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 Schneffer and co-workers 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% H₂. 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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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 maximum rate of carbon deposition occurs at a lower temperature and the amount of carbon which can be formed is decreased. Change in mixture composition has a relatively small effect on rate of carbon deposition or total amount of carbon formed over the iron catalyst; in particular the crystallinity decreases markedly with increasing amount formed.

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°.1-4 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 ⇌ C + CO₂. Some explanations offered for this diminution in rate are decreasing chemisorption of carbon monoxide on the catalyst,5 beginning of appreciable catalyst sintering,6 and absence of carbide formation.7 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.8,10-13 Also, selected nitrogen compounds, particularly cyanogen and ammonia, have been shown to be powerful retarders of carbon deposition.5,11,12 On the other hand, hydro-
rates of carbon formation from carbon monoxide–hydrogen mixtures

Fig. 1.—Three typical rate curves showing carbon formation from a 98.0% CO–1.4% H₂ mixture over 0.10 g. of reduced carbonyl iron at 570°.

gen has been shown to be an accelerator of carbon monoxide decomposition over iron catalysts. Water vapor has been found to both accelerate and retard carbon monoxide decomposition.

There is considerable disagreement as to what the active form of the iron catalyst is in the decomposition of carbon monoxide, but it is generally agreed that an oxide of iron alone is not the active catalyst. Various investigators have attributed the catalytic activity to one or more of the carbides of iron (Fe₂C, Fe₃C, Fe₆C₅), metallic iron, or to the iron–iron oxide interface. This disagreement as to the active catalyst is caused primarily by the concurrent production of free carbon and carbide carbon, which raises the question as to whether or not the carbide carbon is a precursor of the free carbon.

In this research, a detailed investigation of the effect of hydrogen on the rate of carbon deposition from carbon monoxide–hydrogen mixtures was conducted. This involved, in many cases, the obtaining of rate data until the deposition of carbon ceased, since it was of interest to know not only the maximum rate of carbon deposition but also the amount of carbon which could be formed from a starting catalyst weight. Other factors affecting the rate of carbon deposition which were investigated include catalyst pretreatment, gas flow rate past the catalyst, different starting catalyst materials and reactivation of a spent catalyst. Experimental details describing the apparatus, the catalysts used, and operating procedures have been included in an accompanying paper, which presents the properties of the carbons formed from the carbon monoxide–hydrogen mixtures used in this paper.

Results

Determination of Carbon Deposition Rate.—As was discussed, the cumulative weight of carbon formed during a run was determined from the cumulative volumes of gas passing through the wet test meters before and after the reactor. Before the gas entered the exit wet test meter, it was passed through an Ascarite tower to remove carbon dioxide. The gas was saturated with water prior to entering both wet test meters. From the difference in gas volumes between the entering and exit wet test meters, the amount of carbon formed was calculated (predicted), assuming the difference in volumes to be caused by two reactions, CO + H₂ → C + H₂O. For both of these reactions, the wet-test-meter readings indicate a decrease of two moles of gas for each mole of carbon formed. For this calculation the extent of the water–gas shift reaction, CO + H₂O → CO₂ + H₂, is unimportant.

This simplified approach to determining the carbon deposition rate is incorrect insofar as reactions producing hydro-
carbon to produce methane ($\text{C} + 2\text{H}_2 \rightarrow \text{CH}_4$) and the reaction $\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$ are the most likely to produce errors. In addition, the chemisorption of hydrogen at the edges of the carbon crystallites will produce a decrease in gas volume which is not attributable to carbon formation. Results show, however, that for gas mixtures containing less than 40% hydrogen, extraneous reactions have relatively little effect on distorting the true picture of carbon deposition, with agreement between predicted and actual amounts of carbon formed invariably being within 10%. Considering the large variations in carbon deposition rates found for different gas mixtures, temperatures and catalysts, the above agreement is quite satisfactory to allow major conclusions to be made.

