550°. This is presumably connected with the greater retention of ammonia acquired in the treatment with ammonium chloride during the preparation and reflects the higher acid-strength index of the catalyst with 90% silica.

It is evident for both catalysts that the acid determined by butylamine titration reaches a high value at a lower temperature of heat treatment than that required for developing maximum polymerization activity. The latter reaches a maximum only when the temperature of heat treatment is adequate to develop the greatest quantity of protonic acid. This provides additional evidence that the protonic acid is of greater significance in the polymerization of propylene than total acids or Lewis acid alone.

CARBON FORMATION FROM CARBON MONOXIDE–HYDROGEN MIXTURES OVER IRON CATALYSTS.[1,2] I. PROPERTIES OF CARBON FORMED

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Received April 8, 1958

The properties of carbons formed from various carbon monoxide–hydrogen mixtures in a flow system over iron catalysts at temperatures from 450 to 700° and atmospheric pressure have been investigated. The crystallite height, surface area, C–H ratio and electrical resistivity of the carbons are found to be markedly affected by formation temperature, gas composition and amount of carbon formed over the catalyst. The carbons have an unusually well developed crystalline character, considering the relatively low formation temperatures, with crystallite heights in most cases being above 100 Å. and interlayer spacings indicating substantial three-dimensional ordering.

Introduction

The majority of research on the reaction $2CO \rightarrow C + CO_2$ has been prompted by its highly deleterious effects on currently or potentially important industrial processes. Ceramic brick linings containing iron undergo physical disintegration when exposed to carbon monoxide under certain conditions, because of carbon formation within the porous material. The Fischer–Tropsch process used for the synthesis of hydrocarbons is subject to carbon deposition, which may lead to blockage of the reaction vessel and to deactivation and disintegration of the catalyst. The reaction has become of concern in nuclear reactors, when graphite is used as the moderator and carbon dioxide as the coolant. The extent of carbon transfer by the combined reactions of carbon monoxide formation by carbon gasification in the high temperature reactor zone and carbon monoxide decomposition to carbon in the low temperature reactor zone must be understood.

Recently there has been interest shown in using the carbon monoxide deposition reaction to produce carbons of commercial utility. During World War II, the Germans used the reaction to produce a substitute for carbon black.[3] A French patent describes a process and equipment for producing carbon in a falling-bed reactor using a finely divided iron catalyst.[4] A recent American patent describes an apparatus for the production of carbon black at conditions between 700 to 1035° and 10 to 40 atm., where a metallic catalyst is not necessary.[5] An excellent, annotated bibliography of the literature and patents related to the production of carbon by the decomposition of carbon monoxide has been compiled.[6]

This research had two main objectives: (1) to investigate in detail the structure of carbon produced by the decomposition of carbon monoxide over an iron catalyst, as a function of temperature and inlet carbon monoxide–hydrogen composition, and (2) to investigate the effect of temperature and inlet carbon monoxide–hydrogen composition on the rate and amount of carbon formation before deactivation of the iron catalyst occurs. All reactions were conducted at atmospheric pressure. This first paper discusses the properties of the carbons formed.

Experimental

Reactor.—The reactor consisted of a Vycor combustion tube 600 mm. long, 25 mm. i.d., and 31 mm. o.d., heated by a conventional split-tube furnace. The catalyst was held in a Coors porcelain micro combustion boat, glazed inside and outside, size 0000, having a volume of 0.2 cc. A Vycor thermocouple protection tube, 7 mm. o.d. and 5 mm. i.d., extended halfway into the reactor tube and housed a chromel–alumel thermocouple for measuring reaction temperature. A second chromel–alumel thermocouple, located between the reactor and the furnace windings, was connected to a Phen-Trols Electronic Temperature Controller, which held the reactor temperature within ±5°. Auxiliary equipment included wet test meters, before and after the reactor, to determine cumulative gas flow; a rotameter to measure instantaneous helium, hydrogen or carbon monoxide flow into the reactor; water saturators immediately before the wet test meters; Ascarite towers before and after the reactor to remove carbon dioxide; and magnesium perchlorate towers before and after the reactor to remove water.

Catalysts.—The iron catalyst used for the majority of the

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[1] Based, in part, on an M.S. thesis submitted by G. R. Imperial to the Graduate School of the Pennsylvania State University, August, 1957.

[2] At different stages, this work was supported by the Reading Anthracite Company and the Atomic Energy Commission under Contract No. AT(30-1)-1710.

[3] B.I.O.S. Final Report No. 1399, Item No. 22.

[4] French Patent No. 874,681 (August 18, 1942).

[5] U. S. Patent No. 2,716,053 (August 23, 1955).

[6] An Annotated Bibliography, H. Jack Donald, Mellon Institute of Industrial Research, 1956.

work was a Baker Analyzed reagent grade iron powder produced by reducing iron carbonyl in hydrogen (called carbonyl iron, for convenience). The powder consisted of spherical particles having an average diameter on a weight basis of *ca.* 10 μ. Following reduction of the powder in hydrogen for 24 hours at 400° the material had a B.E.T. surface area of 0.99 m.^{2}/g., as given by nitrogen adsorption. The powder packed to a bulk density of *ca.* 2.7 g./cc. in the porcelain boat prior to reaction. Additional information on the catalyst is available from a recent publication.[7]

Because of interest in a cheap, successful catalyst for the carbon monoxide deposition reaction, some runs were made using "Sinter B," which is an iron typical of the sintered by-product made from iron-containing fines blowing from the top of open hearths and blast furnaces.[8] Morton[9] presents detailed physical and chemical properties of a "Sinter B." X-Ray diffraction analysis of the "Sinter B" used in this research yielded lines for Fe_2O_3 and SiO_2 as the main constituents. The B.E.T. surface areas of an 80 × 100 and a −100 mesh fraction of "Sinter B" heated to 528° was 0.41 and 0.46 m.^{2}/g., respectively, as given by nitrogen adsorption.

