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Nature of Surface Species on Supported Iron during CO/H$_2$ Reaction

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The transient method has been used to study the H$_2$/CO reaction over 10% Fe/Al$_2$O$_3$ and 10% Fe/SiO$_2$ at 1 atm and 285°C in a differential reactor. Responses to perturbations in the feed composition to the reactor were measured by on-line mass spectrometry. Additional studies were made with the reactants CO/He, C$_2$H$_4$/H$_2$, and C$_2$H$_4$/He. The effect of water in the feed was also investigated. The nature of the species remaining on the surface or in the bulk of the iron was investigated by hydrogen and by oxygen flushing. The observations are explained by proposing a common surface carbon precursor to the formation of surface CH, surface carbidic carbon, surface graphitic carbon, and bulk iron carbides.

INTRODUCTION

In this work results are presented on the hydrogenation of carbon monoxide on supported iron catalysts (10% Fe/Al$_2$O$_3$ and 10% Fe/SiO$_2$). As in previous studies on this system (*1, 2*) measurements have been made by mass spectrometry of the response of the composition of the effluent from a differential reactor to step changes in feed composition at constant temperature, pressure, and flow rate. In these studies (*1, 2*) several aspects of the sequence of steps of the first part (methanation) of the Fischer–Tropsch synthesis were determined, as follows. The initial rate of methane production over a freshly reduced catalyst upon a switch from pure H$_2$ to 10% CO/H$_2$ is high and then rapidly decreases to a minimum in less than a minute at 285°C, as a surface carbonaceous species builds up. As the reaction continues a second surface species appears, and the rate of reaction increases to a second maximum as the coverage of this second species increases. Studies by Mössbauer spectroscopy during these transients show that the rate of formation of bulk iron carbides is lower than the rate of accumulation of surface species. More than an hour is required for the carburization of the iron bulk, whereas the second maximum in the H$_2$/CO reaction rate occurs after only about 10 min at 285°C. Carbon balances obtained during this initial period show that after the first minute the rate of CO dissociation is constant, so that as the rate of accumulation of intermediates goes down, the rate of hydrocarbon production goes up. After the second maximum in the rate any added carbon accumulation seems to inhibit the rate of the H$_2$/CO reaction.

In the previous work (*1, 2*) the nature of the two surface species was not considered other than to note that they seem to be of different degree of hydrogenation, CH$_x$ and CH$_y$. These surface species may be associated with those observed on iron by Bonzel and Krebs (*3*). In the present work we have studied the reaction of the surface species with oxygen and the influence on their appearance of the CO/H$_2$ ratio and the water content of the feed gas. We have also studied the transformations of the surface species during exposure to helium at 285°C. A series of experiments has also been done by exposure of the freshly reduced catalyst to CO/He. Here the surface intermediate is unhydrogenated carbon, and its behavior

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on exposure to oxygen or helium at 285°C will be shown to be different from that of the two intermediates formed during exposure to CO/H_2. As discussed in what follows, these experiments do seem to confirm that these species are CH_x and CH_y.

EXPERIMENTAL METHODS

In this work the experimental methods and equipment are the same as those described previously (*1*). Transient experiments involving feeding one gas or gas mixture after another for various times will be designated by a nomenclature such as H_2, 15 h → He, 5 min → 10% CO/H_2, 100 s → He, 40 s → H_2 (*t*). The result will then be expressed as a graph of production rates of various compounds (mole/min · g of supported catalyst) as a function of time *t* after the last switch indicated (e.g., H_2 (*t*)). In some figures points on the curves are shown merely to identify them.

The 10% Fe/Al_2O_3–Alon C catalyst is the same as that previously described (*1*). The 10% Fe/SiO_2–Cab-O-Sil catalyst was made by impregnation by the method of incipient wetness, using as the starting salt $Fe(NO_3)_3 \cdot 9H_2O$. Both catalysts were activated by exposure to flowing helium at 270°C for 1 h followed by reduction in flowing hydrogen at 450°C for 15 h.

Unless otherwise indicated, 50 mg of supported catalyst has been used with a feed flow rate of 33.3 ml/min of the various gases or gas mixtures at atmospheric pressure. The reaction temperature is 285°C (558 K).

The alumina-supported catalyst has been characterized by transmission electron microscopy, X-ray diffraction, and CO chemisorption at −74°C (*1*). These three techniques indicate a particle size of about 170 Å, equivalent to about 100 μmole of surface iron site/g of catalyst. In connection with Mössbauer studies (*2*) on the silica-supported catalyst, the crystallite size for 10% Fe/SiO_2 was determined as about 140 Å by transmission electron microscopy and by X-ray line broadening.

RESULTS

Reaction of oxygen with the surface species. Figure 1, from our previous work (*1*), shows the result of the experiment 10% CO/H_2, 5 min → He, 40 s → H_2(*t*) over the 10% Fe/Al_2O_3 catalyst. Unless otherwise specified, the results given here are for this catalyst. The first two peaks have been associated with the hydrogenation of two different surface species, and the final tailing production of CH_4 has been associated with the hydrogenation of bulk carbides. Very little water is produced with the CH_4, so the two peaks have been supposed to be two species of different degrees of hydrogenation, CH_x and CH_y. Here we use the reaction of oxygen with the surface species in order to estimate their hydrogen content.

The effect of oxygen is complicated by the heating of the catalyst particles that oc-

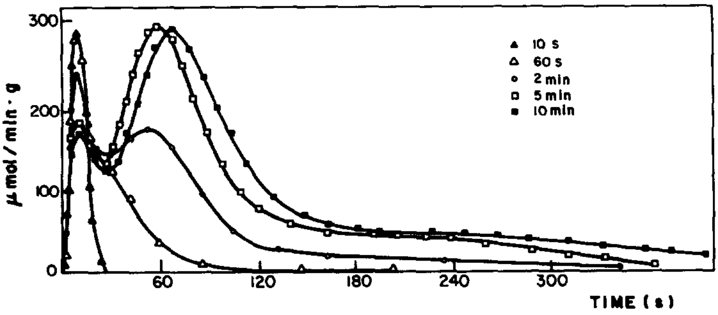


FIG. 1. Methane produced by a switch to hydrogen after various reaction times (10 s to 10 min) of 10% CO/H_2 at 285°C.

curs when metallic iron is oxidized. Some of the water produced during the passage of 10% CO/H_2 is retained on the alumina support so that a switch to oxygen will produce some water by thermal desorption in addition to that originating in the oxidation of CH_x or CH_y. In what follows we describe experiments intended to determine the desorbed water so that the oxidation experiments can be correctly interpreted.

We have studied two times of contact with 10% CO/H_2. An exposure time of 10 s is used first, so that only the first peak is present (50 μmole/g). If 5 min of exposure to 10% CO/H_2 is used, all three peaks appear: the first (still 50 μmole/g), the second (251 μmole/g), and the third (205 μmole/g) representing 33% carburization of the bulk (*1*). Thus the amount of water produced from the 10-s experiment gives an estimate of x in CH_x, and the 5 min experiment gives the water coming from both CH_x (assumed the same as 10 s) and CH_y. Experiments to be described presently (see Table 3) show that the CH_x peak, formed in 10 s, is stable in He. Its stability in H_2/CO was also shown in our previous study (*1*). The oxidation of the carbide, if it occurred, should produce no water.