Figure 1 presents data for the rate of carbon deposition from a 98.0% CO–1.4% H$_2$ mixture over 0.10 g. of carbonyl iron at 576°. The gas flow rate was 5.8 cc./sec. (STP) and the catalyst was pretreated in hydrogen, as previously described. The shape of the deposition curves is typical.

These conditions were used throughout the work unless otherwise specified.
of those usually found—an initial induction period, a period of essentially constant rate of carbon deposition and a period of decreasing rate of carbon deposition until deposition completely stops. The agreement between runs, as shown in Fig. 1, is also fairly typical, with the maximum deposition rates varying by ca. ±3%. The predicted weights of carbon formed in the runs, 6.05, 6.15 and 6.47 g., can be compared with the weights actually obtained, 5.94, 6.18 and 6.27 g., respectively. The final carbons contain ca. 2% iron by weight.

Effect of Variation in Carbon Monoxide-Hydrogen Composition on Carbon Deposition at Different Temperatures.—Figures 2 and 3 present the results of carbon deposition as a function of gas composition and temperature. From Fig. 2, it is seen that as the hydrogen content of the gas mixture is increased, the temperature at which the maximum rate of carbon deposition occurs also increases, it ranging from ca. 528° for the 0.8% H₂ mixture to ca. 630° for the 19.9% H₂ mixture. Also, the deposition temperature is seen to affect markedly the total amount of carbon which can be produced from a starting catalyst weight. For example, for the gas mixture containing 0.8% H₂, carbon deposition has stopped after formation of 2.4 and 1.0 g. of carbon at 576 and 002°, respectively; whereas at the temperature of 528°, 6.0 g. of carbon has been deposited with deposition still continuing. It is seen that increasing the hydrogen content of the gas mixture markedly increases the amount of carbon which can be formed from a given catalyst weight, particularly at the higher temperatures. For hydrogen contents of 5.2% or greater, the reaction at all temperatures had to be discontinued before carbon deposition had ceased because of either plugging of the reactor with carbon or undue duration of a reaction run.

Figure 3 clearly shows the effect of increasing the hydrogen content in the gas mixture on carbon deposition rates at particular temperatures. It is seen that a change in gas composition has a relatively small effect on maximum rate of carbon deposition or amount of carbon which can be formed at the lower temperatures (470 to 528°) but has a major effect at the higher temperatures (above 576°). At the higher temperatures it is seen that the maximum rate of carbon formation increases with increasing hydrogen content in the gas up to a point and then decreases. Also at the higher temperatures, increasing additions of hydrogen to the gas markedly increase the total amount of carbon which can be formed.

Of particular interest in Fig. 3 is the run made with a gas mixture containing less than 0.05%H₂, which clearly shows the relatively high stability of carbon monoxide which is dry and low in hydrogen, even over iron.

In order to show more clearly the effect of change in mixture composition and temperature on the total amount of carbon which can be formed from a given catalyst weight, a series of runs were made using a starting weight of carbonyl iron of only 0.02 g. From Fig. 4, it is again seen that at a relatively low temperature (500°) variations in gas composition have little effect on the extent of carbon deposition and that the catalyst remains active to catalyze carbon deposition for extended periods. Even for the gas mixture containing

(23) The deposition curves at 500° for 9.0 and 36.8% H₂-containing mixtures are very similar to those for 19.9 and 0.8% H₂-containing mixtures, respectively. The experimental points have been omitted from Fig. 4 to avoid confusion.
only 0.8% \text{H}_2 \text{O} is not occurring to a significant extent because of the reactions of hydrogen previously discussed. In this case the total weight of carbon formed was compared with the weight predicted from the amounts of water and carbon dioxide absorbed from the product gas stream, as shown in Table I. It is seen that the agreement in the weights is good at deposition temperatures of 576, 600 and 630°C, indicating that the reaction \( \text{CO}_2 + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O} \) is not occurring to a significant extent. On the other hand, agreement is less satisfactory at 528°C, suggesting that the above reaction becomes a factor at the lower temperature.