The iron catalysts used in this research have a negligible surface area compared to conventional catalysts used commercially for the ammonia synthesis and Fischer–Tropsch processes. Therefore, initially (prior to significant catalyst disintegration) they will be found to be much less active than commercial catalysts.

Reactants.—All gases were obtained from the Matheson Company. Helium and hydrogen, used for pretreatment, were guaranteed at 99.8 and 99.9% purity, respectively. The carbon monoxide–hydrogen mixtures were analyzed by the Matheson Company by either an Orsat apparatus or a mass spectrometer. In addition to the two main constituents, the mixtures contained up to 0.3% carbon dioxide (removed prior to entering the reactor), traces of iron pentacarbonyl (removed by decomposition in the entering end of the reactor), and small amounts of oxygen and nitrogen. A maximum of 0.3 mg. of sulfur per liter of gas was found.

X-Ray Diffraction Apparatus.—A 164° (2θ) General Electric X-ray diffraction unit, XRD-3, was employed to determine interlayer spacings and average crystallite heights of the carbons produced. Copper radiation was used except when analyzing samples containing high concentrations of iron and/or iron carbide. In those cases, iron radiation was substituted because of the excessive absorption of the copper radiation by iron compounds. Standard X-ray procedures and subsequent calculations for graphitic specimens, as discussed in detail in a recent paper,[10] were adopted. Three separate X-ray samples for each carbon were analyzed. With a few exceptions, the interlayer spacing and average crystallite height data varied less than ±0.003 Å. and ±5%, respectively, on a given carbon.

Electrical Resistivity Apparatus.—The apparatus and procedure employed in this determination has been described.[11] Essentially the electrical resistivity of a sample was determined by comparing the voltage drop across a known sample length with that across a fixed resistance, both carrying the same total current. Electrical resistivities could be duplicated within ±2.5% on a given sample.

Low Temperature Gas Adsorption Apparatus.—A standard gas adsorption apparatus[12] was employed to obtain adsorption isotherms, using nitrogen as the adsorbate. Specific surface areas, calculated from the isotherms by the B.E.T. equation, could be duplicated within ±2.5%. An equilibration time of one-half hour for each adsorption point proved more than ample.

Acid Treatment of Raw Carbon.—Some of the raw carbons were treated separately with 12 *N* HCl, 15 *N* HNO_3 and 50% by weight of HF to remove compounds of iron. The procedure for HCl and HNO_3 treatment consisted of boiling 0.63 g. of raw carbon with 50 cc. of acid for a designated period of time, washing the purified carbon with hot water in a Morton bacteria filtering apparatus (containing a fritted disc with openings of less than 2 μ), and drying at 120° in a vacuum oven. The procedure for HF treatment was similar, except that in the initial step 0.63 g. of raw carbon and 10 cc. of acid were held in a platinum crucible and the contents evaporated to dryness.

Typical Carbon-deposition Run.—An iron sample of desired weight was placed in the porcelain boat, which in turn was centered in the Vycor reactor tube. Prior to a run, helium was passed through the entire system (5.8 cc./sec., STP) for one-half hour, during which time the volume of gas passing through the two wet test meters was recorded to check for leaks. Then, with helium flow continuing, the reactor was brought to reaction temperature and allowed to equilibrate during a second half-hour period. After the period of helium flow, the catalyst usually was pretreated by reducing in hydrogen (11.0 cc./sec.), for one hour. In other runs, the catalyst was pretreated by carbiding with carbon monoxide (5.8 cc./sec.) at 359° for varying lengths of time. In some runs, no pretreatment of the catalyst was employed.

In runs using hydrogen pretreatment, the carbon monoxide–hydrogen mixture was passed into the reactor (5.8 cc./sec., unless otherwise specified) immediately following the pretreatment. Following the carbiding pretreatment and prior to the introduction of the carbon monoxide–hydrogen mixtures, helium was passed through the reactor while the catalyst was being brought to reaction temperature. During the passage of the carbon monoxide–hydrogen mixture, the cumulative volumes of gas passing through the wet test meters, before and after the reactor, were recorded. Before the gas entered the exit wet test meter, it was passed through an Ascarite tower, where the carbon dioxide which was formed during the reaction was removed.

At the end of a run, helium was passed (30 cc./sec.) through the reactor while it was cooled to room temperature. Cooling was greatly accelerated by opening of the split-tube furnace and directing a stream of compressed air against the reactor tube. After cooling, the contents of the reactor tube were removed, the weight of free carbon being taken as the difference between the total weight of material removed and the initial weight of catalyst employed.[13,14]

Results and Discussion

Electron Micrographs of Carbon.—Electron micrographs of the carbon produced from the decomposition of carbon monoxide at different temperatures, from different carbon monoxide–hydrogen mixtures, and after varying amounts of carbon formed per weight of catalyst were obtained. The nature of the carbon formed agrees with that shown in previously published electron micrographs of carbon deposited over iron, cobalt and nickel.[15–17] The most characteristic growth consisted of two carbon filaments tightly twisted into a rope over 1 μ in length and between 0.1 and 0.5 μ in diameter. Much bifilamentary growth also was observed, where the carbon threads did not become twisted. It was not possible, however, to associate a particular type of growth with variations in operating conditions.

At the end of the carbon growths, there invariably was located a particle of iron and/or iron carbide, which presumably was the catalyst for the growth of the particular filament. Figure 1 presents a dark-field micrograph of a carbon (78%

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[7] P. L. Walker, Jr., and F. Rusinko, Jr., This Journal, **59**, 1106 (1955).

[8] C. B. Bigelow, *Am. Inst. Mining Met. Engrs.*, **10**, 103 (1951).

[9] R. J. Morton, *ibid.*, **10**, 122 (1951).

[10] P. L. Walker, Jr., H. A. McKinstry and J. V. Pustinger, *Ind. Eng. Chem.*, **46**, 1651 (1954).

