4. Solubility curves have been obtained for $Na_2Si_2O_5$ from undersaturation but they could not be checked from supersaturation.

5. The solubility curve for $\beta 3Na_2O\cdot 13SiO_2\cdot 11H_2O$ changes but slightly with temperature. This composition best fits the experimental data.

6. The solid phases observed at the temperatures used were: $3Na_2O\cdot 13SiO_2\cdot 11H_2O$, $Na_2Si_2O_5$, Na_2SiO_3, $Na_2SiO_3\cdot H_2O$, $\alpha Na_2SiO_3\cdot 6H_2O$, $\beta Na_2SiO_3\cdot 6H_2O$, $Na_2SiO_3\cdot 5H_2O$, $Na_3HSiO_4\cdot 5H_2O$, $Na_3HSiO_4\cdot 2H_2O$, $Na_3HSiO_4\cdot H_2O$, NaOH and $NaOH\cdot H_2O$.

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[CONTRIBUTION FROM THE MELLON INSTITUTE AND THE UNIVERSITY OF PITTSBURGH]

Preparation, Stability and Adsorptive Properties of the Carbides of Iron[1]

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Introduction

The possible importance of metallic carbides in the synthesis of hydrocarbons from hydrogen and carbon monoxide over catalytic Co, Ni or Fe was first suggested by Fischer and Tropsch.[2] They proposed that the carbides might be intermediates in the Fischer–Tropsch process by being formed by the reaction of carbon monoxide with the metals and reduced by hydrogen to form hydrocarbons. In recent years it seems to have been well established that for iron[3a,b] and probably for cobalt[4,5] the bulk carbides are not intermediates. Nevertheless, the carbides are known to be formed during synthesis. It seemed well, therefore, to obtain some information relative to the adsorptive properties of the carbides toward carbon monoxide and hydrogen with a view to assessing more accurately their part, if any, in the Fischer–Tropsch synthesis. The present paper reports such adsorption studies for the various iron carbides and also gives additional information relative to the preparation and properties of the iron carbides including the use of hydrocarbons as carbiding agents, the rate of carbiding as a function of surface area, and the relative stability of samples of Fe_3C, Hägg Fe_2C, and hexagonal Fe_2C.[6]

Experimental

The apparatus employed both for carbiding runs and for adsorption measurements was an adaptation of a standard adsorption apparatus such as has been used in surface area measurements by low-temperature adsorption isotherms and has been described on numerous occasions.[7,8] Surface area measurements with nitrogen at −195° were made on all samples of carbides and metals used in the present work.

The catalyst tube was held at a constant temperature (to within ±0.25°) in the range 100 to 500° by using a furnace control similar to that described by Benedict.[9] A thermocouple in a well down the center of the catalyst tube enabled one to detect any temperature rise in the catalyst during carbiding or adsorption runs. Liquid nitrogen, Dry Ice–alcohol, and ordinary ice were used for the −195, −78.5 and 0° baths, respectively. The bath at −46° was maintained by keeping chlorobenzene at its melting point.

Carbon monoxide was prepared from formic acid and phosphoric acid. Just before use, it was passed over hot copper at 300° to remove traces of oxygen; through soda-lime to remove carbon dioxide: and through a Dry Ice trap to remove water vapor. Helium and tank nitrogen were purified by standard procedures.

Hydrocarbons (Phillips hydrocarbon gases, pure grade) were employed for some of the carbiding in place of carbon monoxide. The hydrocarbons (usually either propane, butane or pentane) were further purified by being passed over hot reduced copper, through a tube containing ascarite and finally through a tube containing freshly-activated alumina. The pentane was carried over the iron catalyst with pure dry helium.

The iron catalysts used for preparing the adsorbents in the present work were fused synthetic ammonia-type catalysts. Except for catalyst 910, which was free of added components, promoted catalysts were used in this investigation. Most of the work was done on promoted catalyst 423 which, in addition to oxygen, contained 72.26% Fe, 2.26% Al_2O_3, 0.62% SiO_2 and 0.21% ZrO_2. The other catalysts employed were 435, with 72.2% Fe, 0.8% Al_2O_3 and 0.25% K_2O; and 422, with 73.26% Fe, 1.55% Al_2O_3 and 0.58% ZrO_2. These fused oxide catalysts were initially reduced with hydrogen at space velocities near 1000 and at successively higher temperatures starting at 350 and extending up to 500° for the promoted catalysts.

