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Hydrogenation of CO and CO_2 over Iron Foils
Correlations of Rate, Product Distribution, and Surface Composition

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The hydrogenation of CO and CO_2 over polycrystalline iron foils has been investigated under highly controlled conditions (6 atm, 3:1 H_2:CO, 300°C). The surface composition of the foil before and after high-pressure reaction was determined by Auger electron spectroscopy. The H_2/CO reaction produced C_1–C_5 hydrocarbons in detectable quantities. In this reaction the initially clean iron surface was rapidly covered by a monolayer of carbonaceous material that appeared to be the active surface. The specific methanation rate on this surface was 1.9 molecules $site^{-1}$ sec^{-1} with an activation energy of 27 ± 2 kcal $mole^{-1}$. The H_2/CO_2 reaction produced almost exclusively methane (97 mole%) and at a higher rate (10.9 molecules $site^{-1}$ sec^{-1}) than did the H_2/CO reaction. In both the H_2/CO and the H_2/CO_2 reactions the active surfaces were eventually poisoned by excessive deposition of carbon. The carbon-poisoned surfaces produced only methane but at much slower rates than did the active surfaces. Iron, without promoters, appears to be predominantly a methanation catalyst that poisons rapidly by the deposition of multilayers of carbon.

I. INTRODUCTION

In the synthesis of hydrocarbons from CO, CO_2, and H_2, iron plays an important role as a catalyst (*1–4*). In the SASOL process, potassium-promoted iron is utilized commercially to catalyze the Fischer–Tropsch reaction (*5*). In spite of the long history of application of this material many fundamental questions that may provide the key to its catalytic activity are unanswered. These questions concern the surface composition of the active catalyst and the atomic surface structure that provides desired activity, reactivity, and long-term stability. We should also know the oxidation states of atoms on the surface and should attempt to identify the role of the promoters that effect activity and product distribution.

The surface reactions of CO and H_2 may be viewed as composed of two parts: (i) the hydrogenation of dissociated or molecular carbon monoxide and (ii) the subsequent insertion of CO that results in the production of hydrocarbon chains. Only the first part of this process takes place during methanation or during the production methanol. There are several transition metals that carry out this reaction but do not exhibit insertion activity. Others, like iron, can catalyze both reactions to yield a broad distribution of products with a wide range of molecular weights.

To understand the mechanism of this important catalytic reaction, we have developed an apparatus that permits determination of the surface composition of the working catalyst by Auger electron

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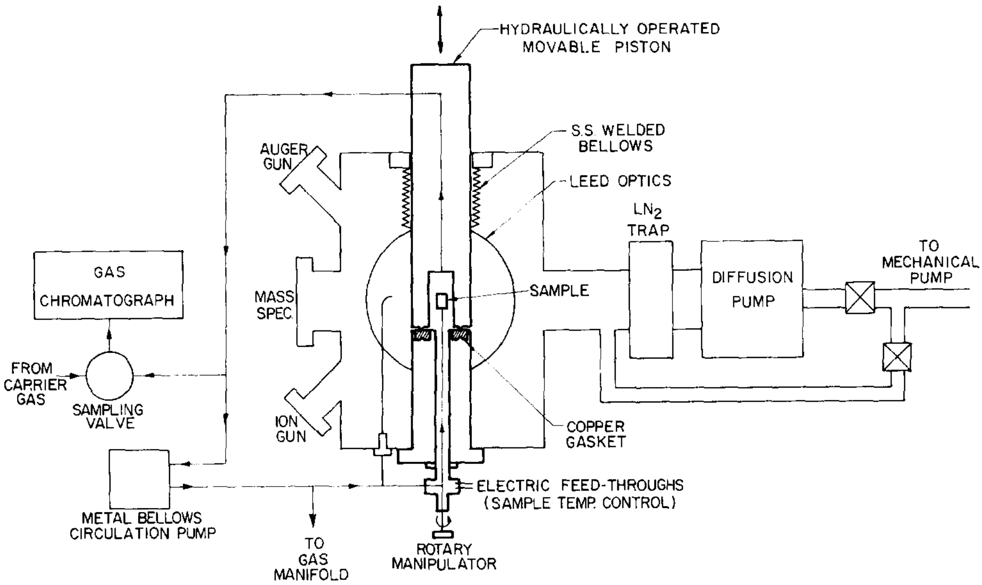

FIG. 1. Schematic of UHV surface analysis system equipped with sample isolation cell for high-pressure (1–20 atm) catalytic studies.

spectroscopy *in situ*, before and after carrying out the Fischer–Tropsch and methanation reactions at high pressures (1–20 atm). The apparatus consists of an isolation cell in an ultrahigh vacuum system, that can be pressurized or evacuated. The catalyst is of small surface area (~1 cm²) but the sensitivity of the gas chromatograph detector is sufficient to determine rates and product distribution under industrially suitable conditions. This apparatus (shown in Fig. 1) has already been employed to study the methanation reaction on rhodium polycrystalline foils (*6*).