[11] P. L. Walker, Jr., and F. Rusinko, Jr., *Fuel*, **36**, 43 (1957).

[12] P. H. Emmett, A.S.T.M. Tech. Publ. No. 51, 95 (1941).

[13] The increase in weight actually represents closely the total carbon (free carbon plus carbidic carbon); but the maximum carbidic carbon present, for all runs reported, represents less than one per cent. of this weight and can be ignored. Therefore, in the future discussion free carbon and carbidic carbon will not be distinguished.

[14] The actual weights of carbon were less than computed values because of competing reactions producing hydrocarbons.

[15] L. V. Radushkevich and V. M. Luk'yanovich, *Zhur. Fiz. Khim.*, **26**, 88 (1952).

[16] L. J. E. Hofer, E. Sterling and J. T. McCartney, This Journal, **59**, 1153 (1955).

[17] W. R. Davis, R. J. Slawson and G. R. Rigby, *Trans. Brit. Ceram. Soc.*, **56**, 67 (1957).

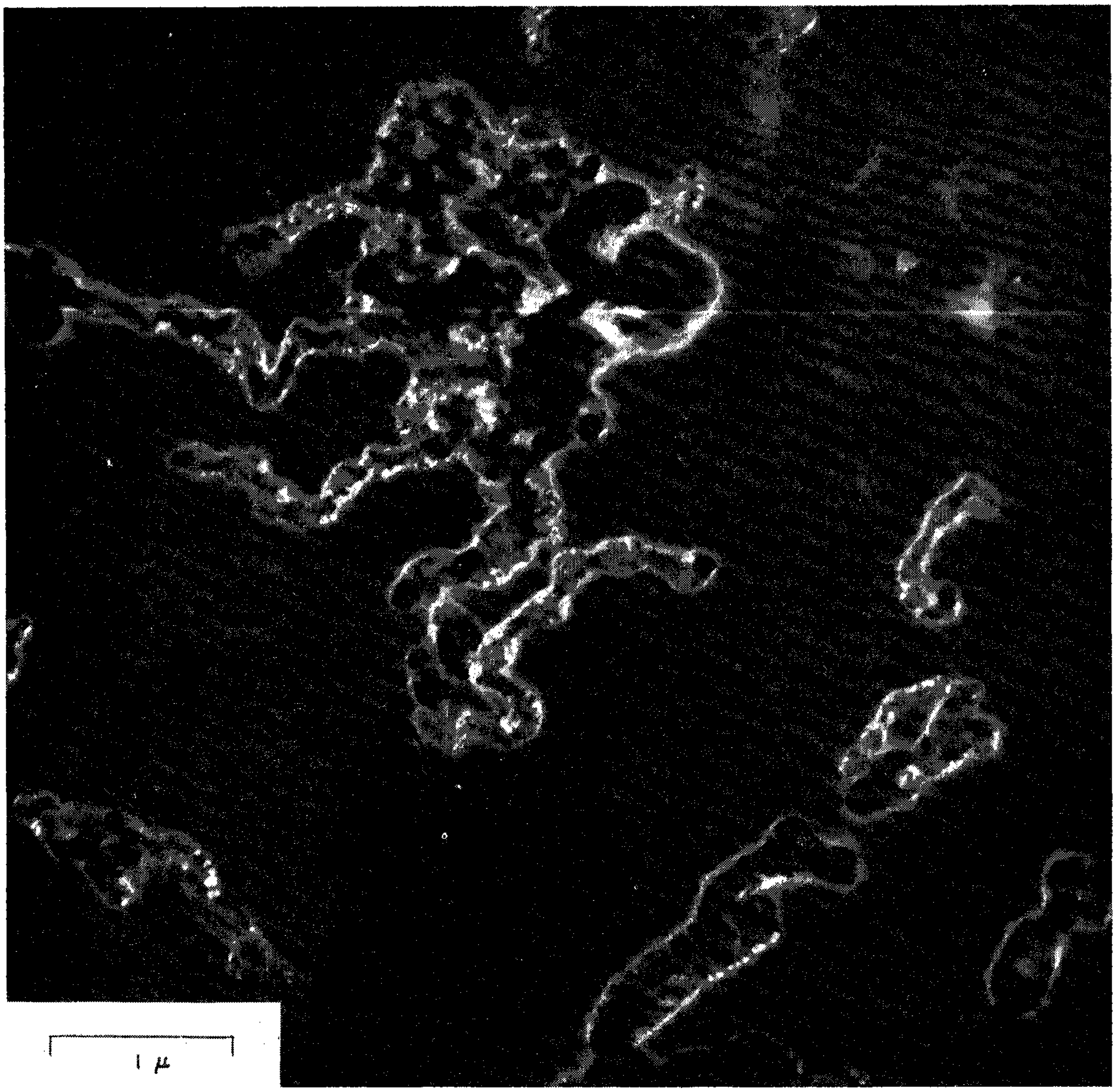

Fig. 1.—Dark-field electron micrograph of raw carbon (78% C–22% Fe) formed at 528° from a 98.6% CO–1.4% H_2 mixture over carbonyl iron.

C–22% Fe) formed at 528° from a 98.6% CO–1.4% H_2 mixture over carbonyl iron. The micrograph clearly shows the location of the iron-containing material. The particle size of this material is markedly less than that of the original carbonyl iron, agreeing with the findings of Tenenbaum and Joseph[18] that carbon monoxide deposition on and within iron disintegrates the material.

Under dark-field conditions, crystalline areas of the solid diffract the electron beam and sharp, light lines are produced. Such diffraction from the carbon filaments is observed in Fig. 1, indicating the crystalline nature of the carbon formed. This has been confirmed by X-ray diffraction studies, to be discussed.

