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Further Results on the Reaction of H_2/CO on Fused Iron by the Transient Method

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Experiments have been continued on a CCI commercial, promoted, fused-iron catalyst. Catalyst stability and long-term activity are improved by an oxygen treatment at 500°C prior to reduction at 500°C. Water is a strong inhibitor of the initial reaction of H_2/CO (9/1) at 250°C and 1 atm to hydrocarbons, and the steady-state catalyst is active for the shift reaction. Experiments with C_2H_4/H_2 and other olefins show that these reactants are both split into lower alkanes (including methane) and added to for the formation of alkanes of higher carbon number than the feed olefin. Reaction on a reduced catalyst at 250°C does not lead to bulk carburization of the iron, whereas of course CO/H_2 under the same conditions forms bulk Fe_2C. These results support a mechanism in which the hydrogenation of surface carbon is the rate-limiting process, and chain growth occurs through C_xH_y fragments, present on the surface in low coverage. ESCA experiments show that the surface of the catalyst used at 250°C has a high concentration of graphitic carbon and that the iron is at least partly oxidized.

INTRODUCTION

In a previous study (*1*) it was proposed that the surface of a promoted fused-iron catlayst is largely covered with carbon during the steady-state reaction of hydrogen and carbon monoxide (90% H_2, 10% CO) at atmospheric pressure and 250°C. This same catalyst, a commercial ammonia synthesis catalyst (CCI), was also evaluated (at 2.0 MPa) in a more applied way in connection with the study of a scheme for energy storage in a central power plant (*2, 3*). It is now clear that is is necessary to consider that each catalyst (i.e., even the same metal on different supports) may operate for reactions of H_2/CO through a unique sequence of steps, or at least with a particular rate-determining step. Thus although the hydrogenation of surface carbon seems to be rate limiting on iron (*1*), on ruthenium the dissociation of adsorbed CO has been proposed as rate limiting (*4*). The present work is a continuation of that of Ref. (*1*); this time the role of CO_2 and H_2O has been investigated, and interesting information has been obtained on the chain-growth process.

EXPERIMENTAL

The properties of the catalyst used are summarized in Table 1. The reactor was made of $\frac{1}{4}$-in. stainless-steel tube and filled with 100 mg of catalyst (particles of 300 μm) mixed with 500 mg of glass beads of the same size. The reactor and the glass beads were confirmed to produce no products at the reaction conditions. Feed rates of H_2/CO (9/1) between 20 and 120 ml/min were explored but if not otherwise noted, 40 ml/min was used; the conversion was always less than 5% of the CO fed.

TABLE 1

CCI Fused Iron Catalyst[a]

Composition	Fe_3O_4, 96.5%; Al_2O_3, 2.5%; K_2O, 0.6%; SiO_2, 0.4%
BET surface area	13.0 m^2/g (135 μmole/g)
CO chemisorption	38 μmole/g

[a] See Ref. (*1*).

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Hydrogen (99.99%, Air Liquide) was purified by a molecular sieve 5A trap, followed by a deoxo reactor, followed by a second molecular sieve 5A. Carbon monoxide (99.9%, Air Liquide) was passed through a glass tube heated to 220°C to decompose carbonyls and then through a trap of activated carbon at 25°C.

Analysis of the reaction products was by gas chromatography. For the separation of the hydrocarbons, a Poropak Q (80–100 mesh) 6-m, ⅛-in. stainless-steel column was used with a flame ionization detector. Column temperature was 195°C, and the carrier gas (He) was used at 30 ml/min. The CO_2 and H_2O were measured by a second identical Poropak Q column at 175°C, leading to a thermal conductivity detector. For the reaction conditions used, only alkanes were found among the hydrocarbon products.

RESULTS AND DISCUSSION

The Basic Reaction

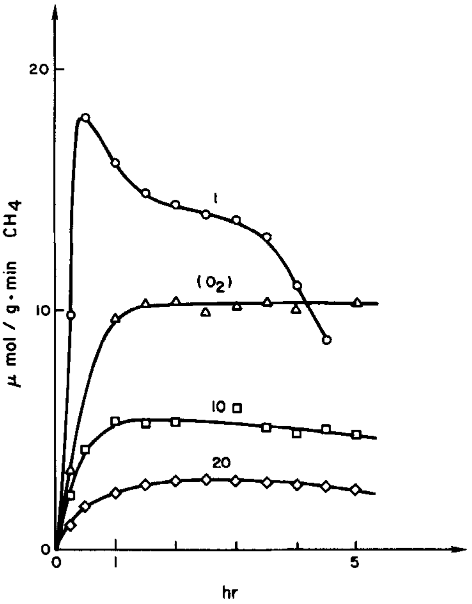

FIG. 1. Rate of reaction after various reactivations as described in text. Feed rate, 120 ml/min of H_2/CO = 9; 250°C.

