ISOTHERMAL DECOMPOSITION OF NICKEL CARBIDE

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INTRODUCTION

The present study of the thermal stability of nickel carbide, like a previous and similar one of a carburized cobalt Fischer-Tropsch catalyst (6), was made to gain more insight into the problem of the formation of free carbon during hydrocarbon synthesis by the Fischer-Tropsch process. This undesirable side reaction leads to plugging of fixed-bed reactors or disintegration and loss of catalyst in fluidized-bed converters, and to a decrease or total loss of catalytic activity. Information obtained from this type of study should be useful in eliminating the conditions responsible for formation of free carbon, which can be produced by way of metal carbide (5, 17):

$$xM + 2CO \rightarrow M_zC + CO_2 \tag{1}$$

and

$$M_x C \rightarrow x M + C \text{ (free)}$$
 (2)

This mechanism of formation of free carbon by decomposition of the metal carbides is supported by the fact that only those metals which form metastable carbides are known to form free carbon from carbon monoxide.

Nickel carbide. Ni₃C, is well known from several investigations (1, 2, 9, 11-15, 17, 18). It has been prepared by passing carbon monoxide, carbon monoxide and hydrogen, methane, benzene vapor, or illuminating gas over nickel oxide or over reduced nickel catalysts (with or without promoters and supports) at 170- 250° C., or at higher temperatures where carbide formation is incomplete and noticeable amounts of free carbon are formed. The carbide, which is relatively stable up to about 250°C., has a close-packed hexagonal crystal structure with a = 2.646 Å., c = 4.329 Å., and c/a = 1.636, according to Jacobson and Westgren (9), or a = 2.65 Å., c = 4.32 Å., and c/a = 1.63, according to Le Clerc (12, 13), whose "hexagonal nickel" must have been Ni₂C according to the method of preparation. Tutiya's (18) results also support this structure. Kohlhaas and Meyer (11) found additional x-ray lines and ascribed an orthorhombic structure to Ni₃C, isomorphous with Fe₃C. This structure has not been substantiated as yet, however. According to Bahr and Bahr (1), Ni₃C is only very weakly ferromagnetic. Their sample was not fully carburized, so that the ferromagnetism was probably due to a small amount of residual nickel. One carbide sample used

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for the present study contained slightly more than the stoichiometric amount of carbon and was nonferromagnetic within the limits of error of the measurements, in accordance with the observation of Le Clerc and Michel (13). Two carbides of nickel are known definitely so far, Ni₃C and Ni₅C. A postulated nickel carbide, Ni₃C₂ (1), has not been found, and its existence was denied by Schmidt (15). Durand (4) has prepared nickel acetylide, NiC₂, by an entirely different method. Tebboth (17) tentatively assumed that Ni₃C decomposes to free metal and carbon by way of Ni₆C. The intermediate formation of this lower nickel carbide at 350°C. (the temperature at which Tebboth's data were taken to support this hypothesis) is unlikely, as will be shown later.

MATERIALS AND PREPARATION

One formula weight (297.7 g.) of nickel nitrate hexabydrate was dissolved in 4 l. of distilled water at 80°C, and a solution of 112 g. of potassium hydroxide in 500 ml. of distilled water at room temperature was added with stirring. The

hki	I*	d† (observed)	d (calculated)	hkl	I*	$d\dagger$ (observed)	d (CALCULATED)
100	w	2.2808	2.2909	200	vw	1.1420‡	1.1453‡
002	W	2.1563	2.1648	112	S	1.1277	1.1293
101	S	2.0189	2.0249	201	M	1.1076	1.1072
102	W	1.5731	1.5734	004	w	1.0827	1.0824
110	M	1.3228	1.3225	202	W	1.0128	1.0123
103	M	1.2213	1.2211		}		

TABLE 1 Determination of lattice constant for Ni₂C

*S = strong, M = medium, W = weak, VW = very weak.

† Corrected by using sodium chloride, $a_0 = 5.628kX$, as an internal standard.