The samples carbided with carbon monoxide were prepared by passing carbon monoxide over the reduced catalysts at temperatures starting at 200° and increasing gradually to 275°. As is well known,[10,11,12] iron under these conditions will form a carbide that can be identified by its X-ray structure and that corresponds approximately in composition to Fe_2C. In the present work, the percentage carbiding was determined in two ways. During the carbiding process a sample of the exit gas was analyzed for carbon dioxide at various time intervals. An integration of this time *vs.* carbon dioxide curve gave values for the total carbon dioxide yield from which the extent of carbiding was calculated by assuming that the carbon monoxide reacted with the iron to form Fe_2C and carbon dioxide. The amount of carbide formed was checked by noting the increase in the weight of the sample. The two methods always agreed to within about ±0.1% carbide carbon when correction was made for a trace of oxygen

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[1] Joint contribution from the Gulf Research & Development Company's Multiple Fellowship, Mellon Institute, and the University of Pittsburgh, Pittsburgh, Pa.

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

[3] (a) Kummer, DeWitt and Emmett, THIS JOURNAL, **70**, 3632 (1948); (b) Browning, Kummer and Emmett, *J. Chem. Phys.*, **16**, 739 (1948).

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

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

[6] Hofer, Cohn and Peebles, *ibid.*, **71**, 189 (1949).

[7] Emmett, *A. S. T. M.*, **41** (1941).

[8] Emmett, "Advances in Colloid Science," Interscience Publishers, New York, N. Y., 1941, pp. 1–36.

[9] Benedict, *Rev. Sci. Instruments*, **8**, 252 (1937); **12**, 36 (1941); **13**, 24 (1942).

[10] Bahr and Jessen, *Ber.*, **66**, 1238 (1935).

[11] Hägg, *J. Krist.*, **89**, 92 (1934).

[12] Jack, *Nature*, **158**, 60 (1946).

taken up as oxide during the carbiding. A final check on the composition of the sample[13] could be obtained by noting the weight loss on reduction. All of the carbidic carbide can be reduced quantitatively at 300° without reducing any appreciable amount of free carbon that might be present.[10]

In an attempt to prepare a carbided iron sample whose surface was free of oxide, hydrocarbon gases were tried for carbiding. The carbiding was effected by simply passing the pure hydrocarbon gas (propane, butane or pentane) over a thoroughly reduced catalyst at temperatures between 250 and 350°.

Results and Discussion

Preparation and Properties of the Carbides of Iron.—In the present work it has been found that preparing the Hägg carbide, Fe_2C, by the reaction of hydrocarbons and iron has numerous advantages over the usual method of preparation employing carbon monoxide as the carbiding agent. To begin with, the carbiding can be carried out rapidly (in a few hours) at 275 to 325° by passing butane, propane or pentane over an iron catalyst[14] without any appreciable temperature rise in the catalyst. In contrast to this, carbiding with carbon monoxide is very exothermic and may easily cause a temperature rise of 20° or more unless one takes the precaution to start the carbiding at a relatively low temperature in the range 200 to 225°. There is no evidence of the formation of any free carbon if a hydrocarbon is used as a carbiding agent, whereas with carbon monoxide there is a considerable danger of forming some free carbon before the sample is completely converted to Fe_2C. With care, however, even with carbon monoxide as a carbiding gas we have found it possible to convert Fe almost completely to Fe_2C without the formation of any free carbon. After the accumulation of about 9.1% carbidic carbon, free carbon tends to form at and above 300° if carbon monoxide is used as a carbiding agent.

A second advantage of carbiding with butane or other hydrocarbon is the possibility of producing the carbides of iron entirely free of any oxide. In contrast to this, we have found that invariably about 0.3% oxygen is taken up by the iron during carbiding with carbon monoxide for carbide contents ranging from 2 to 9.1%. On catalyst 423 on which the experiments to detect oxide were performed, this would correspond to about two layers of iron oxide if the oxygen were uniformly distributed over the surface.

Two striking differences were noted between the carbides formed by using a hydrocarbon gas as a carbiding agent and those formed by carbiding with carbon monoxide. In the first place, it was not found possible to incorporate more than about 7.5% carbidic carbon into a sample by carbiding with a hydrocarbon, whereas at least 9.1% carbidic carbon could be incorporated in an iron catalyst if carbon monoxide were used as a carbiding gas. Even heating the sample in butane for 16 hours at 350° did not cause more than the 7.5% carbidic carbon to be incorporated into the sample. The X-ray photographs of the Fe_2C formed by carbiding with a hydrocarbon gas were identical to the patterns of the Fe_2C formed using carbon monoxide except, of course, that the lines due to free iron were more intense in the sample containing 7.5% carbidic carbon than in one containing 9.1%.

Perhaps the biggest difference between the carbides formed by the two different carbiding agents was the stability of the Fe_3C formed by heating the Fe_2C samples to 400 or 450°. The cementite formed from an Fe_2C that had been prepared by carbiding with carbon monoxide is quite stable and will withstand many hours heating in vacuum at 500° without decomposing into iron and carbon. On the other hand, the cementite formed from Fe_2C samples prepared by carbiding with butane was found to decompose almost completely at 500° in a few hours as judged in all cases by the intensity of the patterns in the X-ray photographs.[15] The cause of this difference is not known with certainty although the oxide impurity present in carbides formed from carbon monoxide and an iron catalyst appears to have a stabilizing influence on the cementite.