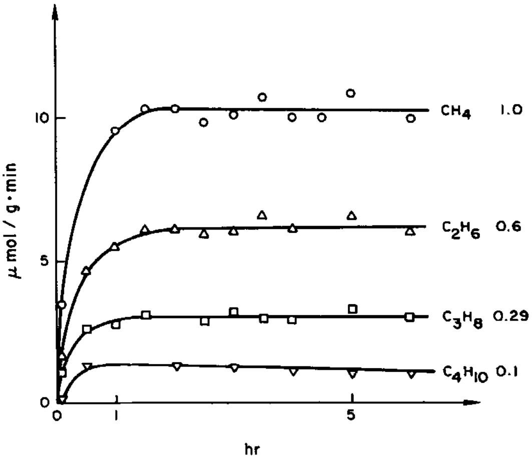

FIG. 2. Formation rates of products at 250°C. Feed, 40 ml/min of H_2/CO = 9.

After an initial reduction in flowing hydrogen at 60 ml/min for 60 hr at 500°C, the reactor is cooled to 250°C and the feed is switched at time zero to 10% CO in H_2. Curve 1 of Fig. 1 results. The deactivation is rapid and the production rate of methane passes through a maximum. A reactivation in H_2 at 500°C for 15 hr increases the activity of the catalyst to a level above what it was at the end of the first run, but below what it was at its maximum. This process continues with further reactivations, and Fig. 1 shows curves after 10 reactivations and after 20 reactivations. However, it was found that short (30-min) treatment by oxygen at 500°C and 1 atm before the usual reduction by hydrogen produced a relatively stable catalyst, as shown by the curve O_2 of Fig. 1. The activity of the catalyst is obviously very sensitive to its state of oxidation and to the concentration of refractory carbon at or near its surface. It may be recalled that Matsumoto and Bennett (*1*) found that short treatments in helium at 250°C converted the active carbon intermediate to a form inactive at this temperature. Similar effects were observed for nickel (*5*).

Figure 2 shows the other hydrocarbons produced corresponding to the curve labeled O_2 of Fig. 1. The numbers by the curves are the steady-state rates of production divided by that for methane. These selectivities are insensitive to the activity level and are about the same for all of the catalyst conditions of Fig. 1. Water and carbon dioxide are also produced, but these production rates are less reproducible. The catalyst has a fraction exposed of only about 5%, and it has been shown that the entire mass of iron is carburized (*1*). Thus small changes in carbon concentration in the bulk may produce CO_2 and H_2O at rates at least as high as the catalytic reaction. Figure 3 shows the history of a freshly reduced catalyst after exposure to CO/H_2 at 250°C, H_2 at 250°C, and finally H_2 programmed to 500°C. The first peak represents the removal of a surface carbon intermediate as methane, and the second large peak comes from the decarburization of the bulk of the catalyst. This result has already been discussed (*1*). When carburization is mentioned in what follows, it refers to the formation of bulk Fe_2C; Fe_3C is not favored at 250°C (*1b*).

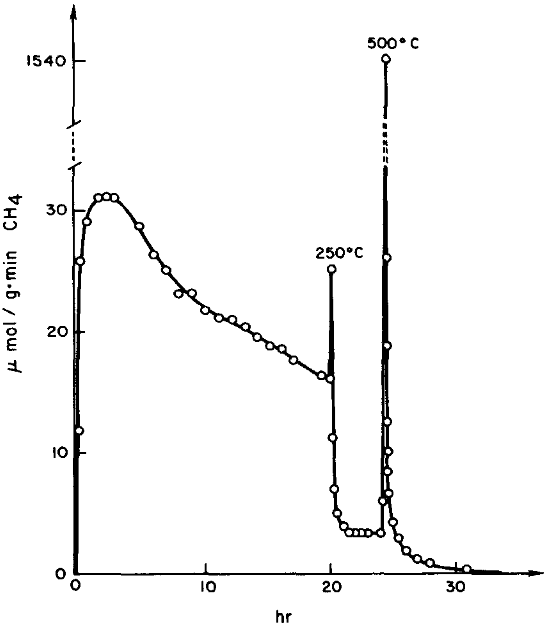

FIG. 3. Hydrogenation of surface carbon over catalyst initially reduced 15 hr at 500°C and then cooled to 250°C. At time zero flow is switched to $H_2/CO = 9$, 250°C. At 20 hr, feed is switched to pure H_2, 250°C; at 24 hr temperature is raised to 500°C.