‡ Line not used in calculation for lattice constant because of faintness.

precipitate was washed five times, each time with a solution of 10 g. of ammonium nitrate in 3 l. of distilled water, after which it was filtered and dried in air. Reduction in a Rose crucible showed that the sample contained 58.4 weight per cent nickel; the theoretical value for nickel hydroxide is 63.3 weight per cent. The x-ray diffraction pattern was identical with that obtained by Cairns and Ott (3).

A portion of this preparation (in four sample tubes) was reduced with hydrogen for 85 hr. at 275°C. to virtually constant weight. One of the tubes was then removed for x-ray diffraction analysis and found to contain face-centered cubic nickel. The remaining tubes were carburized with carbon monoxide at 250°C. for 22.5 hr., at which time another sample was removed for x-ray and magnetic analyses. Only the lines of close-packed hexagonal nickel carbide, Ni₃C, were observed on the x-ray film. After an additional 91-hr. carburization, the rate of carbon uptake of the remaining two tubes had become negligible, and the third sample tube was used for x-ray and magnetic studies. The lattice constant of Ni₃C was determined using this sample. The corrected (8) x-ray diffraction lines

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are listed in table 1. The lattice dimensions found were a = 2.6449 kX., c = 4.3296 kX., and c/a = 1.637 (average values from calculations of six films taken from four samples). The average carbon-nickel weight ratio of the two completely carburized tubes was 0.0725, an excess over the ideal stoichiometric ratio, 0.0682, for Ni₃C. The carbon in the remaining tube was completely removed with hydrogen after 26.25 hr. at 250°C., proving that essentially only carbidic carbon had been present in the sample. The reduced product was, of course, face-centered cubic nickel, as indicated by x-ray diffraction. The course of the carburization and reduction is shown in figure 1.

APPARATUS AND PROCEDURE

The magnetic balance (7, 16) and procedure (6) used for the decomposition study have been described previously.



FIG. 1. Carburization and subsequent reduction, both at 250°C., of finely divided nickel

RESULTS

1. Fully carburized Ni₃C

The first series of experiments was carried out with samples taken from tube No. 3, i.e., fully carburized Ni₈C (weight ratio C:Ni = 0.0722:1). As in the case of Co₂C, the course of the reaction was followed by measuring the increase of ferromagnetism, or the formation of metallic nickel, as a function of time at constant temperature and field strength.

In this case, however, the decomposition was preceded by an induction period which was analogous to that found by Jolivet and Portevin (10) for the decomposition of austenite. Because it was difficult to estimate, this interval has been defined as the time elapsed from the moment the reaction temperature was reached until 5 per cent of the carbide was decomposed. At 333°C., for example, one sample was found to have an induction period of about 9 hr., while 90 per cent of the carbide decomposed during the following 4.5 hr. In order to ascertain whether any internal structural changes occurred during the induction period, another sample was heated to 333° C. It developed ferromagnetism after 6 hr. and was cooled after a total of 7 hr. Only the original carbide and a small amount (about 5 per cent) of nickel metal were present according to the x-ray diffraction pattern; no phase transformation had taken place during the induction period. This period decreased with increasing temperature; it varied, however, within rather wide limits for different samples and could not always be determined accurately.

A typical decomposition-rate curve is shown in figure 2. The decomposition rate of the carbide was linear in the range of about 65-75 per cent to about 5-15



FIG. 2. Thermal decomposition of fully carburized Ni₃C at 323°C.

per cent of remaining carbide. These portions of the curves were used to calculate apparent zero-order rate constants for that range of carbide content. Table 2 contains the induction periods and the apparent specific reaction-rate constants (see also evaluation of data, below) measured between 323°C. and 355°C.

The effect of shortening the induction period upon the quasi-zero-order specific reaction rate was determined on four samples of fully carburized Ni₃C. The procedure was as follows: Each sample was heated to a certain temperature, T, in 5 min. and kept at that temperature for a measured interval, t, then cooled to 343°C. in 2 min. and allowed to decompose completely at 343°C. Table 3 is a summary of the data. There was no apparent effect upon the reaction rate until the (additional) induction period at 343°C. was eliminated; then the reaction rate was approximately twice the former rate. It may be noted here that the calculated induction period for 381°C. is 15.9 min., and that the calculated zero-order reaction rate at that temperature is 3.75×10^{-3} /sec.