Properties of the Carbon Produced by Decomposition of Carbon Monoxide–Hydrogen Mixtures over Carbonyl Iron.—Initially, it was desired to investigate only the effect of temperature and carbon monoxide–hydrogen composition on the character of the carbon formed. To do this, other factors (total gas flow rate, amount of carbon formed per starting weight of iron, and pretreatment of the iron), were held constant. A 0.1-g. sample of iron was used from which *ca.* 0.9 g. of carbon was produced, meaning that the final carbon had *ca.* 10% iron (primarily Fe and Fe_3C) present. Table I presents the data on the average crystallite height and interlayer spacing of the carbon produced.[19] To the authors' knowledge, the crystallite heights (L_c) of the majority of the carbons produced are considerably larger than those reported for other carbonaceous materials having seen comparable maximum temperatures. For example, typical carbon blacks,[20] carbons pro-

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[18] M. Tenenbaum and T. L. Joseph, *Trans. Am. Inst. Mining Met. Engrs.*, **140**, 106 (1940).

[19] Data presented in an accompanying paper show that for the 34.1% CO–65.9% H_2 mixture more of the carbon was formed by the reaction $CO + H_2 \rightarrow C + H_2O$ than by the reaction $2CO \rightarrow C + CO_2$. This suggests that as the hydrogen content of the gas mixture is increased the former reaction becomes of increasing significance.

TABLE I

EFFECT OF CARBON MONOXIDE–HYDROGEN COMPOSITION AND TEMPERATURE ON THE AVERAGE CRYSTALLITE HEIGHT AND INTERLAYER SPACING OF CARBONS FORMED BY CARBON MONOXIDE DECOMPOSITION OVER CARBONYL IRON

Formation temp., °C.	Av. crystallite height and interlayer spacing of carbons produced from various carbon monoxide–hydrogen mixtures 0.8% H_2		2.2		5.2		9.0		19.9		39.8		65.9	
	L_c,Å	d-spacing,Å.	L_c	d-spacing	L_c	d-spacing	L_c	d-spacing	L_c	d-spacing	L_c	d-spacing	L_c	d-spacing
450	38	3.416	...	...	...	...	...	...	...	...	...	...	...	...
470	67	3.408	53	3.418	62	3.410	...	...	...	...	...	...	...	...
500	97	3.384	98	3.388	66	3.394	79	3.404	...	...	40	3.443	132	3.436
528	124	3.377	132	3.372	149	3.373	118	3.377	76	3.398	54	3.431	102	3.430
576	127	3.369	175	3.367	231	3.364	195	3.359	211	3.363	154	3.365	170	3.398
585	...	...	141	3.369	...	...	...	...	...	...	...	...	...	...
602	101	3.380	134	3.372	130	3.369	253	3.361	282	3.360	191	3.360	248	3.364
630	114	3.374	...	...	...	...	168	3.368	192	3.363	280	3.359	263	3.359
700	...	...	...	....	...	...	...	...	128	3.380	137	3.378	...	...

duced from high molecular weight aromatic compounds,[21] and heat-treated coals[22] have crystallite heights in the range of only 10 to 35 Å. Likewise, the interlayer spacings of all the carbons produced from the carbon monoxide–hydrogen mixtures are significantly less than those of other carbons formed at similar temperatures.[20–22] For these other carbons, spacings are always greater than 3.44 Å., the lower interlayer spacing limit of completely amorphous carbons, according to Franklin.[23] The lowest interlayer spacing seen in Table I, 3.359 Å., is indicative of a carbon having *ca.* 85% three-dimensional ordering, according to the Franklin correlation.[23] For the carbons produced by conventional treatment of carbon-containing raw materials, a heat treatment temperature above 2000° is necessary before the high degree of three-dimensional ordering found for most of the carbon samples in Table I is achieved.[21,24] Indeed, for the majority of commercial carbon blacks, it is not possible to produce as high a degree of three-dimensional ordering even after heat treatment to 3200°.[20]

From Table I it is seen that for each carbon monoxide–hydrogen mixture used the crystalline character of the carbon increases with increasing temperature of formation to a maximum and then decreases with further temperature rise. Further, the temperature at which the maximum crystalline character is attained gradually increases with increasing hydrogen content in the gas mixture. The maximum crystallite size attained also increases as the hydrogen content in the gas mixture is increased, at least up to the 19.9% H_2-containing mixture.

The change in surface area of the carbon as a function of temperature of formation and carbon monoxide–hydrogen composition is presented in Table II. The surface area values indicate that the carbon has a high degree of internal porosity and surface roughness; for if a typical particle size is taken to be 0.1 μ in diameter and 1 μ long, the specific surface area of a non-porous particle is calculated to be only 15 m.^{2}/g. The surface areas are considerably larger than those for carbons which are easily graphitized,[25] smaller than the areas for typical active carbons,[26] and comparable to the areas of intermediate grades of carbon black.[27]

TABLE II

EFFECT OF CARBON MONOXIDE–HYDROGEN COMPOSITION AND TEMPERATURE ON THE SPECIFIC SURFACE AREA OF CARBONS FORMED BY CARBON MONOXIDE DECOMPOSITION OVER CARBONYL IRON

Formation temp., °C.	Specific surface area, m.^{2}/g., of carbons produced from various carbon monoxide–hydrogen mixtures 0.8% H_2	2.2	5.2	9.0	19.9	39.8	65.9
450	44	...	...	...	...	...	...
470	106	116	125	...	...	...	...
500	113	131	132	125	161	152	99
528	111	121	157	132	134	156	170
576	87	97	93	61	91	105	172
602	71	76	95	82	77	65	104
630	35	...	...	84	82	89	87
700	...	...	...	...	42	52	...