Therefore we proceed as follows. The experiment 10% CO/H_2, 10 s → He, 5 min → O_2 produces 78 μmole of water/g of catalyst, and this amount includes that from CH_x and from thermal desorption of water produced during 10% CO/H_2 reaction. The experiment 10% CO/H_2, 10 s → He, 40 s → H_2, 30 s → He, 5 min → O_2 produces 52 μmole water/g, and this amount must come from thermal desorption alone, since the CH_x has been completely removed by hydrogen, and a 5-min purge in He is sufficient to desorb water held at 285°C. Thus 26 μmole of water/g come from the CH_x. The reactions are

$$CH_x + H_2 \rightarrow CH_4 \qquad (1)$$

$$CH_x + O_2 \rightarrow \frac{x}{2} H_2O + CO_2. \qquad (2)$$

Thus we have

$$\frac{50}{26} = \frac{CH_4}{H_2O} = \frac{2}{x}$$

so that x is about 1. We have also confirmed that no water is present in the absence of reaction. The experiment H_2, 460°C → H_2, 285°C → He, 5 min → O_2 does not produce any water.

The hydrogen content of the surface is next investigated after a 5-min exposure to 10% CO/H_2. The experiment 10% CO/H_2, 5 min → He, 5 min → O_2 produces 109 μmole/g of water. As previously, this quantity includes the hydrogen from CH_x and CH_y and also the water thermally desorbed. The experiment 10% CO/H_2, 5 min → He, 40 s → H_2, 6 min → He, 5 min → O_2 produces 61 μmole/g. This quantity is somewhat larger than the 52 μmole/g found in the similar experiment above, with only 10 s of exposure to 10% H_2/CO. The difference may be caused by the longer exposure of the support to water of reaction in the 5-min experiment, so that a little more water is desorbed than for the 10-s experiment. From the total water ($109 - 61 = 48$ μmole/g) we subtract 26 μmole/g coming from CH_x, leaving 22 μmole/g coming from CH_y. This time we have

$$\frac{251}{22} = \frac{CH_4}{H_2O} = 2/y$$

so that y is about 0.17. These values of x and y are only approximate, since water is difficult to determine accurately by mass spectrometry. It should also be noticed that, for the measurement leading to $CH_{0.17}$, the thermal effect of the oxidation of the bulk of the iron is not exactly the same for the measurement of 109 μmole/g (iron about 33% carburized) as for the measurement of 61 μmole/g (iron decarburized by H_2).

We have also attempted to use deuterium to estimate x. The experiment 10% CO/H_2, 10 s → He, 40 s → D_2 should lead to the production of CH_xD_{4-x}. However, the OH of the alumina can exchange its H with an adsorbed D so that such experiments are not as useful as they first appear. The reduction of the catalyst in hydrogen at 450°C for 15 h produces an alumina of low surface OH concentration. However, during CO/H_2 reaction at 285°C, the OH on the alumina surface builds up as the support is exposed to water from the reaction. To test the possibility of exchange, we report the experiment H_2/H_2O, 40 s → He, 5 min → 10% CO/He, 5 min → He, 40 s → D_2. The exposure to H_2/H_2O simulates the water that would be adsorbed during the CO/H_2 reaction. CO/He gives unhydrogenated surface C, so this experiment should give CD_4 as the sole product. Such is not the experimental result. Large peaks of CH_2D_2 and CHD_3 are produced as well as CD_4, showing that hydrogen from the support exchanges with adsorbed D_2. This is an example of the H_2 or D_2 spillover.

Influence of hydrogen. In our previous work (*1*), the nature of the surface species resulting from the exposure of the reduced catalyst to 10% CO/H_2 for various times has been studied. Here we study the different surface species involved when CO is used without H_2 (10% CO/He) and when a little hydrogen is added to this mixture (10% CO/1% H_2/89% He). In the previous section we have shown that the exposure of 10% Fe/Al_2O_3 to 10% CO/H_2 for times above about 1 min gives a catalyst exhibiting two surface species proposed to be CH and $CH_{0.17}$, in addition to bulk carbides.

Experiments with 10% CO/He. In Fig. 2 are shown the results of the experiments H_2 (450°C) 15 h → He (285°C), 10 min → CO/He, (t_1) → He, 40 s → $H_2(t_2)$. The rate of methane production is given as a function of t_2 for various times t_1 of exposure to 10% CO/He. The result is quite different from that of Fig. 1, as might be expected, for now the only species involved must be CO and C on the surface, and bulk carbides. No hydrogenated species are to be expected. During the production of CH_4 (Fig. 2) practically no water was produced, so the surface species must be surface carbon. The height and area of this peak increase with t_1, and after 6 min a second peak starts to appear, at first as a tail on the first peak and finally as a region of almost constant methane production. Mössbauer studies carried out at the conditions of this experiment but at 270°C show that there is a long period of approximately constant rate of decarburization. Thus it is logical to associate the long flat tails of the peaks at high t_2 with the production of methane from bulk carbides. This procedure was used in our previous work (*1*), and the carbide peak for hydrogen treatment after exposure to 10% CO/H_2 is the third peak of Fig. 1. The quantities of CH_4 produced in the peaks of Fig. 2 are given in Table 1. The percent carbide calculated is based on the formula $Fe_{2.35}C$, a mixture of χ and ε' carbides, obtained from the Mössbauer results averaged over the first 15 min of reaction (*2*). When the quantities of carbide (second flat peak) are subtracted from the total carbon, the surface carbon given in Table 1 is obtained (first peak).

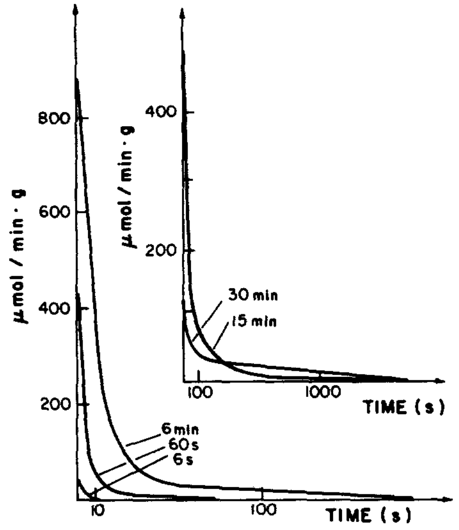


FIG. 2. Methane produced by a switch to hydrogen after various reaction times of 10% CO/He at 285°C.

It is clear that the surface carbonaceous species represented by Fig. 1 are qualitatively different from those represented by

TABLE 1

Species Accumulated during Exposure to 10%CO/He at 285°C, μmole/g of Catalyst

Time (s)	Total	Surface carbon	Carbide	Percent carbide
6	3.5	3.5		
60	40.0	40.0		
360	232.0	174.0	58.0	9.5
900	586.0	378.0	208.0	34.0
1800	553.0	102.0	451.0	74.0

Fig. 2. After 900 s of exposure to 10% CO/He, the peak in Fig. 2 corresponds to 378 μmole/g of surface carbon (Table 2). In Fig. 1, 300 s of exposure to 10% CO/H_2 forms a peak of different shape; the amount of surface carbon is 361 μmole/g (*1*).

Experiments with 10% CO/1% H_2/89% He. Since the rate of carbon buildup on and in the iron is much less with CO/He than with CO/H_2, it is interesting to find out what is the effect of adding a little H_2 to the 10% CO/He mixture. This section considers such experiments.

Figure 3 gives the methane production peaks obtained by a switch to H_2 after various times of exposure to 10% CO/1% H_2/89%He. As in previous experiments the third peak corresponds to the hydrogenation of the bulk carbide. The carbide accumulated (as percent, based on $Fe_{2.35}C$) is plotted in Fig. 4a for the various reaction mixtures. In accord with the Mössbauer results, the rate of carburization increases in the order 10% CO/He, 10% CO/1% H_2/89% He, 10% CO/H_2, and 33% CO/H_2. Figure 4b shows a similar result but for the combined methane peaks arising from all the *surface* species. During the carburization with the mixture containing 1% H_2, no hydrocarbon products and water were detected; the only product was CO_2. It is clear that the presence of hydrogen in CO/He enhances both the rate of accumulation of surface species and the rate of bulk carburization of the iron.