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2. "Ninety-five per cent" carburized Ni₃C

The sample in tube 2 had a carbon-nickel weight ratio of 0.0647, i.e., it was 95 per cent carburized on the basis of an ideal stoichiometric weight ratio for Ni₃C. It was feebly ferromagnetic at room temperature, and this magnetism disappeared upon heating. A comparison of the ferromagnetism before and after decomposition indicated the presence of only 1-3 per cent free nickel. It is possible that some of the nickel was so finely divided as to be magnetically unsaturated

DECOMPOSITION TEMPERATURE	INDUCTION PERIOD	APPARENT SPECIFIC REACTION-BATH CONSTANT, &
°C.	min.	
323	1320	3.4×10^{-5}
323	960	3.9×10^{-5}
323	660	4.0×10^{-5}
333	540	7.8×10^{-3}
333	420	9.7×10^{-5}
333	420	11 × 10 ⁻⁵
343	180	23×10^{-5}
343	240	19×10^{-5}
355	100	51×10^{-5}

TABLE 2

Induction period and quasi-zero-order rate constants for isothermal decomposition of fully carburized $\rm Ni_sC$

TABLE 3

Effect of shortened induction period upon rate of decomposition, at 343 $^\circ$ C., of fully carburized Ni $_{\rm s}$ C

T	t TIME AT T	ADDITIONAL INDUCTION PERIOD AT 343°C.	QUASI-ZERO-ORDER DECOMPOSITION RATE
°C.	min.	min.	sec1
375	10	155	1.8×10^{-4}
381	10	60	2.3×10^{-4}
381	13	0	3.6×10^{-4}
381	15	None; about 20 per cent already decomposed	4.1×10^{-4}

or even nonferromagnetic, thus yielding an apparently lower percentage of nickel by magnetic measurements than was actually present. On the other hand, nickel carbide, being an interstitial alloy, need not necessarily take up carbon stoichiometrically to become the close-packed hexagonal carbide. For the sake of convenience, the preparation is called "95 per cent" carbide, even though it may have been 95–99 per cent carbide.

A preliminary experiment had shown that the induction period of this sample was considerably shorter at 320°C. than that of the fully carburized sample. A study of the variation of the induction period with temperature was therefore made, and a few rate constants of the decomposition were also determined. (The shape of the decomposition-time curves was the same as that observed with fully carburized samples.) The data are summarized in table 4.

EVALUATION OF DATA

The data were treated analogously to those obtained with cobalt carbide (6). The absence of ferromagnetism in the fully carburized sample and the complete

TEMPERATURE	INDUCTION PERIOD	QUASI-ZERO-ORDER RATE CONSTANT
°C.	min.	sec1
320	660	8.6×10^{-6}
328.5	470	
328.5	306	
335	180	
335	211	
342	180	
349	180	2.3×10^{-4}
349	137	
355.5	105	2.1×10^{-4}
355.5	90.5	2.6×10^{-4}
355.5	Heated at 342°C. for 11 hr. initially	2.7×10^{-4}

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TABLE 5

Activation energies and "frequency factors" for the thermal decomposition of Ni₃C and of Co₂C

	E energy of activation	A "frequency factor"		
	kcai./mole		sec1	
Induction period, fully carburized Ni ₃ C	55	3	× 10	15
Ni ₂ C.	61	1	× 10	16
Induction period, "95 per cent" carburized Ni ₈ C Decomposition (zero-order range), "95 per cent"	36	4	\times 10	8
carburized Ni ₃ C.	71	1	× 10	21
Decomposition (zero-order range), Co ₂ C in catalyst 108B*	54.3	3.89	× 10	16

• Described in reference 6.

reducibility of another, identically prepared sample indicated that only Ni₃C was present before decomposition. The final time-independent ferromagnetism —or constant angle of twist of the sample in the magnetic balance—was proof of complete decomposition into metallic nickel and free carbon. Hence, the angle of twist of the sample was directly proportional to the amount of decomposed carbide, with zero angle corresponding to 100 per cent Ni₃C and the final