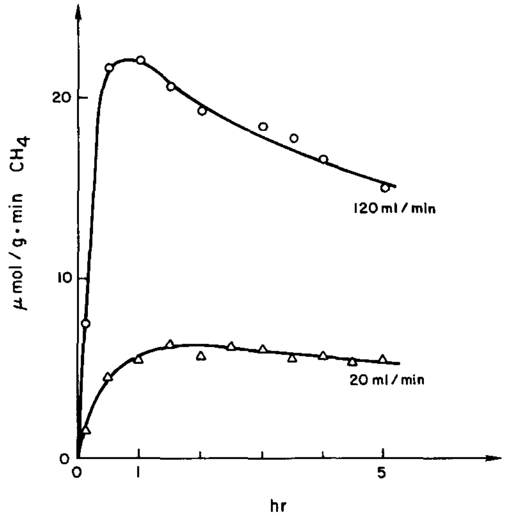

FIG. 4. Effect of flow rate on methane formation at 250°C, feed 9/1 H_2/CO.

Another aspect of the reacting system can be seen in Fig. 4. Experiments were started with a feed rate of 120 ml/min, but the conversion (0.003 to CH_4) was not sufficient to obtain reliable analyses for H_2O and CO_2 by chromatography (thermal conductivity detector). The hydrocarbons, however, were analyzed correctly (flame ionization detector). When the conversion was increased (0.006 to CH_4) by reducing the feed rate to 20 ml/min, a much lower formation rate of methane was observed. This reduction in activity can only be explained by inhibition of the rates by products of the reaction; the reactant concentrations are of course almost unchanged. In other words, even at these low conversions the reactor is not truly differential.

We are thus led to investigate the effect of the products of reaction on the reaction rates, and these experiments will be described later. In order not to be mislead by secular changes in the catalyst, a steady-state condition is first established with 10% $CO + H_2$ feed. The feed is then changed to one containing H_2O, CO_2, etc., as desired, and finally it is changed back to 10% $CO + H_2$.

The base reaction has been studied at several temperatures (230, 250, 270, and

TABLE 2

Effect of Feed Gas Composition[a]

Formation rate (μmole/g min)	Reactants		
	33% CO + H_2	10% CO + H_2	2% CO + H_2
CH_4	2.1	6.0	10.2
C_2H_6	3.0	3.2	3.4
CH_4/C_2H_6	0.7	1.9	3.0

[a] Rates after 4 hr.

300°C) and an activation energy of 20.4 kcal/mole is observed, similar to the value found at 2.0 PMa (*2*).

The influence of the CO/H_2 ratio was also studied, as shown in Table 2. The results are in accord with the previously proposed model (*1*); as the gas composition becomes richer in H_2, the surface coverage of C goes down, and the surface coverage of H goes up. Since under all conditions the surface is mostly covered by C, the observed rates are plausible. The rates of formation of ethane and higher hydrocarbons are little changed.

Influence of CO_2

To the reaction mixture 10% CO + H_2 was added 5% CO_2. The CH_4 production diminished by about 8%, and when the CO_2 was removed the methane formation rate regained its initial value. This effect is not sufficient to explain Fig. 4.

If the CO in the feed gas is replaced by CO_2, the methanation reaction continues at a lower rate, as shown in Table 3. The formation of higher hydrocarbons, however, is drastically reduced.

TABLE 3

Reaction of CO_2 and H_2

Formation rate (μmole/g min)	Feed		
	Before 10% CO + H_2	10% CO_2 + H_2	After 10% CO + H_2
CH_4	7.0	4.4	7.4
C_2H_6	3.2	0.52	3.5
C_3H_8	1.5	0.065	1.5