TABLE 2

Species Accumulated during Exposure to 33% CO/H_2 at 285°C, μmole/g of Catalyst

Time (s)	Total	Peak			Percent carbide
		1	2	3	
6	75	75			
10	122	75	47		
15	168	76	92		
25	263	54	180	29	4
45	405	54	282	69	11
80	578	54	380	144	23
180	656	53	380	223	36
600	728	54	329	334	56
1800	707	50	156	501	82

Figures 4a and b show that the surface species formed with CO/H_2 build up faster than those formed with CO/He and that the same is true for the carburization of the bulk, as shown by the independent Mössbauer studies (*2*). A similar result has been reported by Unmuth *et al.* (*4*).

The effect on the 10% CO/H_2 reaction of the carbon already deposited by 10% CO/He. From the results described so far it is clear that the carbon laid down by CO/He is different from the hydrogenated carbon species laid down by CO/H_2. The question now arises as to what relation may exist between the three surface species proposed: the species deposited by CO/He, and the two species deposited by CO/H_2. To study this we have performed the experiment 10% CO/He, 6 min → He, 40 s → 10% CO/H_2, 60 s → He, 40 s → $H_2(t)$, shown in Fig. 5a along with a previous result, 10% CO/He, 6 min → He, 40 s → $H_2(t)$. It is observed that the short contact with CO/H_2 has greatly modified the production curve of CH_4 from what it was after CO/He only. Curve B resembles that obtained after 10 min of exposure of the fresh catalyst to 10% CO/H_2. The three peaks of Fig. 5 after 60 s in 10% CO/H_2 have the areas 45 μmole/g, 311 μmole/g (close to saturation), and 172 μmole/g (carbide). After 60 s of 10% CO/H_2 over a fresh catalyst, the values would be 50 μmole/g, 100 μmole/g,

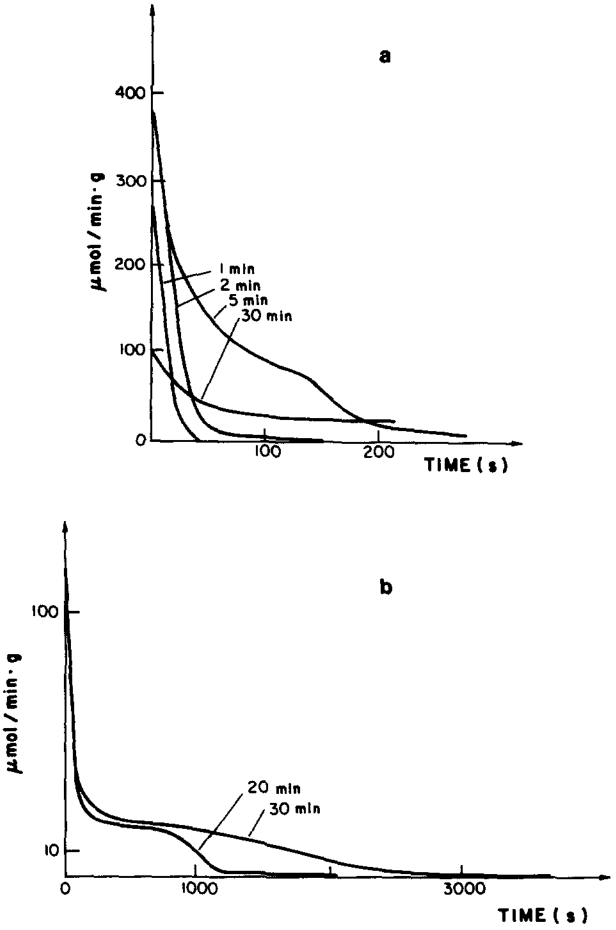


FIG. 3. (a,b) Methane produced by a switch to hydrogen after various reaction times of 10% CO/1% H$_2$/89% He at 285°C.

and 50 μmole/g. The extent of carburization is 9.5% after 5 min in 10% CO/He and then goes to 27% after 60 s additional in 10% CO/H$_2$. On a fresh catalyst, 60 s of this mixture produces a carburization of about 6%.

The influence of the carbon deposited by CO/He on the catalytic activity for the reaction CO/H$_2$ is shown in Fig. 5b. The activity rises quickly, in 80 s, to a value comparable to that which required 10 min of reaction time in the experiment of Fig. 1. (*1*). The interpretation of these results will be discussed in a later section.

Experiments with 33% CO/H$_2$. It is of interest to study the effect of a higher partial pressure of CO than the 10 kPa used in the experiments discussed until now. Figures 6a, b show the results at 285°C of the experiment 33% CO/H$_2$, (t_1) → He, 40 s → H$_2$(t_2). The curves obtained are similar to those for the 10% CO/H$_2$ mixture. For time t_1 greater than 25 s three peaks are observed, and the quantities involved are given in Table 2. As with the 10% CO mixture, the first peak stays at about 50 μmole/g. The second peak increases with t_2 until a maximum of 380 μmole/g at 80 s, and then after a short period of stability (80–180 s) it decreases. The maximum value is higher than that with the 10% CO feed, 309 μmole/g. The third peak, corresponding to bulk carbides, increases continuously. In accord

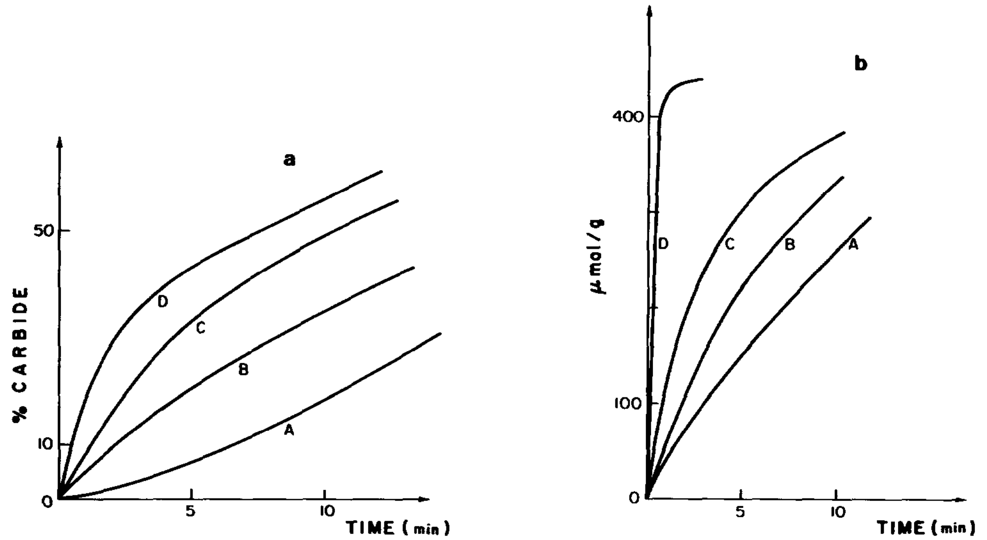


FIG. 4. (a) Carburization of 10% Fe/Al_2O_3 at 285°C with different mixtures. A: 10% CO/He; B: 10% CO/1% H_2/89% He; C: 10% CO/H_2; D: 33% CO/H_2. (b) Quantity of CH_4 produced by hydrogenation of all surface species at 285°C. A: 10% CO/He; B: 10% CO/1% H_2/89% He; C: 10% O/H_2; D: 33% CO/H_2.

with the Mössbauer results, the iron is carburized in 33% CO/H_2 faster than in the other mixtures studied. This is shown in Fig. 4a. In Fig. 4b are also plotted the results for the accumulation of the surface species. The second surface species builds up faster with 33% CO/H_2 than with 10% CO/H_2, and the methane production rate during reaction also rises more quickly to its maximum, as shown in Fig. 6c. For both feed mixtures, the maximum quantity of the second peak is found at the time corresponding to the maximum methane rate in the appropriate reaction mixture.