TABLE III

EFFECT OF CARBON MONOXIDE–HYDROGEN COMPOSITION AND TEMPERATURE ON THE ATOMIC CARBON–HYDROGEN RATIO OF CARBONS FORMED BY CARBON MONOXIDE DECOMPOSITION OVER CARBONYL IRON

Formation temp., °C.	Atomic carbon–hydrogen ratio of carbons produced from various carbon monoxide–hydrogen mixtures 0.8% H_2	2.2	5.2	9.0	19.9	39.8	65.9
470	14.4	13.1	11.4	..	..	..	..
500	21.5	16.4	14.1	9.6	11.4	7.3	9.0
528	25.3	15.4	19.5	10.8	13.3	10.1	9.6
576	27.3	21.1	21.6	23.2	17.3	14.3	12.2
602	..	27.4	26.2	27.4	28.1	16.4	20.4
630	34.2	..	..	34.5	35.2	..	34.6
700.	..	..	..	..	52.7	53.0	..

It is also seen from Table II that the specific surface areas of the carbons exhibit an over-all trend similar to the crystallographic data, despite some scattered inconsistencies. They increase in area

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(20) W. D. Schaeffer, W. R. Smith and M. H. Polley, *Ind. Eng. Chem.*, **45**, 1721 (1953).

(21) C. R. Kinney, Proceedings of the Conferences on Carbon, U. of Buffalo, 1956, p. 83.

(22) H. E. Blayden, H. L. Riley and A. Taylor, *J. Am. Chem. Soc.*, **62**, 180 (1940).

(23) R. E. Franklin, *Acta Cryst.*, **4**, 253 (1951).

(24) A. E. Austin and W. A. Hedden, *Ind. Eng. Chem.*, **46**, 1520 (1954).

(25) "Some Factors Affecting the Reactivity of Sized Particle Carbons to Carbon Dioxide," P. L. Walker, Jr., and J. R. Nichols, Proceedings of the Conference on Industrial Carbon and Graphite, London, 1957, in press.

(26) J. W. Hassler, "Encyclopedia of Chemical Technology," Vol. 2, The Interscience Encyclopedia, Inc., New York, N. Y., 1949, pp. 881–897.

(27) "Cabot Carbon Blacks Under the Electron Microscope," 2nd Edition, Godfrey L. Cabot, Inc., Boston, Mass.

with increasing deposition temperature to a maximum and then decrease with a further temperature increase. The temperature at which the surface area reaches its maximum value for a particular carbon monoxide–hydrogen mixture is less than the temperature at which the crystallite height of the carbon reaches its maximum value. It is seen that the maximum specific surface area obtained generally increases with an increase in the percentage of hydrogen in the carbon monoxide, but the effect is not as marked as in the case of the crystallite height data.

Table III presents data on the effect of temperature of formation and carbon monoxide–hydrogen composition on the atomic carbon–hydrogen ratio of the carbon produced. For a given gas mixture, the amount of hydrogen in the carbon[28] markedly decreases as the formation temperature increases. At lower formation temperatures, the amount of hydrogen in the carbon also increases with an increase in the amount of hydrogen in the inlet gas mixture; but this effect becomes small at temperatures above 602°. If the hydrogen were chemisorbing on the edges of the carbon crystallites, it would be predicted that the hydrogen content in the carbon would decrease with increasing crystallite size. Qualitatively, this fact is suggested at formation temperatures below 576° by comparing the data in Tables I and III; but the correlation doubtless is complicated by the effect of temperature and hydrogen concentration on the extent of hydrogen chemisorption on carbon. Assuming that the fraction of edge atoms on the carbon crystallite which will be occupied by hydrogen is a maximum at the lowest carbon formation temperature, 470°, and taking a crystallite size of L_c = 62 Å. and L_a = 124 Å.,[30] an atomic C–H ratio of 12.5 is calculated, if two atoms of hydrogen are assumed, on the average, to occupy an edge carbon atom.[31] This is in good agreement with the experimental atomic C–H ratios for the carbons produced at 470°.

Table IV presents data on the effect of temperature of formation and carbon monoxide–hydrogen composition on the electrical resistivity of the carbons under a pressure of 2500 p.s.i.a. The effect of formation temperature on the electrical resistivity of the carbon is seen to be a function of the hydrogen content in the gas mixture. For hydrogen contents below 5.2%, the electrical resistivity is seen to decrease monotonically with increasing temperature of formation. For the carbons produced from gas mixtures containing 39.8 and 65.9% H_2, the electrical resistivity is clearly seen to go through a maximum at a formation temperature of *ca.* 528°. At a particular formation temperature, the electrical resistivity is seen to increase, with a few exceptions, with increasing hydrogen content in the gas mixture to a maximum at 39.8% H_2 and then to decrease.

TABLE IV

EFFECT OF CARBON MONOXIDE—HYDROGEN COMPOSITION AND TEMPERATURE ON THE ELECTRICAL RESISTIVITY OF CARBONS FORMED BY CARBON MONOXIDE DECOMPOSITION OVER CARBONYL IRON

Formation temp., °C.	Electrical resistivities, ohm cm. × 10², of carbons under a pressure of 2500 p.s.i.a. produced from various carbon monoxide–hydrogen mixtures						
	0.8% H_2	2.2	5.2	9.0	19.9	39.8	65.9
470	8.90	14.0	17.3	..	..	..	..
500	8.54	13.3	16.9	..	22.3	21.6	12.6
528	..	12.0	..	15.4	..	27.5	22.4
576	5.71	6.9	12.7	12.3	15.9	23.0	18.9
602	5.67	4.1	8.0	..	11.4	18.4	12.3
630	..	..	..	5.3	6.1	9.1	7.4
700	..	..	..	..	4.9	7.3	..

TABLE V

CHANGE OF PROPERTIES OF CARBONS WITH WEIGHT FORMED FROM A 99.2% CO—0.8% H_2 MIXTURE AT 528° OVER 0.1 GRAM OF CARBONYL IRON

Carbon formed, g.	L_c, Å.	Interlayer spacing, Å.	Surface area, m.²/g.	C/H	Electrical resistivity, ohm cm. × 10² at 2500 p.s.i.a.
0.09	145	3.365	83	8.5	*a*
0.92	124	3.370	110	25.3	10.3
2.05	110	3.374	117	18.5	11.6
3.39	94	3.383	131	16.3	10.5
4.63	97	3.384	143	17.3	9.1
6.87	87	3.384	144	18.2	8.7

[a] Insufficient sample.