If the reaction \( \text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O} \) is not a significant factor in determining the composition of the product gas leaving the reactor, it is concluded, from Table I, that a larger portion of the carbon is formed as a result of the reaction \( \text{CO} + \text{H}_2 \rightarrow \text{C} + \text{H}_2\text{O} \) rather than the reaction \( 2\text{CO} \rightarrow \text{C} + \text{CO}_2 \) for the 34.1% \text{CO}–65.9% \text{H}_2 mixture. Unfortunately, for the other gas mixtures studied, the amounts of water and carbon dioxide absorbed from the product gas were not determined; but undoubtedly the relative amounts of carbon formed by the above two reactions is a function of the partial pressures of hydrogen and carbon monoxide and the extent of their chemisorption on the catalyst.

**Effect of Operating Variables on the Deposition of Carbon from Carbon Monoxide–Hydrogen Mixtures. Catalyst Pretreatment.**—The effect of catalyst pretreatment on the subsequent deposition of carbon at 576°C from a 99.2% \text{CO}–0.8% \text{H}_2 mixture over 0.10 g. of carbonyl iron was studied briefly. Carbon deposition after reduction of the catalyst for one hour in hydrogen at 576°C was compared with deposition over the unreduced catalyst and a catalyst which had been partially precarbided using carbon monoxide for three hours at 359°C. Figure 5 presents the data with each deposition curve representing the average of two experimental runs. It is seen that pretreatment affects the three main regions of the deposition curve. Carbon deposition over the reduced catalyst is the most rapid during the early stages of the run. The maximum rate of carbon deposition occurs over the precarbided catalyst from ca. 30 to 50 minutes after the reaction has started. The maximum rate of carbon deposition over the reduced and unreduced catalysts is essentially the same. Pretreatment has a marked effect on the amount of carbon which can be produced from a given weight of catalyst, with the reduced catalyst producing ca. 30% more carbon than the unreduced catalyst and ca. 38% more carbon than the precarbided catalyst.

**Carbon Monoxide–Hydrogen Mixture Flow Rate.**—Figure 6 presents results on the effect of flow rate of a 97.8% \text{CO}–2.2% \text{H}_2 mixture on the deposition of carbon at 528°C over 0.10 g. of carbonyl iron. From the rate of carbon formation in the region of constant deposition rate, it is calculated that the \text{CO}–\text{CO}_2 ratio in the product gas ranged from ca. 2.5 to 12.5% of the equilibrium value as the flow rate was decreased from 5.80 to 0.29 cc./sec.

A plot of reaction rate, expressed as grams of carbon deposited per hour per atmosphere of average carbon monoxide pressure in the reactor, versus the gas flow rate shows a decreasing positive slope with increasing flow rate. This is the usual relation for a heterogeneous reaction which is being controlled to a significant extent by both chemical and mass-transport resistances. With increasing flow rate, the extent of rate control by mass transport resistance continuously decreases, until at a sufficiently high flow rate the reaction rate is independent of further increases in flow rate.

As seen in Fig. 6, changes in gas flow rate over the catalyst can affect not only the maximum rate of carbon formation but also the total amount of carbon produced.