Experiments with water added to the feed mixture. In our preceding work (*1*) it was found that water acts as a reversible inhibitor for the H_2/CO reaction, a result confirmed by others (*5*, *6*). The results of the experiment H_2 → 10% CO/H_2O/H_2 are shown in Fig. 7. The water content was 0.6%, added via a saturator at 0°C. As

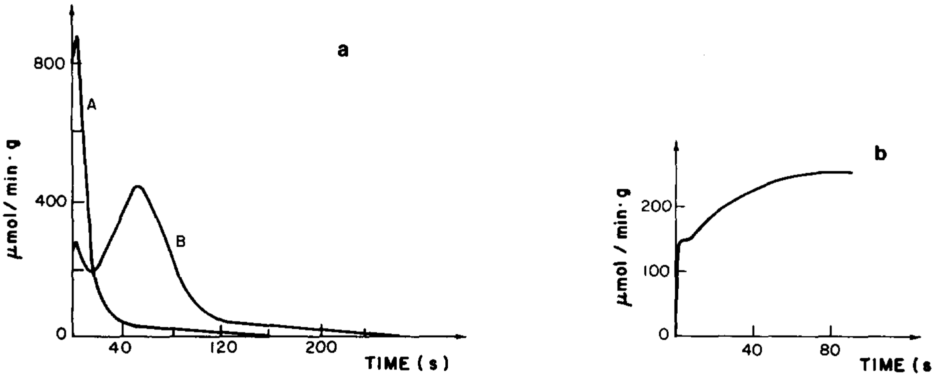


FIG. 5. (a) Transformation of surface carbon behavior by exposure to 10% CO/H_2. Methane produced by A: 10% CO/He, 5 min → He, 40 s → $H_2(t)$; B: 10% CO/He, 5 min → He, 40 s → 10% CO/H_2, 60 s → He, 40 s → $H_2(t)$. (b) Transformation of surface carbon behavior by exposure to 10% CO/He. Methane produced during CO/H_2 reaction by 10% CO/He, 5 min → He, 40 s → 10% CO/$H_2(t)$.

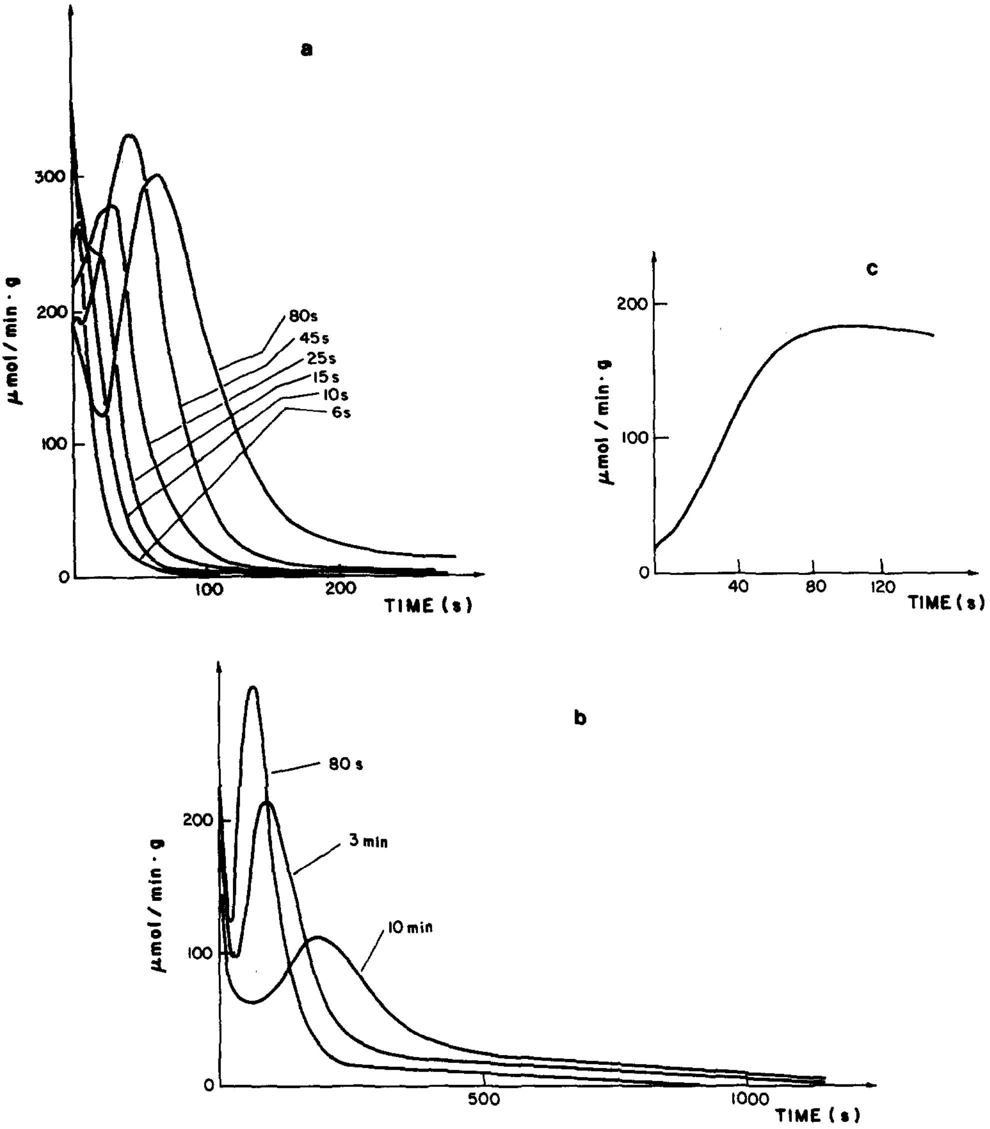


FIG. 6. (a,b) Methane produced after various reaction times of 33% CO/H$_2$ at 285°C. (c) Methane production at 285°C over freshly reduced catalyst after switch from He to 33% CO/H$_2$.

shown, water vapor inhibits the H$_2$/CO reaction, particularly at the time of the minimum rate, at $t = 50$ s. The second maximum in the rate is attained sooner than without added water. The surface and bulk species present after 4 min of reaction are shown in Fig. 8. For curve A, the total species accumulated is 181 μmole/g. For curve B, it is 375 μmole/g. The accumulation of the second, less hydrogenated peak is much greater with water than without. Thus it seems that the rate of CO dissociation remains high but that water has reduced the ratio H/O on the surface so that the rate of hydrogenation of the surface species to products is reduced, so that they build up faster than without water. The CO$_2$ production accompanying Fig. 7 is increased (not shown).

If water is added to 10% CO/He the rate

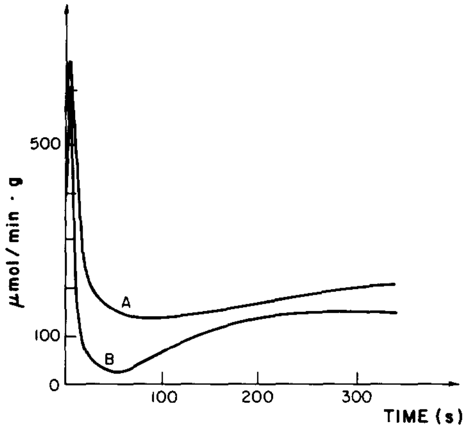


FIG. 7. Initial methane activity of 10% CO/H_2 over freshly reduced catalyst at 270°C. A: No water in 10% CO/H_2; B: 0.6% water in 10% CO/H_2.

of carbon deposition is drastically reduced. The result appears in Fig. 9. Now the surface is relatively oxidized so that H_2 and CO_2 are the main products (shift reaction) rather than surface and bulk carbon species.

The Mössbauer results (*2*) show that bulk carburization is markedly inhibited when H_2O is added to CO/H_2 or to CO/He. As previously, a reduced surface favors carburization whereas an oxidized surface inhibits it.