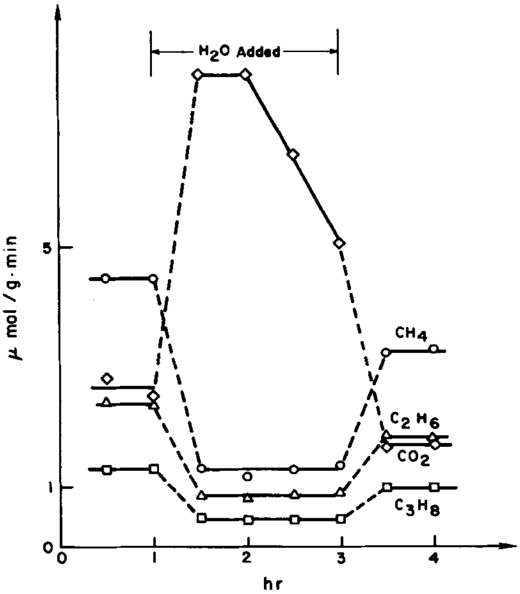

FIG. 5. Effect of water vapor on the reaction at 250°C. Feed H_2/CO = 9 at 40 ml/min.

Influence of Water

A concentration of 0.6% water vapor was added to the 10% CO + H_2 feed mixture at steady-state reaction, and Fig. 5 shows the result. The inhibiting effect of water is clear and it is probable that the lower rates at higher conversion shown in Fig. 4 are explained by the increased water concentration at higher conversion.

It is also interesting to evaluate the capability of the steady-state catalyst surface to catalyze the shift reaction. Figure 6 indicates that when the H_2 in the 10% CO + H_2 mixture is replaced by 0.6% water, all production of hydrocarbons stops, and a large rate of CO_2 formation is observed. These results are further evidence of the power of the iron catalyst to adsorb dissociatively H_2O as well as CO.

Influence of Ethane

The addition of 10% C_2H_6 to the reactants does not change the rates of reaction. However, iron has some activity for hydrogenlysis (*6*). If the 10% CO + H_2 mixture is

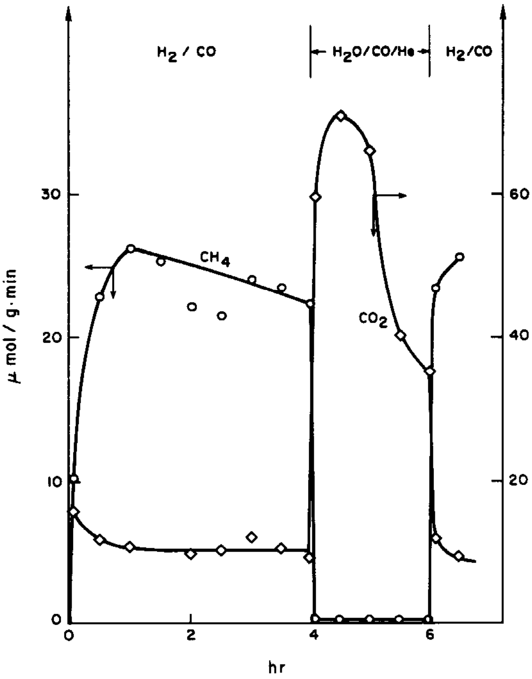

FIG. 6. Reaction of water and carbon monoxide at 250°C.

changed to 10% C_2H_6 + H_2, methane is formed at 0.65 μmole/g min (see Fig. 7), less than 10% of a typical methanation rate.

Influence of Olefins

When 10% C_2H_4 + H_2 is fed to the reactor just after the reduction of the catalyst at 500°C, the curves of Fig. 7 are obtained. There is immediate production of methane, propane, *n*-butane, and *n*-pentane. Ethane is confounded with the large ethylene peak in the analysis by chromatography. The rates do not increase from zero as in Fig. 2. A switch to hydrogen (not shown on Fig. 7) produces no methane peak at 250°C, and programming the temperature to 500°C results in the production of only 4 μmole of CH_4/g of iron. Thus the C_2H_4/H_2 mixture does not lead to bulk carbide at 250°C and does not lead to active surface carbon removable by H_2 at 250°C. The reaction rates after 4 hr with ethylene are about twice those with CO, and the initial rates are an order of magnitude higher. Figure 7 shows also the switch from C_2H_4/H_2 to CO/H_2 and then to C_2H_6/H_2.

Figure 8 shows the usual curves for CO/H_2 over a reduced catalyst, followed by a switch to C_2H_4/H_2 over the now-carburized catalyst. These results are consistent with the idea that the rate-determining step with CO is the hydrogenation of surface carbon. Subsequent chain growth occurs through CH_2 groups (or CH), and if these groups are formed directly from ethylene, the production rates of the products are higher; the rate-limiting step coming from CO is no longer relevant. After exposure of the catalyst to CO/H_2, much of the surface is covered with inactive carbon, so the rate of CH_4 production with C_2H_4/H_2 of Fig. 8 is lower than that of Fig. 7.