**Table I**

<table>
<thead>
<tr>
<th>Reaction temp., ( {\degree} \text{C} )</th>
<th>Wt. H_2O absorbed, g.</th>
<th>Equiv. wt. C, g.</th>
<th>Wt. CO_2 absorbed, g.</th>
<th>Equiv. C wt., g.</th>
<th>Total pred. C wt., g.</th>
<th>Total exp. C wt., g.</th>
</tr>
</thead>
<tbody>
<tr>
<td>528</td>
<td>1.165</td>
<td>0.777</td>
<td>0.445</td>
<td>0.121</td>
<td>0.808</td>
<td>0.779</td>
</tr>
<tr>
<td>576</td>
<td>1.988</td>
<td>1.631</td>
<td>3.158</td>
<td>0.861</td>
<td>2.186</td>
<td>2.081</td>
</tr>
<tr>
<td>600</td>
<td>2.447</td>
<td>1.631</td>
<td>3.038</td>
<td>0.828</td>
<td>2.450</td>
<td>2.370</td>
</tr>
<tr>
<td>630</td>
<td>1.462</td>
<td>0.975</td>
<td>1.597</td>
<td>0.436</td>
<td>1.411</td>
<td>1.426</td>
</tr>
</tbody>
</table>

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(24) X-Ray diffraction studies of the carbided catalyst showed high concentrations of FeC and FeC (Hagg carbide). The amount of free carbon formed was negligible. During the time taken to heat the precarbided catalyst from 330°C to reaction temperature in helium, the reactions \( \text{Fe} + \text{FeC} \rightarrow \text{FeC} \) and \( \text{FeC} \rightarrow \text{Fe} + \text{C} \) undoubtedly occurred. Furthermore, some decomposition of FeC back to \( \text{Fe} \) and \( \text{C} \) was expected. For example, after carboiding another sample of iron at 330°C for 3 hours, heating it in helium to 600°C and holding for one hour resulted in the conversion of the carbide back to \( \text{Fe} \), as revealed by X-ray diffraction studies. Unfortunately an X-ray diffraction pattern was not taken after heating the precarbided catalyst sample to 575°C prior to making the carbon deposition runs.

(25) H. H. Podgurski, J. T. Kummer, T. W. DeWitt and P. H. Em-
carbon which can be formed. For a flow rate of 5.80 cc/sec., the rate of carbon deposition progressively decreases after production of ca. 3.5 g. of carbon and undoubtedly stops after formation of ca. 7 g. On the other hand, for a flow rate of 2.08 cc/sec., carbon deposition remains at a maximum rate up to ca. 7 g. of carbon formed and then decreases in rate very slowly, with the total amount of carbon which can be formed being considerably above 12 g.

Catalyst Type.—The rate of carbon deposition from a 99.2% CO-0.8% H₂ mixture at 528° over 0.10 g. of “Sinter B” catalyst was investigated. “Sinter B” is a sinter of fine iron-containing powder which comes from the top of open hearths and blast furnaces, as previously described. The carbon deposition rate was investigated over both the reduced (the same reduction procedure being used as for carbonyl iron) and the raw catalyst for two different particle sizes. As was found for carbon deposition over carbonyl iron, the initial rate of carbon deposition and the total amount of carbon which can be formed is appreciably greater over the reduced than over the raw catalyst. Also, in this case, the maximum deposition rate over the reduced catalyst is considerably greater than that over the raw catalyst. Change in particle size (representing a change in initial B.E.T. surface area from only 0.41 to 0.46 m²/g.) is found to have a minor effect on rate of carbon deposition.

Comparison of carbon deposition over reduced “Sinter B” with that over reduced carbonyl iron under the same experimental conditions shows that the maximum carbon deposition rate over the carbonyl iron is ca. 25% higher. However, since the specific surface area of carbonyl iron is ca. twice that of the “Sinter B,” the specific activity of “Sinter B,” at the maximum carbon deposition rate, is higher. Total carbon production over reduced “Sinter B” (2.3 g.) is found to be considerably less than over reduced carbonyl iron (greater than 6.0 g.).