Stability of the surface species. After the experiment 10% CO/H_2, 10 s → He, 40 s → H_2 it will be recalled that a single methane peak is formed by hydrogenation (Fig. 1). For longer reaction times this peak changes little and retains its value of 50 μmole/g.

Now we consider the experiment 10% CO/H_2, 10 s → He(t) → H_2. Table 3 shows that this peak is remarkably stable in helium. Also, the maximum rate is about the same as that for the first peak of Fig. 1. This result also indicates that the O_2 and H_2O levels in the helium are low, for otherwise this extremely reactive peak would be changed by the extended exposure to He.

We are also interested in the effect of helium on the second peak of Fig. 1. A reaction time in 10% CO/H_2 of 5 min is chosen, so that the second peak is large but carburization is not complete (peak 1: 54 μmole/g, peak 2: 251 μmole/g, peak 3: 205 μmole/g; 33% carburization (*1*)). This curve is shown in Fig. 1 and is the starting curve for Fig. 10. Then the experiment 10% CO/H_2, 5 min → He(t_1) → $H_2(t_2)$ is performed, with the results shown in Fig. 10. As time of exposure to helium increases, the second peak decreases and the tailing carbide peak increases. As noted in the legend of Fig. 10, the total amount of carbon represented by the methane peaks remains constant, within experimental error, for different exposure times in helium. The Mössbauer studies (*2*) corresponding to this experiment show an increase in carburization during heat treatment in helium, so it is logical to conclude that some of species CH_y has been converted to bulk carbide. The rate is

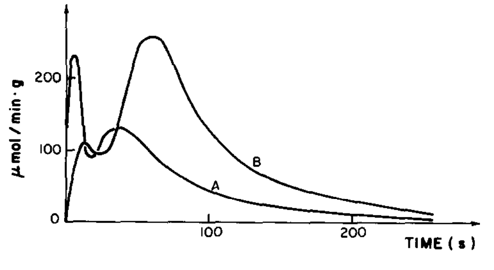


FIG. 8. Methane produced by a switch to H_2 after 4-min exposure of reduced catalyst to 10% CO/H_2 at 270°C. A: No water in 10% CO/H_2; B: 0.6% water in 10% CO/H_2.

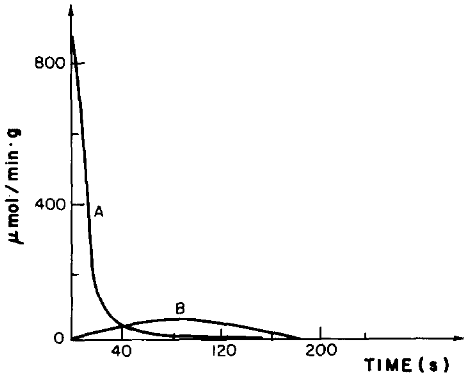


FIG. 9. Methane produced by a switch to H_2 after 6-min exposure of reduced catalyst to 10% CO/He at 285°C. A: No water in 10% CO/He; B: 0.6% water in 10% CO/He.

TABLE 3

Stability of Surface Exposed to Helium (285°C): 10% CO/H_2, 10 s → He(t) → H_2

Purge time t(s)	20	30	60	120	300	600	1800
CH_4 μmole/g	50	46	48	51	52	50	49

quite low when compared to that with 10% CO/He or especially 10% CO/H_2. The rate of carburization by the second surface species can be increased by increasing the temperature during the helium treatment after the surface species are formed. Figure 11 shows the results of the similar experiment, 33% CO/H_2, 5 min → He(t_1) → H_2(t_2).

The experiment 10% CO/He, 5 min → He, 30 min → H_2 (all at 285°C) reduces slightly the corresponding peak of Fig. 2 and also increases its tail. These experiments seem to support the idea that the carbon peak of Fig. 2 as well as the CH_y peak can be transformed into surface carbon and bulk carbide by heat treatment, whereas the CH_x peak is relatively stable.

Experiments with ethylene. Another test of the idea that H_2/CO leads to the surface species CH and $CH_{0.17}$ is accomplished by the experiment 10% C_2H_4/H_2(t_1) → He, 40 s → H_2 (t_2). With the large excess of hydrogen which is used with ethylene it is reasonable to assume that ethylene or CH_2 from it is not appreciably dehydrogenated on the surface. The reaction 10% C_2H_4/H_2 gives, in addition to ethane, a considerable production rate of CH_4. Some C_3H_8 and C_4H_{10} are also produced. Thus the C–C bond is broken on the surface, so that CH_2 surface intermediates are probable. The presence of propane and butane in ratios to methane similar to those arising from 10% CO/H_2 gives support to the notion that for both reactions the polymerization passes through CH_2 groups. No oxygen (CO insertion) seems to be necessary. No bulk carbides are formed during the 10% C_2H_4/H_2 reaction (2).

Upon switching from 10% C_2H_4/H_2 to H_2, the methane peaks shown in Fig. 12 are formed after varying reaction times t_1. At t_1 = 30 s, the area is about 50 μmole/g, and this figure is consistent with the quantity of CH that the iron surface seems to be able to hold. The area under the peak of Fig. 12 increases only slightly with time, and this is further evidence that the peak arising from ethylene is similar to CH. No second or third peaks appear.

The sequence 10% C_2H_4/He(t_1) → He, 40 s → H_2(t_2) gives the results shown in Fig. 13. There is a small production of methane arising from the self-hydrogenation of the

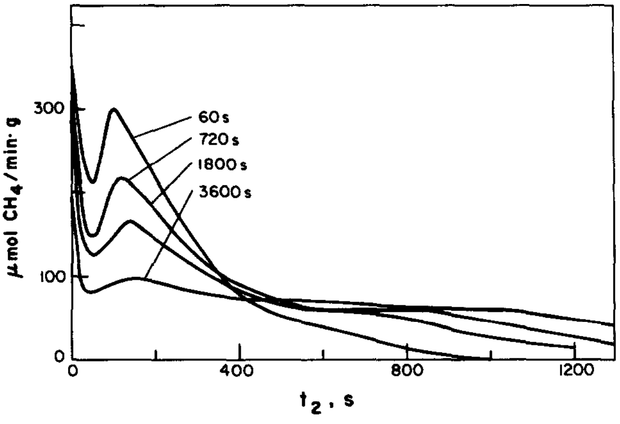


FIG. 10. Effect of exposure to helium at 285°C on the methane peaks formed in the experiment 10% CO/H_2, 5 min → He(t_1) → H_2(t_2). The total quantities of methane in the peaks are 60 s, 480 μmole/g; 720 s, 487 μmole/g; 1800 s, 480 μmole/g.

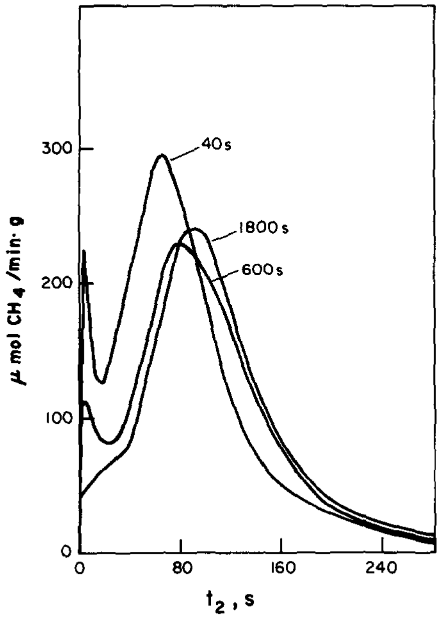


FIG. 11. Effect of exposure to helium at 285°C on the methane peaks formed in the experiment 33% CO/H_2, 5 min → $He(t_1)$ → $H_2(t_2)$. The total quantities of methane in the peaks are: 40 s, 507 μmole/g; 600 s, 498 μmole/g; 1800 s, 480 μmole/g.