Figure 9 shows the reaction of 10% C_3H_6 + H_2 over the reduced catalyst. The results are qualitatively the same as with ethylene. Butene-2/H_2 reacts as shown in Fig. 10, and butene-1/H_2 (always 90% H_2) gives

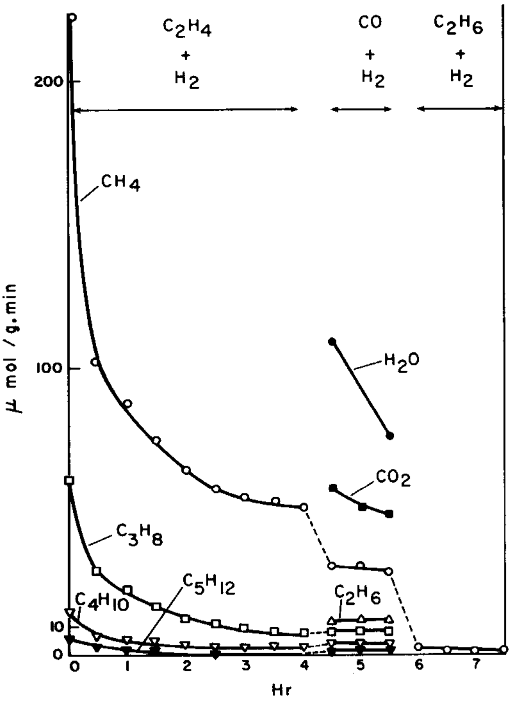

FIG. 7. Reaction of ethylene and hydrogen (1/10) on a reduced catalyst at 250°C, followed by switch to CO/H_2 (1/10) and then C_2H_6/H_2 (1/10).

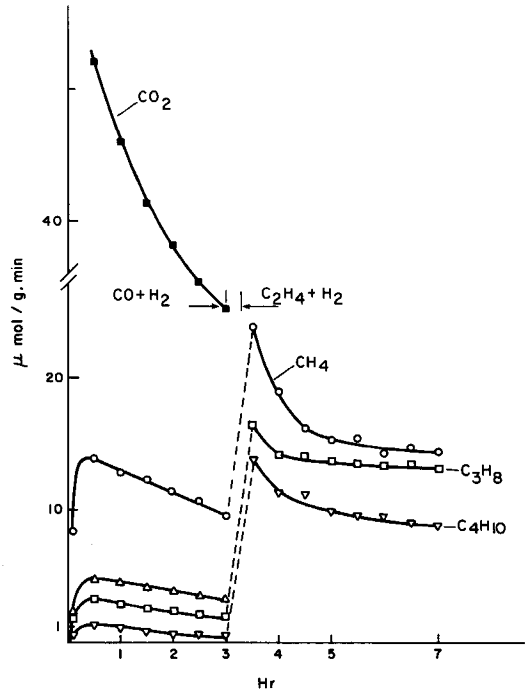

FIG. 8. Reaction of ethylene and hydrogen on catalyst at 250°C after exposure to CO/H_2.

rates that are all a bit lower than for butene-2, as shown. All of these results emphasize that on the iron surface the CH_2 or CH fragments come rapidly to a steady state; the rates of production of the alkane products (no olefins were observed) are not appreciably influenced by the source of the CH_2 groups on the surface. However, there are some differences, as shown in Table 4, which gives the ratios of the production rates after 4 hr. Starting from a given olefin, the products are mostly of shorter chain length and close to the chain length of the reactant. In any event, we are justified in supposing that, starting from CO/H_2, all of the steps after CH_2 or CH formation are rapid, and little of the surface is covered by chain fragments at 250°C and 100 kPa.

TABLE 4

Relative Production Rates[a]

Feed mixture	C_2/C_1	C_3/C_1	C_4/C_1	C_5/C_1
10% $CO + H_2$	0.6	0.29	0.10	0.02
10% $C_2H_4 + H_2$		0.15	0.06	0.001
10% $C_3H_6 + H_2$	0.49		0.087	0.002
10% butene-1 + H_2	0.19	0.76		0.08
10% butene-2 + H_2	0.20	0.92		0.09

[a] 4 hr on stream.