Data in the literature clearly indicate very different rates of carbiding with carbon monoxide that depend on the size, the nature and the purity of the iron samples. We have accumulated in our studies considerable evidence that this rate is approximately proportional to the iron surface area. These data are listed in Table I. It is evident that the initial rate of carbiding per unit area as given in column 4 is fairly constant. However, correcting for the fraction of the surface covered with promoter to obtain a constant rate per unit surface of free iron[16] gives

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(13) Actually, attempts to check the composition by reduction were made on only a few of the carbide samples listed in Tables I and II. However, these reductions corrected for the small amount of water vapor coming from the slight amount of oxide present agreed quite well with the composition established by the weight increase or the CO_2 formation. Reduction at 300° by hydrogen of a number of samples not shown in the present work confirmed the agreement among the three methods for estimating the per cent. carbide present.

(14) Methane can also be used for carbiding but the rate is very much slower than with propane, butane or pentane.

(15) This point has been confirmed by some recent observations by L. C. Browning of this Laboratory. He found that a sample of Fe_2C prepared by carbiding an iron catalyst with butane underwent 93% decomposition to iron and carbon during two hours heating at 500° and 16 hours heating at 470°; similar heating of a sample produced by carbiding this same iron catalyst with carbon monoxide caused only 7% decomposition. Mr. Browning also confirmed the influence of surface oxide on the stability of the iron carbides. He noted that partial removal of some of this oxide from the surface by reduction with hydrogen speeded up the rate of reduction of the carbide and also made the sample decompose to iron and carbon at 500° at about the same rate as a sample carbided with butane.

(16) The free iron surface on reduced iron catalysts was estimated by carbon monoxide chemisorption at −195° by the method developed by Emmett and Brunauer.[17] The total volume of carbon monoxide adsorption at −195° (chemical plus physical) minus the volume of the adsorption at −195° (physical) following an evacuation at −78.5° was called the volume of chemisorbed carbon monoxide

even better agreement among the various catalysts (column 5, Table I). Only catalyst 435 containing alkali in addition to aluminum oxide as promoters has a rate of carbiding that is severalfold greater than the average initial carbiding rate.

Table I

Studies on the Rate of Carbiding Iron Catalysts with Carbon Monoxide

Catalyst sample no.	Initial compn.., wt. % C as Fe_2C	Carbiding rate at 225°[a] cc. (S. T. P.) of CO_2 per min.		
		Per gram of iron	Per unit[b] total surface area	Per unit[b] area of surface iron
910–4	0.0	0.141	0.47	0.51
910–4	2.0	.028	.08	.25
910–4	2.8	.010	.03	.18
910–4	3.9	.0013	.004	.14
910–1	0.0	.072	.33	.61
910–2	.0	.061	.29	.48
910–3	.0	.084	.49	.59
435–1	.0	.59	.42	2.1
435–1	4.2	.212	.14	.24–0.47
423	0.0	.40	.10	0.35
423	.0	1.43	.29	.74
423	.0	0.495	.11	.38
423	6.8	.05	.01	.10
423	9.1	.00017	.00004	.0013

[a] Rates have been corrected to 225° by employing an activation energy of 32.5 kcal. for the carbiding reaction. [b] Unit total surface area is the amount covered by 1 cc. of physically adsorbed nitrogen present as a monolayer. Unit surface area of free iron is based on the number of cc. of CO chemisorbed on the catalyst surface as per reference 17.

The activation energy for carbiding with carbon monoxide was determined for two different types of catalysts (910 and 423) by two different procedures. The carbiding rates at 212° on one sample of catalyst 910 were compared at identical compositions with the rates of carbiding at 245° for another sample of catalyst 910. Activation energies based on rates per unit total area were calculated and compared with values based on rates per unit original free iron surface (obtained from CO chemisorption on the reduced sample). They were found to average 31.5 kcal. when the rates were corrected to a constant total surface and 33.6 kcal. when corrected to a constant area of free iron surface; they were independent of the per cent. carbide over the range studied, 0.2 to 1.13%.

In the second method, assumptions regarding surface areas were avoided by interrupting a carbiding experiment, changing the temperature and resuming carbiding at the new temperature. Calculation of the activation energy was based on the final rate at the first temperature and the initial rate at the second. Activation energies calculated from this type of study of the rate of carbiding (on catalyst 423) yielded a value of 29.6 kcal. at a carbidic carbon content of 6.6% carbon and 34 kcal. at 7.7% carbon. The energy of activation of carbiding iron with carbon monoxide thus appears to be 32.5 ± 3 kcal. per mole of Fe_2C and is independent of the degree of carbiding.