It was found that the initially clean iron surface was rapidly covered by a monolayer of carbonaceous material which appeared to be an active surface for the Fischer–Tropsch reaction, yielding C_1 to C_5 hydrocarbons. This surface proved to be unstable under our reaction conditions and, after several hours, was covered by a multilayer carbon deposit. This deposit produces only methane and at a slower rate than the carbon monolayer.

The turnover numbers and activation energies for methanation have been determined for both H_2/CO and H_2/CO_2 reactions. The H_2/CO_2 reactant mixture produces mostly methane but at a higher rate than does H_2/CO and the composition of the active surface appears to be different (oxide) than the surface composition during the H_2/CO reaction.

Previous studies (*2–4*) of the iron-catalyzed Fischer–Tropsch reaction have shown that the working iron catalysts are composed of carbides, oxides, as well as α-iron. The exact composition depends strongly on reaction time, conversion rates, location in reactor bed, and various catalyst pretreatments. In this paper we report studies of the H_2/CO and H_2/CO_2 reactions on initially clean polycrystalline iron foils that were carried out at 6 atm, in the temperature range of 250–400°C using a 3:1 reactant ratio. Due to the low conversions ($\ll 1\%$) and the short reaction times (<5.0 hr) of the present study, the iron foil did not undergo bulk phase transformations as observed in the previous studies. Thus, we investigate only that part of the Fischer–Tropsch reaction that occurs on iron.

II. EXPERIMENTAL

The apparatus used in the present study has been described in detail elsewhere (*6*). It consists basically of a diffusion-pumped ultrahigh-vacuum (UHV) bell jar (1×10^{-9} Torr) equipped with a retarding grid Auger electron spectroscopy (AES) system, a quadrupole gas analyzer, and a 2-keV ion sputter gun. The unique feature of the apparatus is an internal isolation cell which operates as a micro-batch reactor (100 cm^3 internal volume) in the 1- to 20-atm pressure range while maintaining an UHV in the bell jar around the isolation chamber. An external gas recirculation loop is attached to the cell through which the reactant gas mixture is admitted. The loop also contains a high-pressure bellows pump for gas circulation and a sampling valve which diverts a 0.1-ml sample to a gas chromatograph.

The iron specimen was a 1-cm^2 polycrystalline foil (99.99% pure) which was pretreated in a hydrogen furnace (1 atm of H_2) at 800°C for 4 days prior to mounting in vacuum system. This hydrogen treatment was necessary to remove bulk carbon and sulfur which otherwise diffuse to the surface during the UHV cleaning procedures. The iron foil was mounted such that it could be resistively heated and the temperature was monitored with a chromel–alumel thermocouple spot welded to the foil edge.

The hydrogen and carbon monoxide used to prepare the synthesis gas mixtures were of high-purity research grade. The mixtures were prepared in the circulation loop and then expanded into the isolation cell. Analysis of the synthesis gas by gas chromatography and mass spectrometry indicated that H_2O in very small amounts was the only reactant impurity.

A clean iron surface was prepared in ultrahigh vacuum by ion sputtering the foil (Ar^+, 2 keV, 100 μA) at 800°C for 15 min, then annealing at 700°C for 2 min. This procedure generally produces a surface which is free from sulfur and oxygen. The only detectable surface impurity after this treatment was carbon (10–15% of a monolayer). Once a clean surface was prepared the isolation cell was closed and the synthesis gas (3:1, H_2:CO) was expanded into the cell at a total pressure of 6 atm. The sample temperature was then raised to 300°C and gas chromatographic sampling of the reaction products was commenced. At any point in the reaction the sample could be cooled, the cell and circulation lines could be evacuated, and the cell could be opened to UHV to allow AES analysis of the surface. The pump-down procedure from 6 atm to 5×10^{-8} Torr took approximately 1 min.