Influence of Oxygen

A few experiments were made which confirm that iron can catalyze the oxidation of CO (10% CO + O_2). However, if the iron is first exposed to O_2 (250°C), we find that CO does not react with the surface at 250°C; no CO_2 is formed. 10% H_2 + O_2 gives water at 15 μmole/g min, and of course hydrogen can at least partially reduce oxidized iron, giving water at 250°C.

Since an oxygen pretreatment has been found to be beneficial, a little oxygen was added to the CO/H_2 feed mixture. With 3% O_2, only CO_2 and H_2O were produced. We were not equipped to use only traces of oxygen.

ESCA Results

In order to study the catalyst surface by electron spectroscopy, it was of course necessary to evacuate the sample chamber.

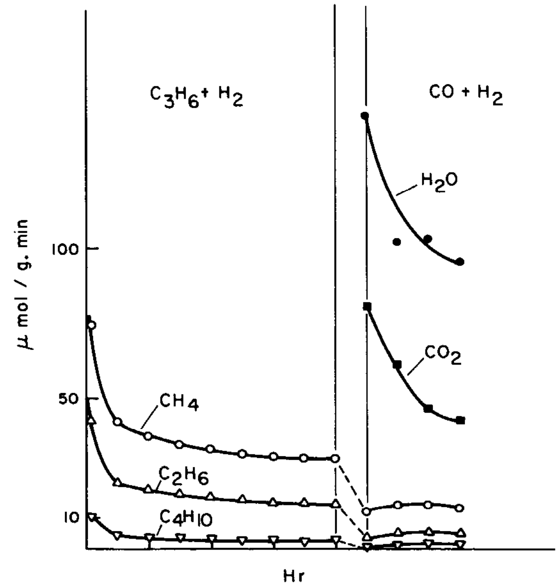

FIG. 9. Reaction of propylene and hydrogen (1/9) at 250°C, followed by CO/H_2.

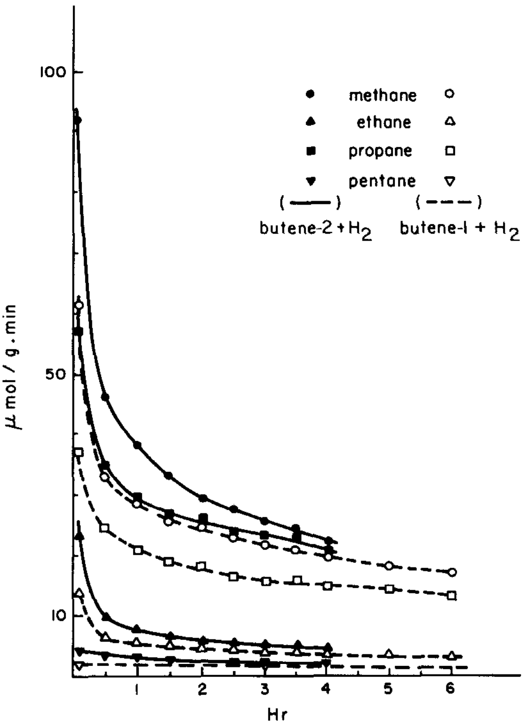

FIG. 10. Reaction of butene-1 and butene-2 with hydrogen at 250°C.

Thus only nonvolatile intermediates could be detected, but the results are of some interest because of the importance of surface C and O. Measurements were made in a V.G. III instrument, which was equipped with a vacuum-tight treatment cell, and the usual computer accessories to smooth curves, subtract background, etc.

Table 5 and Figs. 11 and 12 show the results. Atomic ratios are shown, which should apply to the first few atomic layers, and these were calculated from the appropriate cross sections (*13*). It is clear that the compositions are only qualitative. For sample 5 certain data were not obtained, leading to some blanks in Table 5.

The iron in the reduced catalyst is in the Fe^0 state; the bond energy of iron is close to that observed for metallic iron (e_b = 707.3) (*7*, *8*). As is well known (*9*) the surface of this promoted catalyst is largely covered by K, Al, and O; the ESCA analysis shows more O than accounted for by the stoichiometry of K_2O and Al_2O_3. This state is shown in Figs. 11a and 12a and is sample 1 of Table 5.

The results after the catalyst was used for the CO/H_2 reaction at 250°C under the usual conditions are given by Figs. 11b and 12b; this is sample 4 of Table 5. There is evidence of Fe_2O_3 (e_b $Fe^{2}_{p_{3/2}}$ = 710.8 (*7*, *10*). The surface is also covered by carbon that has a bonding energy close to that of graphite rather than that for a carbide (*11*, *12*). The concentration found by ESCA seems high, but the oxide surfaces are probably covered with carbon also.