Finally, we have made a few observations relative to the formation and properties of hexagonal Fe_2C and the stability of Hägg Fe_2C that may be of interest. The hexagonal carbide mentioned by Hofer, Cohn and Peebles[6] and also by Halle and Herbst[18] is usually prepared from iron catalysts containing Cu. This element supposedly stabilizes the hexagonal Fe_2C by slowing down the rate of transformation to Hägg Fe_2C. Its preparation from iron synthetic ammonia catalysts containing both K_2O and Al_2O_3 has also been reported.[18] We have been able to observe the exclusive formation of the hexagonal Fe_2C by partially carbiding to 2.5% carbidic carbon at 210° iron catalyst 423 which contained neither copper nor alkali. When the carbiding was continued at the same temperature to a total of 6.5% carbon, Hägg Fe_2C appeared though detectable amounts of the hexagonal carbide were still present.

Definite indications have been obtained that the Fe_2C in a partially carbided iron catalyst containing about 6.7% carbidic carbon converts to Fe_3C more readily at 500° by the reaction

$$Fe + Fe_2C \longrightarrow Fe_3C \qquad (1)$$

than by the usual reaction

$$3Fe_2C \longrightarrow 2Fe_3C + C \qquad (2)$$

The evidence is threefold. To begin with, heating a sample containing 6.7% carbidic carbide (50% Hägg Fe_2C, 50% αFe) at 500° for *3 hours* produced a larger fractional conversion to Fe_3C than heating a sample of Hägg Fe_2C containing 9.1% carbidic carbon for the same length of time at the same temperature. In the second place, X-ray photographs showed that the sample containing 6.7% carbidic carbon changed almost completely to Fe_3C and left only a very small amount of iron (<10%) and a trace of Fe_2C. Finally, 93% of the 6.7% carbidic carbon originally present was readily removed from the final Fe_3C sample in 16 hours by reduction by hydrogen at 300°. This shows the absence of any large amount of free carbon in the product since the removal of free carbon at a reasonable rate requires a temperature of about 500°. Hence, reaction (1) apparently occurs preferentially to reaction (2) if free iron is present.

Adsorption of Carbon Monoxide and Hydrogen by Fe_2C.—The study of the adsorption of carbon

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and was used as a measure of the free iron surface. For convenience we shall refer to the "per cent. free iron surface" on the various reduced samples as 100 (volume of chemisorbed CO)/(volume of N_2 in a monolayer). The value so obtained is probably a little high since the area occupied by each chemisorbed carbon monoxide molecule is probably a little smaller than the area occupied by a molecule of physically adsorbed nitrogen.

(17) Emmett and Brunauer, This Journal, **59**, 310 (1937).

(18) Group Leader Conference Ludwigshafen, T. O. M. Reel 26, Bag 2463. Report Dr. Wenzel, T. O. M. Reel 134, Item II/10.

monoxide on partially carbided iron Fischer–Tropsch catalysts had a twofold purpose. In the first place, it seemed to afford a means of judging the amount of free iron left on the surface as a function of the extent of carbiding. For this type of information chemisorption measurements at −195, −78.5 and −46° were used. The second and more direct object was the ascertaining of the extent to which carbon monoxide appears to be adsorbed on a carbided surface at or near synthesis temperatures.

All of the measurements made with carbon monoxide at −195, −78.5 and −46° lead to the conclusion that the "free iron" surface decreases as the per cent. carbiding increases. However, some "free iron" surface still exists as the carbidic carbon content approaches the value corresponding to pure Fe_2C. In other words, the carbon monoxide chemisorption results tend to confirm the conclusion reached previously in some experiments using radioactive carbon[3a] to the effect that carbiding proceeds through the formation of carbide nuclei and not with the laying down of uniform layers of carbide over the entire surface.

The experimental evidence for this conclusion is contained in the adsorption data for −195° given in Table II and in plots for adsorption data for −78.5 and −46° given in Figs. 1 and 2, respectively. The data indicate that about 3% of the surface of catalyst 423 consists of "free iron" even when the sample was carbided with carbon monoxide to 9.1% content of carbidic carbon or was carbided with butane to 7.5% carbidic carbon content.