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angle to 0 per cent Ni_3C . The small amount of metallic nickel present in the incompletely carburized sample (see above) was neglected in calculating the amount of decomposed carbide, the error being within the limits of accuracy of the measurements. To evaluate the temperature dependence of the induction period, the reciprocal of the induction period was treated as a specific reactionrate constant and used in the Arrhenius equation:

$k = A e^{-B/RT}$

The activation energies, E, and "frequency factors," A, computed by the method of least squares from the data in tables 2 and 4, are summarized in table 5, where the earlier data for Co₂C are included for comparison. The dimensions of A and of the specific reaction-rate constants in tables 2 to 4 are sec.⁻¹, because the calculations were carried out using "fraction of the original carbide remaining at any time."

DISCUSSION

It has been shown that thermal decomposition of unpromoted and unsupported nickel carbide, Ni₃C, is preceded by an induction period during which no apparent structural change takes place and that this is followed by the simple reaction Ni₃C \rightarrow 3Ni + C. Thus, Tebboth's (17) hypothesis that Ni₆C is an intermediate in the decomposition was not substantiated, and it appears unlikely that Ni₆C plays such a role in the decomposition of promoted and/or supported Ni₃C catalysts. That does not mean, of course, that Ni₆C may not be present in such catalysts before decomposition, especially at lower temperatures.

In some of the older literature Ni₃C is said to be stable below 400°C. \pm 20° (1, 11, 14). This statement, originally based on faulty thermodynamic studies, is obviously incorrect (12, 13, 15, 17, 18).

Since Ni₃C is metastable, its observed "stability" is purely a result of the small rate of decomposition at low temperatures. This "stability" is a kinetic effect and is, therefore, subject to the mode of preparation of the carbide, addition of inhibitors or accelerators of the decomposition, thermal treatment, etc. In view of the fact that an induction period precedes the decomposition, one may assume that some of the early investigators of Ni₃C did not permit enough time to elapse to notice decomposition below about 380°C. It is very doubtful, however, that the carbide could be stabilized sufficiently to withstand heating for 8 hr. at 420°C. without any sign of decomposition, as was claimed by Kohlhaas and Meyer (11) for one of their preparations.

Over the temperature range investigated, the induction period has the same properties as that of decomposing austenite (10) (corresponding to the lowertemperature branch of Jolivet's curves). The whole course of the decomposition suggests an autocatalytic reaction mechanism. The formation of reaction centers appears to be necessary to start the decomposition. The temperature dependence of the decomposition of fully carburized nickel was similar to that found for a carburized cobalt Fischer-Tropsch catalyst (6). Also, the activation energy and "frequency factor" of the induction period were of the same order of magnitude as those of the decomposition. Changing the induction period appeared to have little, if any, effect on the reaction rate over a wide range of time. When the induction period was shortened to a few minutes' heating at a higher temperature, however, the reaction rate at a lower temperature was approximately doubled. An incompletely carburized preparation exhibited a greatly shortened induction period at 320°C., and the induction period was much less sensitive to temperature changes than that observed for completely carburized Ni₃C. Contrary to the induction periods, however, the half-life of the "95 per cent" carbide, as calculated from the quasi-zero-order rate constants, was three times that of the pure carbide at 325°C. and twice that of the pure carbide at 355°C. (see table 6). If one assumes a nucleation mechanism for the thermal decomposition of nickel carbide, then it appears that some nuclei form much more readily in incompletely carburized nickel carbide, but that they are not as numerous as in a fully carburized carbide, or that their rate of growth is slower than in fully carburized carbide. It is also possible that the metal-carbide interface is a catalyst

TABLE	6
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Time necessary to decompose 50 per cent of the carbide after completed induction (calculated from quasi-zero-order rates)