After exposure to CO_2/H_2, the peak for Fe^{3+} replaces Fe^0 in Fig. 11c, sample 5 of Table 5; the surface must be more oxidized than in the presence of CO/H_2 after equal exposure times. However, no additional O is observed.

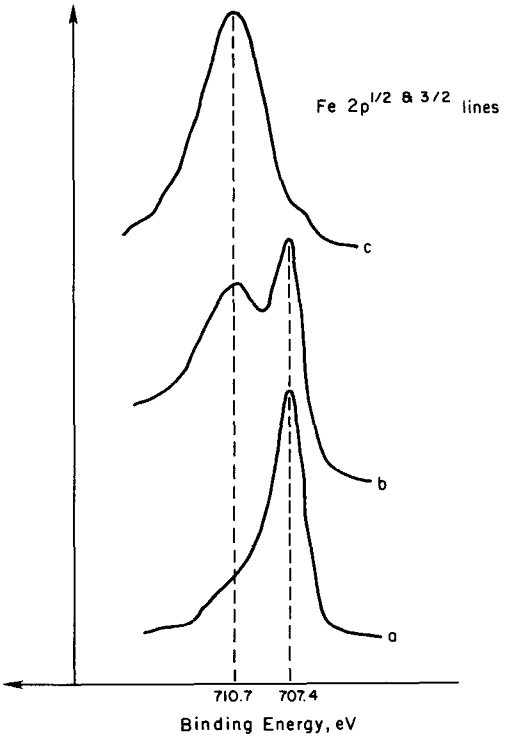

FIG. 11. Electron energy spectrum for iron. (a) Sample 1; reduced at 500°C in H_2 for 24 hr. (b) Sample 4; sample 1 subsequently exposed to H_2/CO (9/1) for 1 hr at 250°C. (c) Sample 5; sample 1 subsequently exposed to H_2/CO_2 (9/1) for 1 hr at 250°C.

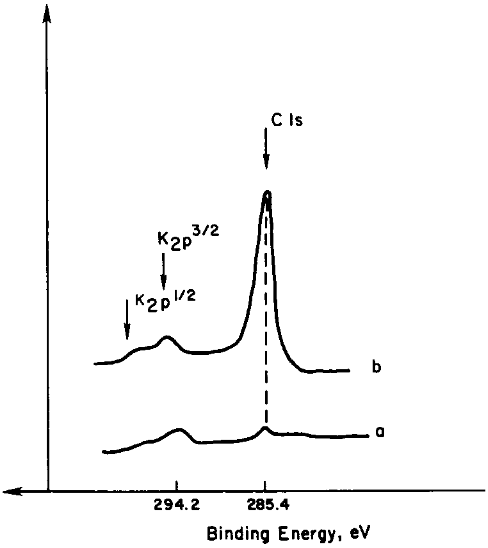

FIG. 12. Electron energy spectrum for carbon and for potassium. (a) Sample 1; reduced at 500°C in H_2 for 24 hr. (b) Sample 4; sample 1 subsequently exposed to H_2/CO (9/1) for 1 hr at 250°C.

The experiments leading to samples 3 and 4 described in Table 5 show that the catalyst surface after reaction in CO/H_2 for 1 hr at 250°C as measured by ESCA is not appreciably changed by exposure to air at 25°C.

SUMMARY

The new results of the present study support most aspects of the sequence of steps proposed by Matsumoto and Bennett (*1*). CO is adsorbed as C + O, and the freshly formed surface carbon is the most abundant surface intermediate; its hydrogenation by adsorbed hydrogen present as H is the rate-determining process. Carbon dioxide added to CO/H_2 is not strongly enough adsorbed to affect the rate appreciably. However, in the absence of CO, CO_2/H_2 makes methane at a lower rate; the surface is more oxidized (note the ESCA