TABLE II

INFLUENCE OF CARBIDING ON THE LOW TEMPERATURE (−195°) CHEMISORPTION OF CO

Catalyst sample no.	Composition (wt. % C as Fe_2C)	N_2 monolayer cc. (S.T.P.) per g. of Fe	Chemisorbed CO,[a] cc. (S. T. P.) per g. of Fe		Ratio of (5) to (3)
			Before carbiding	After carbiding	
910–4	0.0	0.30	0.276	0.276	0.92
910–4	2.0	.33	.276	.114	.346
910–4	2.8	.33	.276	.055	.167
910–4	3.9	.35	.276	.010	.030
435	0.0	1.4	.28	.28	.20
435	4.2	1.5	.28	.04–0.09	.03–0.06
423A	0.0	4.6	1.43	1.43	.31
423A	2.3	4.7	1.43	0.71	.15
423A	6.8	4.5	1.30	.50	.11
423A	9.1	4.5	1.30	.14	.03
423B	4.3	4.7	1.46	.71	.15[b]
324B	6.8	4.6	1.40	.37	.08[c]
423C	2.9	4.4	1.27	.70	.16[c]
423C	7.3	4.5	1.26	.14	.03[b]
423C	7.1	4.4	1.29	.14	.03[b]

[a] See reference 17. [b] Butane was used as a carbiding agent in these runs. [c] Propane was the carbiding agent in these runs. All samples other than those marked (b) or (c) were carbided with carbon monoxide.

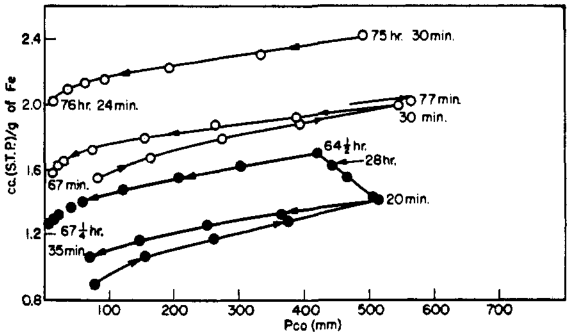

Fig. 1.— -●-, CO adsorption at −78.5° on iron catalyst 423 carbided with CO to 6.8% carbon. Nitrogen monolayer was 4.5 cc. (S.T.P.) per gram of Fe; -○-, CO adsorption at −78.5° on iron catalyst 423. Nitrogen monolayer was 4.6 cc. (S.T.P.) per gram of Fe. The times allowed for equilibration are shown.

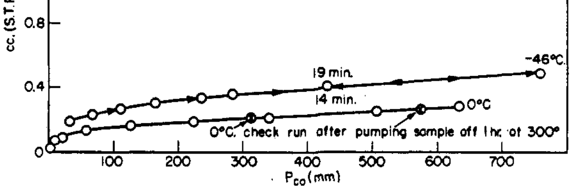

Fig. 2.— -●-, CO adsorption at −46° on iron catalyst 423 carbided with CO to 1.54% carbon. Nitrogen monolayer was between 4 and 4.5 cc. (S.T.P.) per gram of Fe. One additional adsorption point taken at the end of 5 minutes at 64 mm. pressure was 0.97 cc. per gram; -○-, CO adsorption at −46 and 0° on iron catalyst 423 carbided with CO to 9.1% carbon. Nitrogen monolayer was 4.5 cc. (S.T.P.) per gram of Fe.

Figure 3 reveals the presence of a form of weak chemisorption of carbon monoxide on all of the partially carbided samples in addition to the strong chemisorption that has been described above. On the reduced iron catalyst the isotherms for the physical adsorption of carbon monoxide [designated as CO(P)] always fall nearly directly upon the nitrogen adsorption isotherm. This is not surprising since the physical properties of the two gases are so similar. However, when any carbide is present, the repeat isotherm for carbon monoxide after the −78.5° evacuation[19] is always a little larger in extent than the nitrogen isotherms. This is consistent with the existence of a loosely bound type of chemisorption that is formed under the layer of physical adsorption on these partially carbided samples but that is not sufficiently tightly bound to withstand the one-hour pumping at −78.5°. Some

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[19] The evacuation proceeded as the temperature was raised from −195 to −78.5°.

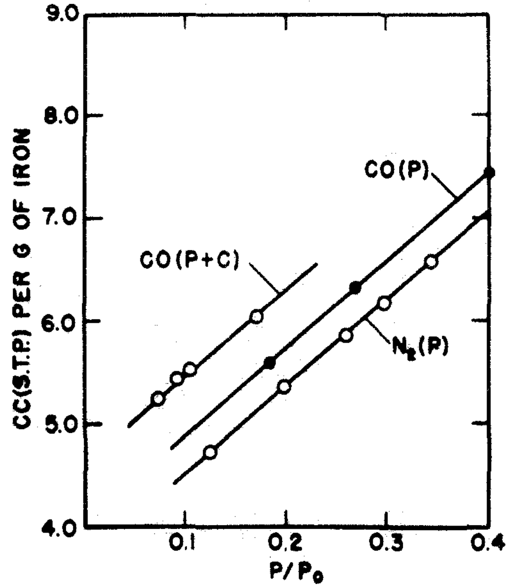

Fig. 3.—Isotherms for physical adsorption of nitrogen. N_2(P); physical adsorption of carbon monoxide, CO(P); and physical plus chemical adsorption of carbon monoxide. CO(P + C) at −195° on iron catalyst 423 carbided with CO to 6.8% carbon at 250°. Nitrogen monolayer was 4.5 cc. (S.T.P.) per gram of Fe.