The electrical resistivities of these carbons are considerably less than that of a widely used channel black, Spheron 6 (resistivity of 2.4 ohm cm. and a surface area of 95 m.²/g.), somewhat less than that of a second channel black, Excelsior (resistivity of 0.25 ohm cm. and a surface area of 210 m.²/g.), and comparable to that of acetylene black (resistivity of 0.09 ohm cm. and a surface area of 64 m.²/g.)

The electrical resistivity of the carbon would be expected to increase with an increase in surface area, a decrease in size and orientation of the crystallites, and an increase in hydrogen content.[32] Comparing these properties with the resistivity data, it is seen that for carbons produced at different temperatures from gas mixtures containing less than 9.0% H_2, variations in the hydrogen content of the carbons appear to have the dominant effect on the electrical resistivity. Both the surface area and crystallite size data go through maximum values with increasing formation temperature—a trend which is not found for the resistivity data. For the carbons produced from the gas mixture containing 19.9% H_2, both the change in surface area and C–H ratio are in the proper direction to explain the electrical resistivity data. For carbons produced from gas mixtures containing 39.8 and 65.9% H_2, the resistivity appears to be primarily determined by the surface area of the carbon, the electrical resistivity and surface area reaching their maximum values at the same temperature.

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(28) It is calculated[29] that the amount of hydrogen chemisorbed on the catalyst constitutes a negligible part of the hydrogen present.

(29) H. H. Podgurski and P. H. Emmett, THIS JOURNAL, **57**, 159 (1953).

(30) It was approximated from the (112) X-ray diffraction peak of the carbons that the crystallite diameter is roughly twice the crystallite height.

(31) R. H. Savage, *Ann. N. Y. Acad. Sci.*, **53**, 862 (1951).

(32) H. T. Pinnick, Proceedings of the Conferences on Carbon, U. of Buffalo, 1956, p. 3.

For carbons produced at the same formation temperature up to 576°, the increase of electrical resistivity with increase in hydrogen content in the gas mixture primarily parallels the decrease in the C–H ratio. However, at formation temperatures of 602, 630 and 700°, a change in electrical resistivity with an increase in hydrogen content in the inlet gas mixture occurs in spite of the relative constancy of the surface area and C–H ratio data. This suggests that the crystallite size of the carbon also is affecting its electrical resistivity, even though its effect is masked by variations in C–H ratio and surface area for many of the other data.

If the electrical resistivity were determined primarily by scattering of electrons at crystallite boundaries, it would be expected that the electrical resistivities of the carbons would decrease with increase in crystallite size. That this is not the case is best seen by two examples. At a temperature of 630°, carbons formed from gas mixtures containing 9.0% or more hydrogen have very similar surface areas and C–H ratios. For these carbons, electrical resistivity increases as crystallite size increases. The carbons prepared at 470° from a gas mixture containing 0.8% H_2 and at 576° from a gas mixture containing 39.8% H_2 have almost identical C–H ratios and surface areas, and yet the electrical resistivity of the carbon prepared at 576° is 2.6 times that of the carbon prepared at 470°. The crystallite height of the carbon prepared at 576° is 2.3 times as great as that prepared at 470°. It is suggested, therefore, that the crystallite size of the carbon is not affecting the resistivity primarily by scattering of electrons at crystallite boundaries but is determining the number of positive holes formed by π electrons jumping from the π band into the σ state, forming a spin pair at the edge of the crystallite.[32] For equal C–H ratios, the percentage of edge carbon atoms having their unshared electrons satisfied by the formation of a spin pair would increase as the crystallite size decreases. This in turn would increase the positive hole concentration within the crystallite and result in a decrease in electrical resistivity with a decrease in crystallite size, as is found in the two examples cited above. In conclusion, then, it can be said that the electrical resistivities of the carbons appear to be a complex function of surface area, C–H ratio, and crystallite size, with variations in C–H ratio having the dominant effect on the electrical resistivities of most of the carbons produced.

Table V presents data on the change of properties of the carbon with weight formed from a 99.2% CO–0.8% H_2 mixture at 528° over 0.1 g. of carbonyl iron. The maximum amount of carbon formed, 6.879 g., represents that formed under the above conditions before the catalyst was completely deactivated. It is seen from the crystallite size and interlayer spacing data that there is a marked decrease in crystalline character of the carbon during the early stages of carbon formation. When the concentration of iron in the carbon becomes less than *ca.* 3%, there is little further change in crystalline character observed.

With increasing amounts of carbon formed, the specific surface area increases, becoming essentially constant when the iron concentration in the carbon becomes less than *ca.* 2%. Some of the sharp, initial rise in surface area probably is caused by the decrease in percentage of iron (with its lower specific surface area) in the sample; but with the decrease in particle size of the iron during carbon formation, the extent to which the iron affects the over-all surface area is not known. A close parallel between the decrease in crystallite size and increase in surface area is found, suggesting that a significant part of the crystallite area is available to the adsorbate. This is confirmed, for example, for the 6.87-g. carbon sample (Table V) where the surface area of a crystallite 87 Å. in height and 174 Å. in diameter is *ca.* 200 m.^{2}/g., as compared to the B.E.T. area of 144 m.^{2}/g., or an area ratio of only 1.39. In comparison to this, a non-porous commercial carbon black, such as P-33 has a crystallite area (L_c = 17 A. and L_a = 28 Å.[20]) of *ca.* 1300 m.^{2}/g. and a B.E.T. area of 15 m.^{2}/g.,[20] or an area ratio of 87, indicating the small extent to which the crystallite surfaces are available to the adsorbate.