The importance of a major difference in state of subdivision of the starting catalyst on its activity to formation of carbon from carbon monoxide-hydrogen mixtures has been brought out by using an iron rod, containing only 0.02% nickel as a major impurity, as a catalyst. The rod had an apparent density of 7.85 g./cc., agreeing well with the true density of iron, 7.86 g./cc., indicating negligible internal porosity. Following hydrogen reduction, a 98.6% CO-1.4% H₂ mixture was passed (5.80 cc/sec.) over a piece of the iron rod (5.1 mm. in diameter and 1 mm. long) for 230 minutes at 576°. A total weight increase of
0.124 g., which would include both free and carbonyl carbon, was found. The carbon, which was in the form of a thin film deposited over the rod, had a similar appearance in electron micrographs to that formed over carbonyl iron. Also, submicron particles of iron were located at the ends of the carbon filaments. The rate of carbon formation over the reduced iron rod, expressed as grams of carbon formed per 230 minutes per gram of starting catalyst weight, is 0.0305 in comparison to a carbon formation rate of 46.5 over the reduced carbonyl iron (Fig. 2). On the basis of activity per square meter of starting catalyst surface, however, if the surface area of the iron rod is taken as its geometric area, the rates of carbon formation are 304 and 47 over the iron rod and carbonyl iron, respectively. The greater specific activity of the iron rod is probably primarily a result of the reaction being controlled to a lesser extent by mass transport resistance for the rod than for the carbonyl iron.

Reactivation of Spent Catalyst.—In an attempt to find the true catalyst for the carbon-deposition reactions, possible reactivation of the spent catalyst once carbon deposition had stopped was investigated. Figure 7 presents the results for three different runs in which the deposition of carbon from a 99.2% CO-0.8% H₂ mixture over an initial weight of 0.10 g. of reduced iron was studied. For runs 1 and 2, 0.39 and 0.25 g. of material were removed from the reactor for X-ray diffraction analysis after reaction times of 210 and 200 minutes, respectively. After these periods of reaction, it is seen that carbon deposition had practically stopped.

X-Ray diffraction patterns of the products, in both cases, showed strong peaks for cementite (Fe₃C) and carbon. No diffraction peaks were found for Fe₃O₄, Fe₂O₃ or α-Fe.²⁸ Since it is known that hydrogen readily converts Fe₃C to α-Fe,²⁹,³⁰ possible reactivation of the spent catalyst by passing 0.5 cc/sec. of hydrogen through the reactor at different temperatures and for different times was attempted. For run 1, an additional 0.05 g. of the product was taken for X-ray diffraction analysis after hydrogen treatment. Analysis showed that the cementite present before treatment with hydrogen had been completely converted to α-Fe. From Fig. 7, it is evident that hydrogen treatment reactivates the catalyst to a marked extent. Indeed, in run 3 the maximum rate of carbon formation after reactivation of the catalyst with hydrogen is greater than in the first carbon deposition cycle. It is seen for each run, however, that the reaction time which elapses before carbon deposition again stops is much less than in the initial cycle. X-Ray diffraction patterns of the product taken at the end of runs 1 and 2 once again show strong cementite peaks and no Fe₃O₄, Fe₂O₃ or α-Fe peaks. No X-ray diffraction patterns were taken of the carbon during run 3, but similar results are expected.

For runs 1 and 3, where hydrogen reactivation was conducted at the relatively high temperatures of 600° and 576°, respectively, wet-test-meter readings indicated that hydrogen was reactivating to a considerable extent with the free carbon. If it is assumed that the cumulative increase in difference between the wet-test-meter readings was caused by the reaction C + 2H₂ → CH₄, it is calculated that 0.50 and 0.49 g. of carbon had reacted in runs 1 and 3, respectively. The addition of these weights to the amounts of carbon recovered from runs 1 and 3 give total weights of carbon formed of 0.89 and 3.91 g.—in excellent agreement with 0.89 and 3.94 g., the weights predicted from the reactions 2CO → C + CO₂ and H₂ + CO → C + H₂O.