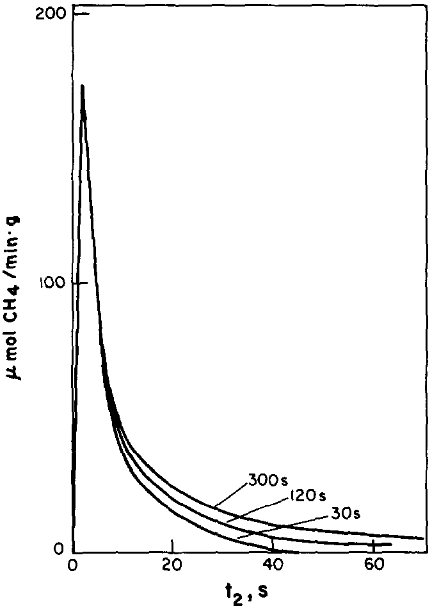


FIG. 12. Methane produced by 10% C_2H_4/H_2 at 285°C by the experiment 10% $C_2H_4/H_2(t_1)$ → He, 40 s → $H_2(t_2)$.

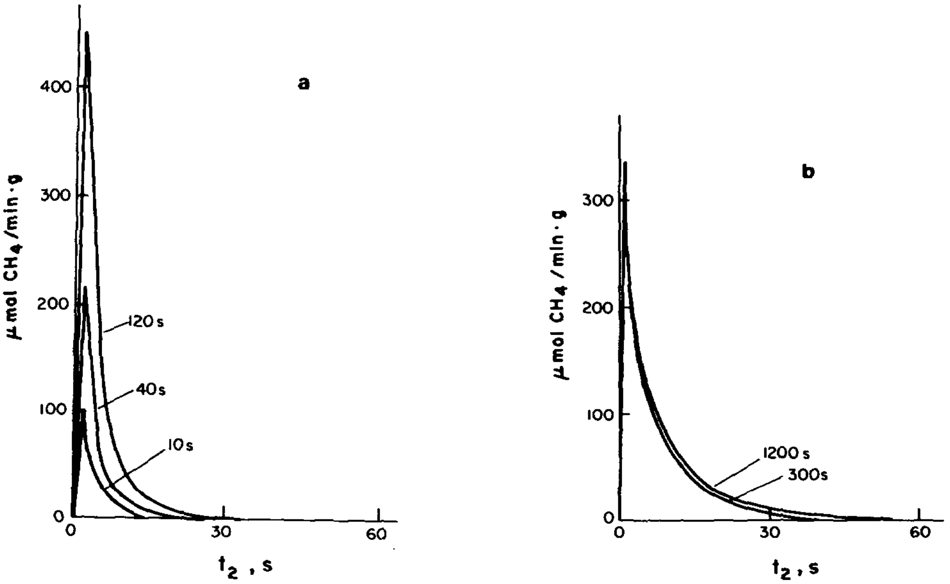


FIG. 13. (a,b) Methane produced at 285°C by the process 10% $C_2H_4/He(t_1)$ → He, 40 s → $H_2(t_2)$. The amounts of methane formed are 10 s, 11 μmole/g; 40 s, 25 μmole/g; 120 s, 46 μmole/g; 300 s, 57 μmole/g; 1200 s, 62 μmole/g.

ethylene (not shown). The switch to hydrogen gives methane peaks of increasing quantity as carbonaceous species arising from the self-hydrogenation of the ethylene build up on the surface. The species originating from C_2H_4/He seems similar to the CH peak arising from CO/H_2, since it is of the order of 50 μmole/g and is stable. It does not increase as does the C peak arising from CO/He. Since we have found CH very stable on iron, it is logical to propose that adsorbed ethylene loses H only to the extent of becoming CH. This proposal is supported by the fact that no species like the second peak of Fig. 1 is formed, and no carbide is formed. The latter especially should require free surface carbon.

Specificity of the behavior of iron. The application of the transient method to the CO/H_2 reaction over 10% Ni/Al_2O_3 and 10% Co/Al_2O_3 will be presented in a separate study. However, it is of interest here to report that the basic experiment 10% CO/$H_2(t_1) \rightarrow H_2(t_2)$ for Ni and Co gives results which differ greatly from those for Fe. For both of these catalysts, there is a rapid rise of methane production to steady state after exposure to 10% CO/H_2. Then after the switch to hydrogen there is a large methane peak which is over by $t_2 = 40$ s. For contact times t_1 greater than 300 s the subsequent peak formed by H_2 does not vary. For Ni, the saturation peak quantity is about equivalent to the surface Ni atoms. For iron the surface species may amount to more than four times the number of surface Fe atoms at 285°C. Both Ni and Co are more active than Fe, so these results are for experiments at $t = 220°C$. There is no bulk carburization.

Thus it is clear that the sequence of steps for the CO/H_2 reaction over iron is different in several ways from that over Ni and Co, for example. Over Ru, the sequence is also different (*7, 8*). The differences are so complex that it seems unlikely that the kinetics over these various metals can be understood in terms of a single expression like $r = k(CO)^x(H_2)^y$.

Results over 10% Fe/SiO$_2$. Iron is a metal for which interaction with oxide supports may be expected. In a separate study we are investigating Fe/TiO_2, Fe/MgO, and Fe/C, for which the effect of the support is considerable. Here we mention briefly results on 10% Fe/SiO_2 (Cab-O-Sil). All the different kinds of transient experiments already described for 10% Fe/Al_2O_3 have been performed, albeit in less detail, for the 10% Fe/SiO_2 catalyst. In every case the results are qualitatively similar, although the silica-supported iron is about 60% as active as the alumina-supported iron. Two surface species and bulk carbide are produced as before. Mössbauer experiments (*2*) on the silica catalyst also give similar results. In summary, there seem to be no qualitative differences in the behavior of the two catalysts. The silica supported iron crystallites (140 Å) are smaller than those on alumina (170 Å) (*2*).

DISCUSSION

The results of the experiments that have been described are quite complicated, and a model accounting for all the experimental features is difficult to devise. Here we present such a model, but until there are more data on surface composition during the experiments the model must be considered tentative.

General Reaction Scheme

First we consider a few general aspects of the results. From Fig. 1, and our previous work (*1*), the quantity in the first (CH) peak has been found about constant at 50 μmole/g. This means that while the first peak is being removed by hydrogen there is little contribution from the second peak ($CH_{0.17}$). If the second peak started to be formed during this time, the first peak would appear to increase with reaction time. It seems that the formation of the second peak (by hydrogenation of $CH_{0.17}$) is inhibited by the presence of the first peak (CH). We have found that 3 s is sufficient for the complete desorption of surface hydrogen, and adsorption is of course faster. Thus the second peak might be expected to have a shape such that the maximum rate would be at the switch to hydrogen; by contrast, its experimental shape is a peak starting at zero and having its maximum at times after the decay of the first peak (Fig. 1). Thus we assume that there are relatively active sites S_1 which adsorb hydrogen and CO and give rise to a very rapid formation of CH. The CH quickly covers almost all these sites, reducing the HS_1 concentration. To explain the slow start of the second peak, we must assume that $CH_{0.17}$ forms on other sites S_2, and that HS_1 forms from the gaseous H_2 and gets to the S_2 sites via the S_1 sites. Thus as the CH is removed from the S_1 sites, HS_1 goes up, sending HS_2 up and producing the second peak with its delayed maximum.

These hydrogenations can be expected to follow the approximate equation, $r = k(CH_z)(H)$ where z is 0.17 or 1. For the first peak, CH starts high and goes down as H goes up producing the observed shape. A similar equation applies to the second peak, but H stays low until the CH is gone, as proposed above.