	HALP-LIFE AT	
	325°C.	355°C.
	hours	hours
Fully carburized nickel, Ni ₂ C	3.0	0.26
"95 per cent" carburized nickel, Ni ₃ C.	9.1	0.53

for nucleus formation. Whatever the exact mechanism may be, the quasi-zeroorder range of decomposition appears to be only slightly affected by a shortening of the induction period (effected by heating at temperatures higher than the temperature at which the reaction rate is measured), provided not more than about 20 per cent of the carbide has been decomposed at the higher temperature. In other words, the zero-order range of the decomposition is relatively insensitive to the previous history of the carbide. Clearly, thermal decomposition of the carbide can be avoided by keeping it at suitable low temperatures; once the carbide has been exposed to higher temperatures long enough to produce sufficient decomposition, it will then decompose at about the zero-order rate of the temperature at which it is subsequently kept. To illustrate this point, one may consider the following example³: If fully carburized Ni₃C is heated to 300°C., it can be kept at that temperature for about 108 hr. until about 5 per cent of the material is decomposed. If this carbide is overheated at 381°C. for 13 min. and then cooled to 300°C., 50 per cent of it will decompose in (probably less than) 28.5 hr.

^{*} It is assumed here that the data can be extrapolated to 300°C.

SUMMARY

1. The thermal stability of nickel carbide, Ni₃C, was studied magnetically and by x-ray diffraction between 320° and 355° C. on a fully carburized and on an almost fully carburized sample.

2. An induction period precedes the decomposition. This period is analogous to that found for the decomposition of austenite. There is no detectable structural change in the carbide during the induction period.

3. The carbide decomposed into free metal and free carbon without intermediate formation of a lower carbide.

4. Shortening the induction period by temporary overheating did not affect the zero-order rate of the decomposition except when the normal induction period was completely suppressed. In that case, the zero-order rate was approximately doubled.

5. In the range from about 70 to 10 per cent nickel carbide, the decomposition rate was constant; hence the reaction was of apparent zero order in that range.

6. Empirical activation energies were found for the induction periods (i.p.) and quasi-zero-order range of decomposition (d.) of the fully carburized carbide (100) and the almost fully carburized carbide (95) as follows: $E_{i.p.100} = 55$, $E_{d.100} = 61$, $E_{i.p.95} = 36$, $E_{d.95} = 71$ kcal./mole.

REFERENCES

- (1) BAHR H. A., AND BAHR, T.: Ber. 61, 2177 (1928).
- (2) BAHR, H. A., AND BAHR, T.: Ber. 63, 99 (1930).
- (3) CAIRNS, R., AND OTT, E.: J. Am. Chem. Soc. 55, 527 (1933).
- (4) DURAND, J. F.: Compt. rend. 177, 693 (1923).
- (5) HOFER, L. J. E.: U. S. Bur. Mines Rept. Investigations 3770 (1944).
- (6) HOFER, L. J. E., COHN, E. M., AND PEEBLES, W. C.: J. Phys. & Colloid Chem. 53, 661 (1949).
- (7) HOFER, L. J. E., COHN, E. M., AND PEEBLES, W. C.: J. Am. Chem. Soc. 71, 189 (1949).
- (8) HOFER, L. J. E., AND PEEBLES, W. C.: J. Am. Chem. Soc. 69, 893 (1947).
- (9) JACOBSON, B., AND WESTGREN, A.: Z. physik. Chem. 20B, 361 (1933).
- (10) JOLIVET, H., AND PORTEVIN, A.: Compt. rend. 213, 687 (1941).
- (11) KOHLHAAS, R., AND MEYER, W. FR.: Metallwirtschaft 17, 786 (1938).
- (12) LE CLERC, G., AND LEFEBVRE, H.: Compt. rend. 208, 1650 (1939).
- (13) LE CLERC, G., AND MICHEL, A.: Compt. rend. 208, 1583 (1939).
- (14) SCHEFFER, F. E. C., DOKKUM, T., AND AL, J.: Rec. trav. chim. 45, 803 (1926).
- (15) SCHMIDT, J.: Z. anorg. allgem. Chem. 216, 85 (1933).
- (16) STORCH, H. H., ANDERSON, R. B., HOFER, L. J. E., HAWK, C. O., AND GOLUMBIC, N.: U. S. Bur. Mines Tech. Paper 709 (1948).
- (17) TEBBOTH, J. A.: J. Soc. Chem. Ind. 67, 62 (1948).
- (18) TUTIYA, H.: Bull. Inst. Phys. Chem. Research (Tokyo) 10, 951 (1930).