The C–H data, in Table V, for small amounts of carbon formed are not understood, but are seen to reach an essentially constant value when the iron concentration in the carbon becomes less than *ca.* 5%. The electrical resistivities of the carbon, as a function of amount produced, show relatively little change, suggesting that the effects which surface area and crystallite size changes may have on electrical resistivity are counterbalancing each other.

The effect of several other operating variables on the properties of the carbon produced by carbon monoxide decomposition were investigated. It was found that varying pretreatment times in hydrogen at 528°, no pretreatment, or precarbiding with carbon monoxide at 359° had minor effects on the crystallite size of an equal weight of carbon produced at 528°. A 20-fold decrease in the carbon monoxide volume flow rate, from that which was usually used, resulted in an increase in the crystallite size, a decrease in the surface area, little change in the C–H ratio, and an increase in the electrical resistivity of the carbon formed.

Properties of the Carbon Produced by Decomposition of a Carbon Monoxide–Hydrogen Mixture over "Sinter B."—Carbon was produced by the decomposition of a 99.2% CO–0.8% H_2 mixture at 528° over 0.1-g. samples of the raw and reduced (H_2 pretreatment for one hour at 528°) "Sinter B." Table VI presents data on the crystallite size and interlayer spacing of the carbon formed over two particle sizes of "Sinter B," with the weight of carbon reported being the amount produced before complete deactivation of the catalyst in each case. For equal weights of carbon formed, the crystallite height of the carbon produced over the reduced "Sinter B" catalyst compares closely with that of the carbon (105 Å.) produced over the reduced carbonyl iron. The interlayer spacings of the carbon formed over the reduced "Sinter B" are slightly higher than that of the carbon formed over the reduced carbonyl iron, indicating a smaller degree of three-dimensional ordering in the carbon.[23] The crystallite heights of the carbons formed over the raw "Sinter B," are substantially smaller than that of the carbon (120 Å.) formed over the reduced carbonyl iron catalyst, for the same weight of carbon produced. The interlayer spacings of the carbon formed over the raw "Sinter B" are substantially higher than that of the carbon formed over the reduced carbonyl iron. It is seen that for either the raw or reduced "Sinter B" catalyst, reduction in catalyst particle size, within limits, has essentially no effect on the crystallite size or interlayer spacing of the carbon produced.

It is apparent from the results given in Table VI that reduction of an iron catalyst, high in oxygen, prior to carbon deposition can affect the crystalline character of the carbon formed. On the other hand, for iron catalysts low in oxygen, such as carbonyl iron, use of a raw or reduced catalyst has been found to have a minor effect on crystalline character of the carbon, as previously discussed.

TABLE VI

AVERAGE CRYSTALLITE HEIGHT AND INTERLAYER SPACING OF CARBONS FORMED FROM A 99.2% CO–0.8% H_2 MIXTURE AT 528° OVER 0.1-GRAM SAMPLES OF RAW AND REDUCED "SINTER B" CATALYST

Mesh size of "Sinter B"	Catalyst treatment	Carbon produced, g.	L_c, Å.	*d*-spacing, Å.
80–100	Reduced	2.42	100	3.382
–100	Reduced	2.24	91	3.387
80–100	Raw	1.15	84	3.390
–100	Raw	1.23	81	3.392

TABLE VII

CHANGE IN CHEMICAL COMPOSITION OF A CARBON PRODUCED AT 528° FROM A 98.6% CO–1.4% H_2 MIXTURE AFTER ACID TREATMENTS

Treatment		Anal. of carbon, wt. %			
Acid	Purif. time, hr.	C	H	Fe	Diff.
None[a]	None	94.24	0.29	5.40	0.07
HCl	2.8	97.39	.57	0.40	1.64
HCl	8.0	97.34	.53	.35	1.78
HNO_3	8.0	88.60	.84	.24	10.32
HF	2.0	97.57	.45	.38	1.60

[a] Original material.

TABLE VIII

EFFECT OF HEAT TREATMENT ON A TYPICAL PETROLEUM COKE AND A CARBON PRODUCED AT 528° FROM A 98.6% CO–1.4% H_2 MIXTURE OVER CARBONYL IRON

Sample	Temp., °C.	L_c, Å.	*d*-spacing, Å.	Ash content
CO carbon	528	144	3.373	5.40
CO carbon	2500	217	3.373	0.15
CO carbon	3000	269	3.371	0.08
Petroleum coke	*ca.* 1000	34	3.482	0.32
Petroleum coke	3000	840	3.362	0.03

Acid Treatment of Raw Carbons.—The carbon made by the decomposition of carbon monoxide over iron has a certain percentage of iron impurity present depending upon the extent of carbon formation. It was desirable to investigate the ease with which the iron and/or iron compounds could be removed by acid treatment and the effect of such treatment on the properties of the carbon formed over carbonyl iron powder. In all cases, the amount of acid added to the carbon represented a considerable excess over that required to combine with the iron present. Table VII presents data on the change in chemical composition of a carbon produced at 528° from a 98.6% CO–1.4% H_2 mixture upon acid treatment. The percentage iron reported was obtained by weighing the ash (Fe_2O_3) at the end of an analysis and converting it back to iron. It is seen that the raw carbon essentially contains only carbon, hydrogen and iron. Acid treatment substantially reduces the percentage of iron in the carbon, but even the rather severe treatments used are found not to remove the iron completely.[33] Electron micrographs of the acid-treated carbon almost invariably show the removal of iron and/or iron compounds from the tip of the carbon filaments. X-Ray diffraction patterns of the above carbon clearly show the complete removal of strong Fe_3C peaks after acid treatment.

