was transformed to χ-carbide as the synthesis proceeded: Between 3.5 and 10 hours, about 10% of the ε-carbide was converted to χ-carbide. Their rate of transition from ε- to χ-carbide is not much different from the rates observed in the present study of copper-free catalysts, indicating that in their catalyst, at least, copper did not appreciably affect the rate of transition. Furthermore, the fact that they found ε-carbide under conditions where the transition took place indicates that ε-carbide may be the precursor of χ-carbide not only in an atmosphere of carbon monoxide but also in synthesis gas.

As mentioned in footnote *b* of Table I, the catalyst treated for 0.5 minute at 350° could not be ana-

lyzed magnetically for ε-carbide because of the presence of cementite. The synthesis of cementite from higher iron carbide and free iron is known to proceed at that temperature[8]; hence it is reasonable to assume that χ-carbide (and, indirectly, ε-carbide) is a precursor of cementite during the carbiding of iron.

The mechanism of the carbiding of iron catalysts may be closely related to the mechanism of the tempering of martensitic steels. ε-Carbide has been found[10] as an intermediate in the decomposition of martensite, which is therefore a precursor of ε-carbide in that reaction. It is conceivable that martensite, or a martensite-like substance, is also a precursor of ε-carbide in the carbiding reaction. If, as is likely, carbide nuclei are formed in the interior of crystallites of α-iron, carbon must diffuse from the surface through α-iron. It is known that carbon diffuses through α-iron only as carbon atoms. The solid solution of carbon in iron resulting from such diffusion cannot deposit carbon in ε-carbide unless it is supersaturated with respect to ε-carbide. Since martensite is a solid solution of carbon in α-iron which can contain enough carbon to deposit ε-carbide and which decomposes in about the right temperature range, martensite may be the precursor of ε-carbide in carburization.

Acknowledgment.—Thanks are due to Mrs. W. C. Peebles for X-ray diffraction analyses.

(10) K. H. Jack, *Acta Cryst.*, **3**, 392 (1950).

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(9) H. Merkel and F. Weinrotter, *Brennstoff-Chem.*, **32**, 289 (1951).

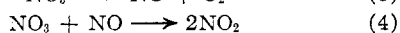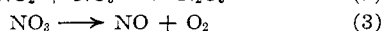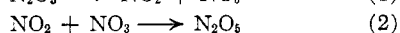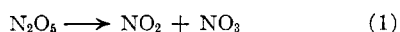[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

Kinetics of the Exchange of N^{15} between $N^{15}O_2$ and N_2O_5[1]

BY ALEXANDER R. AMELL AND FARRINGTON DANIELS

RECEIVED AUGUST 14, 1952

The rate of the exchange reaction $N^{15}O_2 + N_2O_5 \rightarrow NO_2 + N^{15}NO_5$ in the gas phase has been followed at -9, 0 and 10° using chemical separations and a mass spectrometer. The equation $k = 6.0 \times 10^{12} e^{-19,000/RT}$ can be used to express the experimental data. The agreement between this reaction rate and that for the reaction between nitrogen pentoxide and nitric oxide leads to the conclusion that the first step in both reactions is the bond-breaking step $N_2O_5 \rightarrow NO_2 + NO_3$. No effect of total pressure on the specific rate constants for isotopic exchange at low pressures was found, but no conclusions can be drawn concerning the existence of a pressure effect. Qualitative experiments are described in which the rate of decomposition of nitrogen pentoxide is increased by several gaseous reducing agents, as well as by nitric oxide.

In an effort to clear up some of the unanswered questions on the decomposition of N_2O_5, Smith and Daniels studied the rapid bimolecular reaction between NO and N_2O_5. As a result of this study Smith, in his Ph.D. thesis,[2] proposed the following mechanism for the N_2O_5 decomposition:

$$N_2O_5 \longrightarrow NO_2 + NO_3 \qquad (1)$$
$$NO_2 + NO_3 \longrightarrow N_2O_5 \qquad (2)$$
$$NO_3 \longrightarrow NO + O_2 \qquad (3)$$
$$NO_3 + NO \longrightarrow 2NO_2 \qquad (4)$$

Smith pointed out that this mechanism leads to a rate equation in which the decomposition of N_2O_5 is dependent on the concentration of NO_2, while the experimentally found decomposition is independent

of the NO_2 concentration. Smith and Daniels proposed the same mechanism with the elimination of equation (3) as fitting the experimental data for the NO + N_2O_5 reaction.[2-4]

In 1947, Ogg offered a clever explanation for the independence of the rate of decomposition of N_2O_5 on NO_2.[5] By the addition of NO_2 to both sides of equation (3) above (which then becomes $NO_3 + NO_2 \rightarrow NO + O_2 + NO_2$) he obtained a mechanism leading to a rate equation in which the decomposition of N_2O_5 is independent of the concentration of NO_2. Ogg also reported the exchange of N^{13} between N_2O_5 and $N^{13}O_2$ in CCl_4 solution as the first experimental evidence of the reversibility of the first step, i.e., $N_2O_5 \rightarrow NO_2 + NO_3$.

It seemed desirable to use the stable isotope N^{15}

(1) Further details of this investigation may be obtained from the Ph.D. thesis of Alexander R. Amell, filed in the Library of the University of Wisconsin, September, 1950.

(2) J. H. Smith, Ph.D. Thesis, University of Wisconsin, June, 1941.

(3) J. H. Smith, St. Louis Meeting, Am. Chem. Soc., April 9, 1941.

(4) J. H. Smith and F. Daniels, THIS JOURNAL, **69**, 1735 (1947).

(5) R. A. Ogg, *J. Chem. Phys.*, **15**, 337, 613 (1947)