evidence has been obtained showing that both Fe_3O_4 and Fe_2O_3 exhibit this same loosely bound type of chemisorption of carbon monoxide on 10 to 30% of their surfaces. It is, therefore, possible that this loosely bound chemisorption is due to the small amount of surface oxide that is known to accompany the carbiding with carbon monoxide and that probably was not completely eliminated even in the samples using butane as a carbiding gas.

Numerous carbon monoxide adsorption isotherms were obtained but all were not permitted to reach final equilibrium and were not included here. Nevertheless, they indicate as well as those shown in Figs. 1 and 2 that the carbon monoxide chemisorption decreases as the per cent. carbide builds up. Indeed, the reduction in adsorption at −78.5 and −46° that results from carbiding is approximately the same as at −195°. Incidentally, it will also be noted that even at 0° the chemisorption of CO is very small (~0.1 cc. per gram at 50 mm.) on a sample containing 9.1% carbidic carbon.

One of the −46° experiments merits special comment. In the run shown in Fig. 2 for a sample containing 1.54% carbidic carbon, the adsorption was permitted to continue for more than 50 hours until an equilibrium isotherm was obtained that apparently was not undergoing any additional drift. Points taken at five minutes and at 203 minutes showed clearly that even the 1.55% carbidic carbon was retarding the adsorption of carbon monoxide. However, the total adsorption in about 50 hours was surprisingly large. This raises the question of the nature of this slow adsorption. The high chemisorption shown in Fig. 2 would indicate that only about 45% of the surface was covered with promoter and carbide and that the other 55% was covered with "free iron."[17] However, as judged by the −195° chemisorption, only 32% of the surface is covered with free iron. Clearly, one possible explanation of the difficulty can be that at the higher temperature the chemisorbed carbon monoxide is able to reorient itself slowly in such a way as to occupy a much smaller area per molecule at −46° than at −195°. A glance at the average size of the iron atoms in the 100, 111 and 110 faces makes this explanation rather reasonable. The areas per surface iron atom for these three planes are, respectively, 8.2, 14 and 5.8 Å.[2] If the exposed faces were mostly 110 and if these at −195° were able to hold only one carbon monoxide for each two iron atoms but at −46° were slowly able to pick up additional carbon monoxide to make one carbon monoxide for each iron atom, the results could be explained. Another possibility that cannot be definitely excluded is that some formation of iron pentacarbonyl slowly takes place and that this product might be adsorbed in such a way as partially to overlap the promoter and carbide molecules. Regardless of which explanation proves to be the right one, it is definitely certain from desorption measurements that the large volume of carbon monoxide taken up by the catalyst containing 1.5% carbidic carbon is either chemisorbed or held in a compound (such as iron carbonyl) which on being raised to a higher temperature at low pressure gives up carbon monoxide. Thus by pumping first at −46° (at which temperature 2.2 cc. of CO was still retained by the catalyst when the pressure was lowered to less than 10^{-4} mm.) and then at gradually increasing temperatures, it was possible to recover 2.5 cc. (±0.2 cc.) of carbon monoxide that had been taken up by the sample at −46°.

Chemisorption measurements on carbon monoxide at 100 and 200° indicate that the carbide does not chemisorb carbon monoxide at these temperatures. In contrast, iron itself will chemisorb carbon monoxide extensively both at 50° and at 100°. At 150° iron begins to carbide with carbon monoxide so rapidly as to make adsorption measurements difficult. However, on the completely carbided samples (9.1% carbon when put on by carbiding with carbon monoxide and 7.5% carbon when carbided with butane) no detectable chemisorption of carbon monoxide occurred at even 200°.

Two types of activated adsorption of hydrogen exist[20] on iron synthetic ammonia catalysts. One variety, called type A, begins to take place at an appreciable rate at −78°; it decreases in volume

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[20] Emmett and Harkness, This Journal, **57**, 1631 (1935).

at equilibrium at a given pressure as the temperature is increased. At or above 100° a second kind of activated adsorption (type B) sets in at such a rate as to reach equilibrium in a reasonable time. The equilibrium value for type B is considerably above the extrapolation of the isobar for type A. However, type B like type A decreases in amount as the temperature is increased over the range 100 to 450°. The exact nature of these two types of adsorption has never been ascertained but there seems to be little doubt that they have very different properties.