To continue the discussion, let us propose the sequence of steps that follows; we shall then try to show how the experimental results support the scheme:

$$CO + S_1 \rightleftarrows COS_1 \qquad (1)$$

$$COS_1 + S_1 \rightarrow CS_1 + OS_1 \qquad (2)$$

$$COS_1 + OS_1 \rightarrow CO_2 + 2S_1 \qquad (3)$$

$$H_2 + 2S_1 \rightleftarrows 2HS_1 \qquad (4)$$

$$2HS_1 + OS_1 \rightleftarrows H_2O + 3S_1 \qquad (5)$$

$$CS_1 + HS_1 \rightarrow CHS_1 + S_1 \qquad (6)$$

$$\left.\begin{array}{ll} CHS_1 + HS_1 \rightleftarrows CH_2S_1 + S_1 & (7) \\ CH_2S_1 + HS_1 \rightleftarrows CH_3S_1 + S_1 & (8) \\ CH_3S_1 + HS_1 \rightarrow CH_4 + 2S_1 & (9) \end{array}\right\} \text{fast}$$

$$CS_1 + x\text{Fe} \rightarrow \text{Fe}_xC + S_1 \qquad (10)$$

$$CS_1 \rightarrow \text{C (graphite)}\ S_1 \qquad (11)$$

$$CS_1 + S_2 \rightleftarrows CS_2 + S_1 \qquad (12)$$

$$HS_1 + S_2 \rightleftarrows HS_2 + S_1 \qquad (13)$$

$$HS_2 + CS_2 \rightarrow CHS_2 + S_2 \qquad (14)$$

$$CHS_2 \rightleftarrows CH_2S_2 \rightleftarrows CH_3S_2 \rightarrow CH_4 \text{ (fast)}. \qquad (15)$$

In this sequence CHS_1 is associated with the first peak of Fig. 1, CS_2 with the second peak, and Fe_xC with the third peak. We shall discuss a little later the nature of CS_2, which we have written in place of $CH_{0.17}$ or CH_y.

First of all, it is clear that CHS_1 is not the precursor of CS_2 in the existing hydrogen-rich atmosphere. The opposite is not true either, since Fig. 1 shows that CHS_1 is formed before CS_2. Thus we conclude that these two species are formed competitively from a common precursor, CS_1, which comes from the dissociation of COS_1. As mentioned above, the presence of CHS_1 inhibits the hydrogenation of CS_2, so we must propose (Eq. (4)) that H_2 adsorbs from the gas onto the sites S_1. HS_1 can then transfer to the S_2 sites by Eq. (13), at a rate determined by the concentration HS_1. Thus in Fig. 1, for which a switch from He to H_2 is made at time zero, the hydrogen attacks first the CHS_1 (Eq. (7) plus rapid further hydrogenation). As CHS_1 is used up, HS_1 goes up, goes over to HS_2, and then reacts with CS_2.

Nature of the Surface Species

The species CHS_1 gives, when hydrogenated, not only CH_4, but higher paraffins (*1*). Its apparent stability has been mentioned, and it is also clearly highly reactive to hydrogen. Except for reaction times less than 10 s, its quantity is always found to be about 50 μmole/g.

The second species CS_2 is more difficult to characterize. As reaction time goes from 0 to 10 min, its quantity increases to 309 μmole/g, much greater than the approximately 100 μmole of surface iron sites found by chemisorption (*1*). Thus the species must be either a carbon chain, or there must be several carbons bound to single iron atoms. If chains form during reaction (10% CO/H_2) it does not seem logical that such chains, when the CO is removed, should give only CH_4, when we know that the CHS_1 does give higher hydrocarbons (*1*). We recall that exposure of the second peak to helium causes its conversion to bulk carbide, as shown by Fig. 10 and the Mössbauer studies (*2*). Table 3 shows the relative stability of the CHS_1 peak to such treatment. These results all favor the existence of several carbon atoms grouped around iron, rather than chains of carbon extending away from the surface.

When the catalyst is reacted with 10% CO/He, a switch to hydrogen (Fig. 2) causes a methane peak associated with surface carbon which rises and falls as shown in Table 1. Bulk carbide forms simultaneously. A switch from CO/He to He alone shows continued carburization (*2*). Thus it appears tempting to associate the surface carbon formed by CO/He with the CS_2 species formed by CO/H_2. The latter we have found to be slightly hydrogenated ($CH_{0.17}$), but these arguments, with others to come, lead us to propose that the two surface carbons discussed are the same.

However, how can the peaks of Fig. 2, which appear very rapidly, be said to come from the same surface species as those of Fig. 1, which appear slowly? This difference is explained by the sequence of steps already discussed, that is, the CHS_1 formed in the presence of CO/H_2 inhibits the hydrogenation of CS_2. Strong support for these ideas is furnished by the results of Fig. 5. A treatment in CO/He gives curve A of Fig. 5a after a switch to hydrogen. However, if there is a brief passage of CO/H_2 before the switch to hydrogen, we get curve B of Fig. 5a. The surface carbon of A has not been changed to a different form, but the S_1 sites have been almost filled by CHS_1, so that the carbon from CO/He now looks like the second peak after CO/H_2 reaction. Figure 5b supports this argument also. A switch from CO/He to He to CO/H_2 gives a rapid increase of the CH_4 production rate, and the final maximum rate occurs sooner than following a switch directly from the reduced catalyst (in H_2 or He) to 10% CO/H_2. In other words, the maximum CH_4 production rate during CO/H_2 reaction occurs in both these experiments at the time when the accumulated CS_2 on the surface goes through its maximum.

Thus we propose that the second peak of Fig. 1 comes from the same surface carbon as the first peak of Fig. 2. Although the carbon produced by CO/H_2 is slightly hydrogenated, we prefer the approximation that it is carbon alone, based on its behavior as discussed above.

The nature of the surface species may be discussed in the light of the work of Bonzel and Krebs (*3*). They have studied the surface of Fe(110) after CO/H_2 reaction at atmospheric pressure by Auger electron spectroscopy and by X-ray photoelectron spectroscopy. They find three phases, designated by them as follows: (1) a CH_x phase which the Auger studies suggest is CH, E_B (C1s) = 283.9 eV; (2) a carbidic carbon–hydrogen phase, E_B (C1s) = 284.2 eV; and graphitic carbon with E_B (C1s) = 284.7–285.0 eV. This phase is more difficult to hydrogenate then the first two.

Although our iron is in the form of small polycrystalline particles, we seem to have reached conclusions about the nature of the surface species which are similar to those of Bonzel and Krebs. We propose CHS_1 (CH), CS_2 ($CH_{0.17}$), and C(graphitic) S_1. In addition to the surface species, we have observed that the bulk iron, for sufficient time in CO/H_2, is completely carburized to a mixture of ε'-$Fe_{2.2}C$ and χ-$Fe_{2.5}C$ (*1, 2*), determined by Mössbauer spectroscopy. To explain our kinetics, it has been necessary to propose an added (unobserved) surface species CS_1, a very active nascent carbon which is not so closely bound to iron as the other species.

In accord with the work of Krebs *et al.* (*9*) on polycrystalline iron foil, we observe a simultaneous increase in the CO/H_2 reaction rate and the coverage of carbidic carbon (CS_2), and then a decrease in the rate as graphitic carbon build up (*1*).

The carbidic carbon CS_2 must be considered as a grouping of carbon atoms around iron atoms in the top layers of the iron crystallites. Because of the low percentage exposed of our catalyst, this surface carbide, of unknown structure, contributes little to the MES spectra. In the bulk we observe mainly ε' and χ carbides, and no θ-Fe_3C (at 285°C). There must be an activated process for the transformation of the CS_2 into dissolved carbon, which then diffuses rapidly into the bulk (*2*) and reacts in another activated step with iron to form the observed bulk carbides.