TABLE 5

ESCA Results

Treatment	Sample number	Elements[a]									
		Fe	$2p_{3/2}$	O	1s	K	$2p_{3/2}$	Al	$2s_{1/2}$	C	1s
Reduction for 24 hr at 500°C in flowing H_2, 760 Torr, in the spectrometer cell	1	1[c]	707.3	3.5	531.8	0.68	294.2	1.22	74.6	1.17	285.3
		see Fig. 11a				see Fig. 12a				see Fig. 12a	
	2	1	707.4	3.2	531.6	0.53	294.3	0.70	74.6	1.05	285.2
Sample 1 heated in spectrometer cell at 250°C in CO/H_2 for 1 hr[b]	3	1	707.6 708–709	3.9	531.6	0.70	294.3	1.3	75.7	11.5	285.5
Reduced at 500°C in reactor, then used for H_2/CO at 250°C for 1 hr, transferred to spectrometer in air	4	1	707.5 710.7	3.13	531.8	0.56	294.4	0.82	74.7	9.1	285.4
		see Fig. 11b				see Fig. 12b				see Fig. 12b	
Same treatment as sample 4 but CO is replaced by CO_2	5	1	710.7	3.09	530.3 532.0						285.4
		see Fig. 11c									

[a] The first figure gives the concentration in arbitrary units; iron is always taken as unity. The effective cross sections are from Scofield (*13*). The second figure is the bonding energy in electron volts.

[b] If the reaction is continued in the spectrometer cell for 18 hr, this spectrum becomes identical to that for sample 5.

[c] *Precision:* concentration, ± 10%; binding energy, ± 0.2 eV.

results) and the active C is present in lower concentration than in the presence of CO.

However, water can compete with CO for the surface, and it oxidizes the surface while reducing the active C coverage by forming CO_2. When water is added to H_2/CO, the high reaction rate to CO_2 rather than CH_4 shows the strong affinity of the surface of the iron catalyst for oxygen (Fig. 5); the carbon intermediate is replaced at least in part by oxygen.

We recall that the rate of hydrocarbon production over a freshly reduced catalyst rises from an initial value of zero. The carbon formed from CO reacts with the bulk iron of the catalyst, and the surface carbon necessary for hydrocarbon production gradually increases in coverage as the bulk of the iron is carburized to Fe_2C at 250°C. However, when C_2H_4/H_2 is passed over the reduced catalyst, no active C intermediate seems to be necessary. The rate starts at a maximum value, and the bulk of the iron is not carburized. Thus the observed formation of CH_4 and C_3H_8 shown in Fig. 7 arises through a CH_n fragment. No oxygen is present. Iron thus seems to behave differently from cobalt, for which CO is said to be necessary for chain growth (*14, 15*).

When a CO/H_2 feed is changed to C_2H_4/H_2 (Fig. 8), the rate of hydrocarbon production is higher from ethylene than from CO. Methane is an important product from C_2H_4/H_2. This result is not inconsistent with the lack of $^{14}CH_4$ formed when $^{14}C_2H_4$ is added in a small quantity to CO/H_2 (*16*). With CO present the C_1H_n groups must originate principally from CO, so that the added ^{14}C will be concentrated principally in C_xH_y groups of $x \geqq 2$.

It is clear that the reaction of ethylene takes place on the iron surface, since the rate decreases as the inert graphitic carbon builds up (Figs. 7 and 8). It was shown previously (*1*) that the reaction from CO also occurs on the iron part of the surface; after steady state under CO/H_2, a brief exposure to H_2 alone and then a switch back to CO/H_2 lead to a temporary increase in the rate. If the exposure to hydrogen is long enough to decarburize some of the bulk, the subsequent CO/H_2 reaction rate is lowered as recarburization lowers the concentration of the active surface carbon.

In conclusion, the results of the experiments presented here support certain aspects of the mechanism proposed by Matsumoto and Bennett (*1*). A freshly reduced catalyst is carburized by the H_2/CO mixture in about an hour (recall that carburization in CO alone is much slower (*1*)). During this period the hydrocarbon formation rate gradually increases as the surface carbon concentration rises, as influenced by the bulk carbon (carbide) concentration. A switch to pure H_2 gives a methane peak, meaning that hydrogen reacts as H on the surface and that the surface coverage by C is high. The rate-determining process is the formation of CH_n from the surface C; subsequent chain growth is rapid and occurs through these groups, and the product distribution is determined by the rate of propagation and termination (desorption) of chains arising from CH_n. The presence of H_2O and to some extent CO_2 in the gas phase increases surface O at the expense of C and/or H, inhibiting the reaction. However, active surface carbon is gradually coverted to inert (at 250°C) graphite, and activity slowly declines as the part of the iron covered with labile C decreases. For a much regenerated catalyst, oxygen followed by hydrogen cleans off a higher fraction of inert graphite than H_2 alone.

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