Experiments done in conjunction with the present measurements confirmed the existence of these two types of adsorption on reduced catalyst 423. Thus at 600 mm. pressure, the equilibrated isotherms showed adsorption values of 1.08, 0.95, 0.92, 1.1 and 0.52 at −78.5, −46, 0, 200, and 375°, respectively. To conserve space, only the isotherm showing a few measurements at various short time intervals in addition to the final equilibrated values at 200° are given for the reduced iron in Fig. 4.

Carbiding the iron catalyst with carbon monoxide or with butane practically eliminated the low-temperature type A adsorption, but had only a slight effect on type B adsorption until the carbon content was built up in the range 7.7 to 9.1%. The influence of carbiding on the adsorption of hydrogen both in the −78.5 to 0° region and the 100 to 200° region is illustrated by the curves in Fig. 4 for a sample containing 6.8% carbidic carbon. In an experiment on the sample containing 9.1% carbidic carbon, it was found that even at 55° the type A adsorption at 600 mm. was only about 3% of the value that would occur rapidly at this temperature on the reduced catalyst. For the 9.1% carbon content the hydrogen adsorption at 200° was appreciably decreased, but even for this sample the adsorption was two-thirds as great as on the reduced catalyst.

There is no way of knowing from the results in the present paper the extent to which the residual adsorptive capacity of the carbided samples for hydrogen at and above 100° may have been influenced by the small amount of surface oxide that is formed by carbiding with carbon monoxide. An indication that the amount of surface oxide is related to the sorption capacity for hydrogen was obtained on a sample carbided with butane to 7.45% carbon. The hydrogen adsorption at 100° following a surface oxidation (by addition of O_2 at −195°) was increased more than twofold to a value of 0.25 cc. per gram at 100 mm. pressure during a 20-minute run. Another evidence pointing in this same direction is the fact that the hydrogen adsorption at 200° on a sample carbided with butane to a 6.5% carbon content was only about one-half as great (0.3 cc. per gram at 100 mm.) as on a sample carbided with carbon monoxide to a carbon content of 6.8%[21] (0.6 cc. per gram at 100 mm. as shown in Fig. 4). At any rate, it is certain that an appreciable residual hydrogen adsorption exists even on a nearly completely carbided sample at temperatures near those at which synthesis will take place and that unless the sample contains more than about 6.8% carbidic carbon, the adsorption is nearly as large as is obtained at the same temperature on the reduced catalyst.

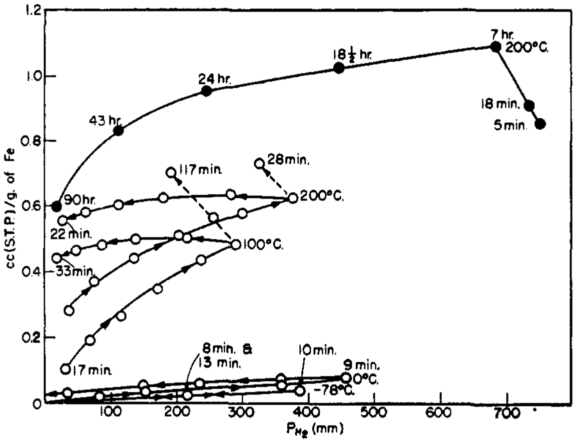

Fig. 4.—-●-. H_2 adsorption at 200° on iron catalyst 423 reduced at 500°. Nitrogen monolayer was 4.3 cc. (S.T.P.) per gram of Fe; -○-. H_2 adsorption at −78.5, 0, 100 and 200° on iron catalyst 423 carbided with CO to 6.8% carbon. Nitrogen monolayer was 4.5 cc. (S.T.P.) per gram of Fe.

Two runs were made on the adsorption of hydrogen and carbon monoxide from a mixture of these two gases at 150 and 200° on a sample that had been carbided with carbon monoxide to a total carbidic carbon content of about 8%. At a partial pressure of about 150 mm., 0.32 cc. H_2 and 0.04 cc. CO were chemisorbed per gram at 150° in 50 minutes; from CO alone at this temperature, partial pressure and time, 0.017 cc. was adsorbed. At 200°, in 25 minutes at 150 mm. partial pressure of each gas, 0.39 cc. of H_2 and 0.11 cc. of CO were adsorbed per gram. These CO adsorption values from hydrogen and carbon monoxide mixtures are about 5% as large as had been obtained on the same catalyst before carbiding; the hydrogen adsorption is about 50% as great from the mixture on the carbided sample as from pure hydrogen on a reduced sample.