Concurrent with the removal of iron from raw carbon it is seen from Table VII that acid treatment increases the percentage of hydrogen and other elements present in the carbon. To be particularly noted is the 10% of other elements present in the carbon after nitric acid treatment—probably existing primarily as peripheral carboxyl, carbonyl and hydroxyl groups. Considering the extensive washing of the acid-treated carbons, it is not likely that the increase in other elements after HCl and HF purification is caused primarily by adsorption of these species (HCl or HF) on the carbon surface, but probably is caused by formation of chlorine and fluorine surface complexes. After purification with HCl or HF, the carbon was washed easily in the filtering apparatus, with the water flowing through the fritted disc at a good rate. By comparison, after purification with HNO_3, the water flowed through the fritted disc extremely slowly. Qualitatively, purification with HCl or HF did not change the appearance or texture of the carbons, whereas, after HNO_3 purification, the carbon had agglomerated considerably and had changed from a soft to an extremely hard material. X-Ray diffraction studies showed that there was no appreciable change in crystallite size or interlayer spacing of the carbon following purification with any of the acids used.

Heat Treatment of the Carbon.—It was of interest to investigate the effect of heat treatment of the carbon on the extent of its purification and crystallite size growth. Samples of carbon produced at 528° from a 98.6% CO–1.4% H_2 mixture were heat treated at 2500 and 3000°. For comparison, a sample of petroleum coke, produced by conventional delayed coking procedures,[34] also was heat treated, at the same time, to 3000°. Table VIII shows that the petroleum coke is considerably more graphitizable than the carbon produced from the carbon monoxide–hydrogen mixture despite its much poorer crystalline character in the raw state. The superior graphitizing character of the petroleum coke is in line with its low

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(33) In other runs not reported, it is found that there is always a small amount of residual iron left after acid treatment which cannot be removed, independent of the percentage of iron in the raw carbon.

(34) H. W. Abbott, "Encyclopedia of Chemical Technology," Vol. 3, The Interscience Encyclopedia, Inc., New York, N. Y., 1949, pp. 1-23.

surface area (0.8 m.^{2}/g.) as compared to that of the carbon from the carbon monoxide–hydrogen mixture (120 m.^{2}/g.), agreeing with the findings of Schaeffer and co-workers[20] on the effect of surface area on graphitizability for a series of carbon blacks. As expected, heat treatment to 2500° and above is effective in removing the majority of the impurities from the carbons.

Conclusions

Carbons formed from various carbon monoxide–hydrogen mixtures over iron catalysts are highly crystalline, considering the relatively low formation temperatures at which they can be produced. For each carbon monoxide–hydrogen mixture used, the crystallinity of the carbon shows a maximum in the temperature range of *ca.* 576 to 630°. The maximum crystallite height of the carbon increases with increasing hydrogen content in the gas mixture, at least up to 19.9% H_2. The specific surface areas of the carbons show a maximum in the temperature range of *ca.* 500 to 576°. The atomic C–H ratio of the carbons is found to increase monotonically with increasing formation temperatures over the entire temperature range for each carbon monoxide–hydrogen mixture investigated and to decrease with increasing amounts of hydrogen in the gas mixture up to formation temperatures of *ca.* 600°. The electrical resistivity of the carbons is found to be a complex function of their crystallinity, surface area and C–H ratio. The properties of the carbon are found to be affected by the amount formed over the iron catalyst; in particular the crystallinity decreases markedly with increasing amount formed.

CARBON FORMATION FROM CARBON MONOXIDE–HYDROGEN MIXTURES OVER IRON CATALYSTS.[1,2] II. RATES OF CARBON FORMATION

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Received April 8, 1958

The effect of temperature and inlet carbon monoxide–hydrogen composition on the rate of carbon formation and amount of carbon which can be formed over iron catalysts before the catalysts are deactivated has been investigated. As the hydrogen content of the gas mixture is increased, the temperature at which the maximum rate of carbon deposition occurs also increases, this temperature ranging from *ca.* 528° for a 99.2% CO–0.8% H_2 mixture to *ca.* 630° for a 80.1% CO–19.9% H_2 mixture. Change in mixture composition has a relatively small effect on rate of carbon deposition or total amount of carbon which can be formed from a given catalyst weight at lower temperatures (470 to 528°) but has a major effect at higher temperatures (above *ca.* 576°). At the higher temperatures, the maximum rate of carbon formation increases with increasing hydrogen content in the gas up to a point and then decreases. Also, increases in hydrogen content in the gas markedly increase the total amount of carbon which can be formed before catalyst deactivation occurs. The type of catalyst pretreatment and nature of catalyst used is also seen to affect carbon deposition. A spent catalyst consists primarily of cementite. Upon hydrogen treatment the cementite is converted to iron and the spent catalyst is reactivated for additional carbon production. It is proposed that iron, on which carbon monoxide can chemisorb and dissociate, is the active catalyst for carbon deposition and that complete conversion of iron to cementite, on which carbon monoxide cannot chemisorb at elevated temperatures, is responsible for stopping carbon deposition.

Introduction

There is general agreement in the literature that the rate of carbon formation from carbon monoxide decomposition over iron catalysts is significant between *ca.* 400 and 750°, with the maximum rate occurring between 500 and 600°.[3–8] Considerable uncertainty exists, however, as to why the rate of carbon deposition decreases above *ca.* 600°, but it is known not to be caused by equilibrium in the reaction $2CO \rightleftarrows C + CO_2$. Some explanations offered for this diminution in rate are decreasing chemisorption of carbon monoxide on the catalyst,[3] beginning of appreciable catalyst sintering,[4,7] and absence of carbide formation.[8] There is some suggestion that the rate of carbon formation increases again at higher temperatures (850°),[9] but this has not been well confirmed.

It has been shown that the addition of small amounts of sulfur compounds to carbon monoxide greatly retards the decomposition of the latter over iron.[5,8,10–13] Also, selected nitrogen compounds, particularly cyanogen and ammonia, have been shown to be powerful retarders of carbon deposition.[8,11,12] On the other hand, hydro-

(1) Based, in part, on an M.S. thesis submitted by G. R. Imperial to the Graduate School of the Pennsylvania State University, August, 1957.

(2) At different stages, this work was supported by the Reading Anthracite Company and the Atomic Energy Commission under Contract No. AT(30-1)-1710.

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