For run 2, where hydrogen treatment was conducted at 416°, there was no detectable difference in cumulative wet-test-meter readings during the treatment. If, prior to treatment, all of the iron existed as cementite, total conversion of it to α-Fe and methane would result in a difference of only 0.0004 ft.³ in the wet-test-meter readings. This difference could not be detected. Unfortunately an X-ray diffraction analysis was not made on a sample after hydrogen treatment in run 2, but conversion of cementite to α-Fe is suggested because of the subsequent significant increase in carbon deposition rate over the rate just prior to hydrogen treatment. Since the maximum rate of carbon deposition and the amount of carbon formed following hydrogen treatment in run 2 is seen to be not as great as that for run 1, probably decarbonization was not complete.

Discussion

On the basis of results presented in this and an accompanying paper,³¹ in addition to key findings by other workers, a qualitative mechanism for carbon formation from carbon monoxide-hydrogen mixtures over iron catalysts is proposed. First, Fischer and Bahr³¹ appear to have adequately explained how the iron catalyst is able to permeate the carbon formed. They report that an iron-copper catalyst, when heated with carbon monoxide at 500° results in the formation of a carbon which contains copper as well as iron, well separated from the main catalyst mass. They conclude that if the iron were carried into the carbon phase as volatile carbonyls of iron, the copper, which forms no carbonyl, would be left behind. The copper and presumably the iron, therefore, must be carried into the carbon phase by some other method, possibly mechanical. The key point in the mechanism is the supposition that carbon monoxide chemisorbs on iron but not on cementite, at the temperatures employed in this research. Emmett and co-workers³² find that iron chemicabs carbon monoxide extensively at 100° but at 150° the iron begins to carbide with carbon monoxide rapidly enough so as to make adsorption measurements on pure iron difficult. They find that at 200° pure carbon monoxide does not chemisorb on Hägg carbide (Fe₃C). As Hägg carbide and cementite have essentially the same ferromagnetic moment, it is expected that their capacities for chemisorption are essentially the same.³³ Therefore, carbon monoxide is not expected to chemisorb on cementite at elevated temperatures.

Consider the case of the passage of a carbon monoxide-hydrogen mixture over reduced carbyliron. After reduction, the carbonyl iron contains chemisorbed hydrogen, probably in atomic form.³⁴ Since chemisorption of carbon monoxide on iron is only slightly inhibited by chemisorbed hydrogen,³³ carbon monoxide will adsorb on iron atoms occupied by hydrogen, as well as on free iron atoms. A fraction of the chemisorbed carbon monoxide will react with chemisorbed hydrogen by the reactions CO + H₂ → C + H₂O and CO + 3H₂ → CH₄ + H₂O, decreasing the amount of hydrogen chemisorbed on the surface, the extent of the decrease being a function of the hydrogen content in the carbon monoxide-hydrogen mixture and the changing nature of the surface. Another fraction of the chemisorbed carbon monoxide will dissociate into carbon and oxygen atoms (the amount and the rate of dissociation depending upon the temperature and the crystallographic plane of iron on which chemisorption takes place,³⁵ among other factors). The majority of the oxygen atoms produced by the decomposition of carbon monoxide will react rapidly with additional undecomposed carbon monoxide to produce carbon dioxide or with hydrogen to produce water, which leave the iron surface.

(28) This does not necessarily mean that these substances were not present in small concentrations, since it is usually not possible to pick up peaks for constituents present in concentrations of less than 3% by X-ray diffraction.
(31) V. J. Kehler, Jr., and H. Lidehiser, Jr., This Journal, 550 (1954).
(32) Private communication from R. B. Anderson.
The carbon atoms produced from carbon monoxide dissociation have a high mobility and the majority of them (some react with hydrogen to form methane) migrate across the surface to a nucleating center (probably a dislocation), where they begin forming concurrently both free carbon and carbidic carbon (cementite). The production of free carbon will stop when the catalyst has been completely carbided to cementite, since the necessary chemisorption of carbon monoxide also will stop.

This general picture of carbon deposition from carbon monoxide-hydrogen mixtures is consistent with the major findings reported in this research. X-Ray diffraction studies clearly show that the major constituent in a spent catalyst is cementite. Following reduction of the cementite to α-Fe by hydrogen, the activity of the catalyst for carbon deposition is restored.