In view of the extreme difficulty of obtaining samples of pure Fe_2C for the adsorption measurements, it is hard to evaluate with certainty the sorptive capacity of this carbide. However, the work in the present paper definitely indicates that carbon monoxide chemisorption at synthesis temperature is blocked out by carbiding the iron catalyst either with carbon monoxide or with

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(21) This evidence based on the low adsorption of hydrogen by a sample carbided with butane is subject to some uncertainty because of the recent discovery that some carbon–hydrogen fragments and some adsorbed hydrogen are left on the sample even after a thorough evacuation at 300°.

butane. It therefore appears safe to conclude that the Fe_2C formed during synthesis is not capable of strongly adsorbing carbon monoxide either by itself or in the presence of hydrogen. On the other hand, the carbided samples are capable of holding hydrogen by activated adsorption at temperatures close to those at which synthesis will occur. Since any likely mechanism for the synthesis would seem to involve the adsorption of the carbon monoxide as well as the hydrogen, it seems probable that the catalyst in Fischer–Tropsch synthesis is not Hägg Fe_2C. A final discussion of the relation of the adsorption measurements to the conclusions that can be drawn as to the mechanism of synthesis will be made in a forthcoming paper after the presentation of adsorption data for carbon monoxide and hydrogen both as separate gases and as mixtures on metallic iron and on Fe_3O_4.

Summary

1. Hägg Fe_2C can be formed by carbiding finely-divided iron catalysts with a hydrocarbon such as propane, butane or pentane equally as well as carbiding with carbon monoxide. The carbiding process using a hydrocarbon is not accompanied by a lay-down of free carbon or by any strong exothermicity.

2. The samples of Fe_2C formed by using butane as a carbiding gas still contain a little residual iron after the carbiding reaction at 300° apparently comes to an end. Only about 7.5% carbon seems capable of being incorporated by this procedure in the catalyst employed.

3. It is possible to form hexagonal Fe_2C by carefully carbiding an iron synthetic ammonia catalyst at about 215° with carbon monoxide, even though the catalyst does not contain copper.

4. Carbon monoxide is still chemisorbed by a partially carbided iron catalyst at −195, −78.5 and −46°, indicating that the carbiding proceeds through the formation of nuclei of carbide rather than by the formation of a smooth layer of carbide over the catalyst surface.

5. The formation of carbide eliminates most of the chemisorption of carbon monoxide at 100 and 200°. It also eliminates the chemisorption of hydrogen in the temperature region −78.5 to 0°. On the other hand, it has little effect on the higher temperature type of hydrogen adsorption occurring at and above 100° until the catalyst samples are almost completely converted to Fe_2C.

6. The energy of activation for carbiding iron with carbon monoxide to form Fe_2C is about 32.5 kcal. per mole.

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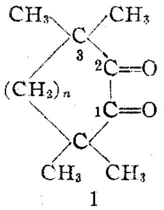
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Influence of Steric Configuration on the Ultraviolet Absorption of 1,2-Diketones

BY NELSON J. LEONARD AND PAUL M. MADER

An excellent method for arriving at the relationship between ultraviolet absorption and steric orientation of the carbonyl groups in the 1,2-dicarbonyl chromophore would appear to be through the preparation of a series of alicylic 1,2-diketones of type I and the determination of their absorption spectra. In such a system there will be a dependence of the angle between the planes of the carbonyl groups upon the size of the ring. Thus, when $n = 1$ (Ia) the dicarbonyl groups are constrained to a *cis* relationship due to the fixity of the five-membered ring, and the absorption spectrum of the compound (Ia) should therefore be representative of *cis* coplanar dicarbonyls. As the ring size is increased (from $n = 1$ to $n = 2, 3, 4$, etc.), the angle between the carbonyls is gradually increased from 0°, or *cis* coplanarity, until the ring becomes large enough (*e. g.*, $n = 14$) to accommodate the carbonyl groups at 180°, or *trans* coplanarity. The absorption spectra of these diketones with increasing ring size will therefore be representative of two adjacent carbonyl groups with regularly increasing interplanar angles. In this system (I) selected for study, there will be no extraneous influence on the absorption due to enolization[1] since the α-carbons are completely alkyl-substituted.



I

a, $n = 1$; b, $n = 2$; c, $n = 3$; d, $n = 4$; e, $n = 14$

Experimental[2]

Special Apparatus.—The low-temperature crystallization apparatus shown in Fig. 1, which was necessary for

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(1) (a) Schwarzenbach and Wittiner, *Helv. Chim. Acta*, **30**, 663 (1947); (b) Wallach, *Ann.*, **437**, 148 (1924); (c) Wheland, *J. Chem. Phys.*, **1**, 731(1933); (d) French and Holden, THIS JOURNAL, **67**, 1239 (1945).

(2) All melting points are corrected. The authors are indebted to Miss Emily Davis, Miss Rachel Kopel, Mrs. Jane Wood and Mr. Maurice Dare for the microanalyses reported herein and to Mrs. James Johnson, Miss Elizabeth Petersen, Mrs. John C. Brantley and Mr. John Gardner for their aid in obtaining the absorption spectra data.