The experiments with ethylene, reported in Figs. 12 and 13, confirm some aspects of the differences between CHS_1 and CS_2. Neither C_2H_4/H_2 nor C_2H_4/He leads to any bulk carburization, as does CS_2. The CH_2 species formed by ethylene apparently do not dehydrogenate beyond CH, but they do transform in the opposite direction to produce methane eventually. The quantity of CH_4 formed by the hydrogenation of these surfaces CH species is of the same order (60 μmole/g) as that of CHS_1 and the species is rapidly removed by hydrogen.

To summarize this part of the discussion, we then propose that after exposure to 10% CO/H_2 for times in the order of 10 min there are associated with the iron: surface CHS_1; surface CS_2, a carbidic carbon; surface graphite, an inhibitor; and bulk carbides, as discussed in our other studies (*1, 2*).

Evolution of the Activity of the CO/H_2 Reaction

A number of experimental results remain to be discussed, in particular the shape of curves like curve A of Fig. 7 (*1*). Why does the reaction rate go back up after its initial maximum has been passed? To explain this, and a number of other results, the sequence of steps contains the carbon species CS_1, which we propose as extremely active surface carbon which has just been formed from the dissociation of COS_1. This CS_1 is the common precursor of Fe_xC, CHS_1, and CS_2. We propose that the general increase in reaction rate is related to the competitive modes of reaction of CS_1. It is transformed to CHS_1 almost instantly and to carbide rather slowly (~40 μmole/g min). The CS_1 is also transformed to CS_2, as soon as the CHS_1 has been formed. All of these sinks for carbon eventually saturate; in particular CS_2 reaches its maximum at about the same time (10 min) as the reaction rate reaches its maximum. Measurements (material balances) on the rate of disappearance of CO, appearance of surface and bulk C, and appearance of gaseous products (*1*) have shown that after about 1 min the rate of CO dissociation is constant while the rate of bulk and surface carbon accumulation decreases and corresponds to the observed rate of increase in gaseous CO_2 and hydrocarbons. We have made this argument previously (*5*), and more recently Niemantsverdriet *et al.* (*11*) have argued persuasively in support of this scheme. However, in these previous papers (*5, 11*) it was thought that the bulk carburization was the principal competitor to hydrocarbon production. Here we see that the formation of the surface carbide, CS_2, is also very important. During these first 10–20 min the role of surface graphite is minimal, but over the long term it will be the principal inhibitor. We note also that when the time to reach the maximum CS_2 accumulation is reduced, the time to reach the maximum in the CH_4 production rate is correspondingly changed. This relation is illustrated by the use of a higher partial pressure of CO (33% CO/H_2), by preformation of CS_2 from 10% CO/He, and by addition of H_2O to 10% CO/H_2 feed.

We are also proposing that the gaseous products are formed from CHS_1; CS_2 is not hydrogenated rapidly in the presence of CHS_1. How can the rate of CH_4 production go up when the CHS_1 measured is about constant after the first 10 s of reaction? To answer this question we propose that the coverage of CHS_1 during reaction with CO/H_2 is lower than its saturation value (50 µmole/g). The concentration of CS_1 is always low. However, when a switch to helium is made, HS_1 goes down, and CH_2S_1 and CH_3S_1, present on the surface in small concentrations, revert to the stable (in the absence of HS_1) form CHS_1. This reversibility of the hydrogenation of CH_x groups has been observed by Calvert and Shapley (*12*) for some homogeneous systems. More pertinent to our heterogeneous system is the recent work of Yamasaki *et al.* (*13*), who have studied the CO/H_2 reaction on Ru/SiO_2 by *in situ* infrared spectroscopy at 150–200°C. They observe the formation of CH_2 and CH_3 in chains present on the ruthenium. Upon evacuation their results suggest that the CH_x species lose hydrogen and revert to carbon by reactions like

$$CH_2 \rightleftarrows C + 2H$$
$$2H \rightleftarrows H_2.$$

For iron, our results indicate that the dehydrogenation goes no further than CH, which has a remarkable stability in the absence of hydrogen.

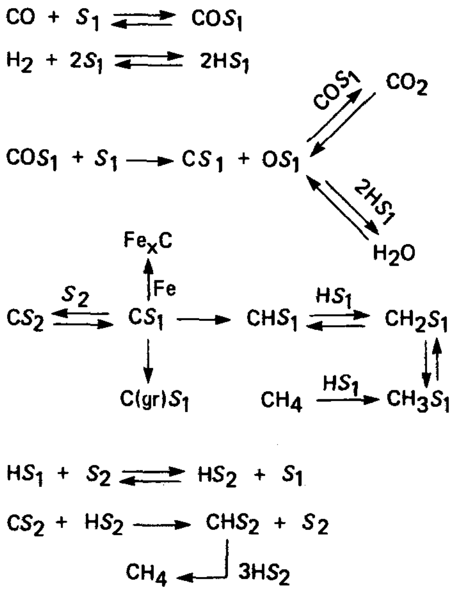
Demuth, in a number of studies, has investigated the interaction of acetylene with the principal crystal faces of nickel by ultraviolet photoemission spectroscopy (*14, 15*) and by electron energy loss spectroscopy (*16*). The adsorbed C_2H_2 leads to CH, CH_2, and CCH species in the UHV conditions of the experiments. Thus the stability of CH_x species on nickel is demonstrated. As discussed previously, we suggest that CH_2 groups from ethylene do not dehydrogenate beyond CH on our iron surfaces.

Thus, we propose that during the first 10 min of reaction, when the rate is increasing, the concentration of CS_1 is increasing, although this concentration cannot be measured by our techniques. The concentration of CHS_1 is also increasing, but we do not measure this dynamic concentration. When the switch to helium is made, CHS_1 goes up to its saturation value, as observed by its subsequent hydrogenation.

Support for this part of the scheme is given by the results with CO/H_2/H_2O, shown in Figs. 7 and 8. Water is known to inhibit the CO/H_2 reaction (*1, 5, 6*) and this overall effect is shown in Fig. 7. The species OS_1 goes up at the expense of HS_1, already present only in small concentration in the presence of CHS_1. Thus the hydrogenation reactions are decreased, but the dissociation rate of COS_1 is not changed so much, so that CS_1 is now converted preferentially into CS_2, as shown by curve B of Fig. 8. Note that curve B of Fig. 7 does rise, almost in parallel with curve A. As already noted, the increased rate of CS_2 accumulation decreases the time to the maximum CH_4 rate in this region. It has been found that the water inhibition effect is reversible (*1*), in accord with these ideas.

CONCLUSIONS

We suggest the following reaction scheme, in accord with Eqs. (1)–(15):



The common precursor of the various species is CS_1, active surface carbon not closely bound to iron. This intermediate is then transformed competitively, at least during the initial reaction period, into bulk carbides (ε'-$Fe_{2.2}C$ and χ-$Fe_{2.5}C$); surface carbidic carbon CS_2, probably with some associated hydrogen ($CH_{0.17}$); inert surface graphitic carbon; and, finally, into reaction products via the stable surface intermediate CHS_1. After a burst of products formed on the clean iron surface, the CO/H_2 reaction rate falls as the bulk and surface carbide accumulate. If the catalyst is saturated with H_2 before the switch to 10% CO/H_2, the initial methane peak is high and sharp, the reaction rate quickly falls as the accumulated surface hydrogen is consumed (*1*). A switch from He to 10% CO/H_2 produces only a small overshoot. Beyond this first maximum, as the sinks for relatively inactive carbon fill up the hydrocarbon production rate goes up, but it soon reaches a maximum as graphitic surface carbon starts to accumulate. The reduced surface of the catalyst obtained under CO/H_2 favors rapid reaction and bulk carburization. More oxidizing gases ($CO/H_2/H_2O$ or CO/He) lead to a lower concentration of carbon precursor and lower rates of hydrogenation and bulk carburization.

It should be recalled that we base these conclusions on our work at 270–285°C. The phenomena may be altered at other temperatures.

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