As was seen in Figs. 2, 3 and 4, hydrogen addition to carbon monoxide can also result in marked increases in maximum carbon deposition rate and total amount of carbon formed. At 630°C, the rate of production of carbidic carbon is high and relatively little free carbon can be produced from a carbon monoxide-hydrogen mixture low in hydrogen (0.8% H₂, for example) before the catalyst is completely carbided. As the hydrogen content in the gas mixture is increased, the rate of conversion of cementite back to iron is increased; and this results in an increasing rate of free carbon formation and a prolonging, or perhaps removing, of the time of complete conversion of the iron to cementite. The optimum hydrogen content to produce a maximum amount of free carbon is a balance between the fraction of surface which is iron and the concentration of carbon monoxide in the inlet gas. Obviously, in the limit, the complete absence of carbon monoxide will result in the production of no free nor carbidic carbon. That the addition of hydrogen, up to a point, can result in an increase in the net amount of free carbon recovered is a consequence of the considerably higher reactivity of carbidic carbon than free carbon with hydrogen.20,30

From Fig. 4, it was seen that additions of hydrogen to carbon monoxide have little effect on the carbon deposition rate at 500°C. At this relatively low deposition temperature, the rate of formation of carbidic carbon is low and, therefore, the presence of a large amount of hydrogen to prevent early catalyst deactivation is not necessary. The fact that the carbon deposition rate at 500°C is so insensitive to gas composition also indicates that the reactions 2CO → C + CO₂ and CO + H₂ → C + H₂O have very similar rates; this primarily implies similar rates for the reaction of carbon monoxide and hydrogen with an oxygen atom to produce carbon dioxide and water, respectively.

The fact that in many runs extended periods of constant carbon deposition rates are found in spite of a probable build-up of carbidic carbon content in the catalyst should be noted. It is suggested that, during these periods, disintegration of the catalyst into smaller particle sizes is taking place. This can result in the total surface area of the iron remaining constant, even though the percentage of the total surface which is iron continues to decrease. At some point, probably when the crystallite size of the catalyst equals the particle size, disintegration of the particles stops and a gradual reduction in carbon deposition rate is noted, as conversion of iron to cementite continues.

The effect which reduction of particle size (greater specific surface area) of the catalyst can have on carbon deposition rate is perhaps best seen in the reactivation runs, shown in Fig. 7. For run 3, following reactivation, the maximum rate of carbon deposition is considerably higher than in the initial deposition cycle. Furthermore, the time for deactivation of the catalyst following its reactivation is considerably less than in the initial cycle. This is consistent with a catalyst of greater surface area on which greater rates of production of both free and carbidic carbon occur. Runs 2 and 3 in Fig. 7 also show a very much shorter catalyst deactivation-time following reactivation. They do not show a greater maximum carbon deposition rate following catalyst reactivation because of the removal of part of the catalyst for X-ray diffraction analysis and/or lack of complete reactivation.

Partially precarbidizing a carbonyl iron catalyst was shown in Fig. 5 to decrease the time for catalyst deactivation, when using a gas mixture low in hydrogen. This is consistent with the overall picture. The fact that an unreduced catalyst also is deactivated in a shorter time than a reduced catalyst, resulting in less free carbon formation should be noted. This is possibly a result of the stabilizing influence of oxygen on cementite, as noted by Emmett and co-workers.22

It is interesting to compare the qualitative mechanism proposed by the authors for the formation of free carbon over an iron catalyst with that proposed by Hofer and Hofer, Peebles and Bean for the formation of free carbon over a cobalt–thoria–kieselguhr catalyst. Hofer proposes that free carbon formation follows two routes, one a surface process and the other process passing through a carbide intermediate. He bases his statement on the findings of the latter workers who studied carbon formation over two identical catalyst specimens, except that the cobalt in one had been converted to Co₃C by carburization with carbon monoxide. These two specimens were then carburized with carbon monoxide at 285°C for 22 hours. Carbon deposition initially was 20 times faster on the metallic catalyst than on the carbided catalyst. During the carburization process, the rate of carbon deposition on the metallic specimen decreased markedly, whereas the rate on the carbided catalyst remained constant. It is concluded that the carbide inhibits the deposition of free carbon in line with the conclusion expressed in this paper; but, unlike the present conclusions, a completely carbided catalyst is still considered partially active to carbon formation. Because of the complexity and possible differences in these
LOW TEMPERATURE HEAT CAPACITIES AND THERMODYNAMIC
FUNCTIONS OF HYDROUS SODIUM PALMITATE

BY HENRY E. WIRTH, JOHN H. WOOD AND JOHN W. DROEGE

Introduction

The water present in sodium palmitate (NaP) containing 0.31% H₂O has been shown to be strongly bound to the soap. Above 3.1% H₂O the water is probably weakly adsorbed on the surface of the soap crystallites. The upper limit of 3.1% for the strongly bound water suggested a definite hydrate, NaP.1/2H₂O (3.14% H₂O), but other interpretations were not excluded by the experimental results.

To obtain further information on the nature of the strongly bound water, heat capacities of NaP containing 0-4.5% H₂O were determined. The original intention was to make all determinations on the same phase of the soap, but it was found subsequently that the phase chosen, the β-phase, undergoes an irreversible transition to the ε-phase when cooled to low temperature and when the moisture content is greater than 3%. Data were therefore obtained on two samples of low moisture β-NaP (0.064 and 2.56% H₂O) and on two samples of ε-NaP (3.02 and 4.48% H₂O).

Experimental

Materials.—Palmitic acid (99.8%), from the same sample used for heat capacity determinations, was dissolved in ethylene dichloride and filtered to remove any impurities to be about equally divided between higher and lower molecular weight fatty acids.

The molecular weight of NaP was taken as 278.42. The palmitic acid regenerated from this sample was 99% pure, but the experimentally determined equivalent weight indicated the impurities to be about equally divided between higher and lower molecular weight fatty acids.

C₃H₅O₂H and less than the theoretical amount of carbonate-free NaOH was added to the hot solution. The solution was evaporated, the recovered soap was ground to a fine powder and heated to 180°C under vacuum for 12 hours to remove excess palmitic acid. This treatment gave the anhydrous β-phase.

A mixture of 65 parts of ε-NaP and 35 parts of H₂O was converted to neat soap by holding it at a temperature of 100°C for 1 hour. The neat soap was cooled to 67°C and held at this temperature for 24 hours to give “tempered” ε-NaP. This material was cooled to room temperature and dried over 60% H₂SO₄ until its moisture content was reduced to 4.5%. Portions of this sample were dried over 65% H₂SO₄ and over P₂O₅ in a vacuum desiccator to obtain samples containing 2.56 and 0.064% H₂O, respectively. All samples were equilibrated for several months in closed containers before use. Water content was determined with an average deviation of ±0.05% by loss of weight at 105°C for six hours under vacuum.

All solutions and high-moisture soaps were protected from atmospheric CO₂ by keeping them under a blanket of N₂. Tests for carbonate in the final samples were negative.

A fourth sample containing 3.02% H₂O was from the lot used for dielectric constant measurements. The palmitic acid regenerated from this sample was 99.8% pure, but the experimentally determined equivalent weight indicated the impurities to be about equally divided between higher and lower molecular weight fatty acids.

The molecular weight of NaP was taken as 278.42. X-Ray powder patterns of samples before and after the heat capacity runs were taken and interpreted for us by Dr. F. B. Rosevear of the Procter and Gamble Co.

Procedure.—Measurements were made in a copper calorimeter (laboratory designation No. 5) using procedures described previously. All samples had a low bulk density and