III. RESULTS

A. H_2/CO Reaction on the Initially Clean Iron Surface

The H_2/CO reaction was investigated at a total reactant pressure of 6 atm and a 3:1, H_2/CO ratio. Prior to the reaction, the iron surface was cleaned by ion sputtering and the surface purity was verified by AES. The foil was then isolated in the high-pressure cell, the reactant gas mixture was admitted, and the foil was heated to 300°C. The ac-

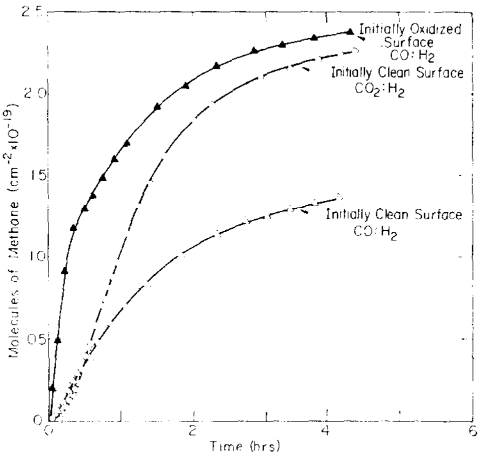

FIG. 2. Accumulation of methane in the isolation cell as a function of time. All reactions are carried out at 6 atm, 3:1 H_2:CO, 300°C.

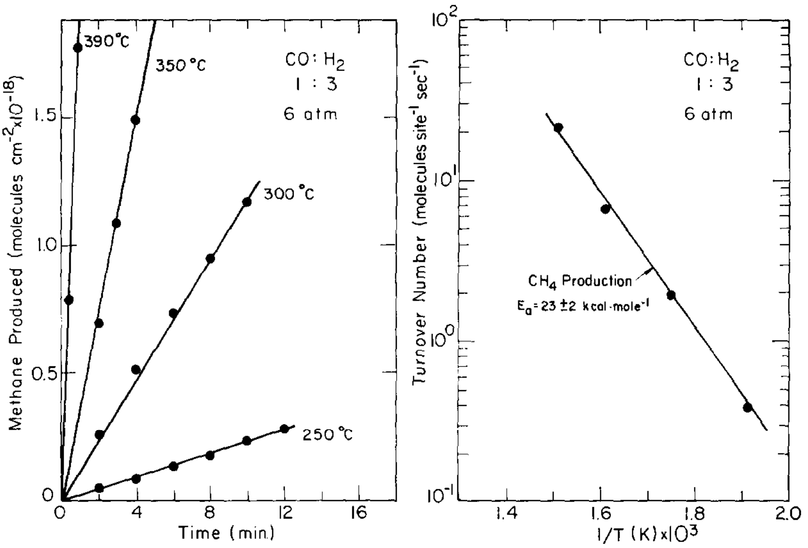

FIG. 3. The influence of temperature on the methanation rate and the corresponding Arrhenius plot.

cumulation of hydrocarbons in the batch reactor was then measured as a function of time. Under these reaction conditions the dominant product was methane (85 mole%) but hydrocarbons up to C_5 were produced in detectable quantities. The chain products were predominantly primary olefins: ethylene, propylene, 1-butene, and 1-pentene. The corresponding saturated straight-chain hydrocarbons were also detected but no branched products were observed. The olefin : paraffin ratio was approximately 4 : 1. A very small amount of methanol (less than 0.1 mole%) was also detected.

The activity of the foil decreased with time as can be seen from the accumulated methane versus time curve in Fig. 2. Chain growth stops after approximately 2 hr but methanation continues at a slow rate.

The specific reaction rate or turnover number for methanation was determined in the following manner. Since a short induction period (approximately 5 min) of low reactivity was generally observed, the first 10 min of methane accumulation were ignored. The accumulation of methane was assumed to be approximately a linear function of time over the next 15-min interval (10–25 min). The slope of the accumulated methane versus time curve, which is the reaction rate, was then evaluated over this time period by linear regression. The slope of the curve was then divided by the concentration of iron atoms in the metal surface (1×10^{15} cm^{-2}) to determine the specific reaction rate. The turnover number for the foil at 300°C thus determined was 1.9. This procedure probably results in a conservative estimate of the turnover number since it assumes that all of the iron atoms in the surface are active. It will be seen from later discussion that the iron surface undergoes chemical changes during the reaction which result in a much lower concentration of iron sites present on the surface.

Figure 3 displays the influence of foil temperature on the initial methanation rate over the temperature range 250–390°C. The methane reaction rate increases rapidly with temperature from a turnover number of 0.33 at 250°C to 32.8 at 390°C. However, at the higher temperature the formation of chain products is severely curtailed, and above 400°C only methane is produced. An Arrhenius plot of the temperature dependence of the reaction rate is shown in Fig. 3. This plot yields an activation energy of 23 ± 2 kcal $mole^{-1}$ which agrees favorably with the 21.3 kcal $mole^{-1}$ activation energy determined for alumina-supported iron by Vannice (7).

A series of experiments was performed in which the reaction was interrupted at various times to permit surface analysis by AES. The results of these experiments are summarized in Fig. 4. It is seen that the clean iron surface is unstable under the reaction conditions and is rapidly covered with carbon. Carbon deposition continues during the reaction with the eventual formation of a multilayer carbon deposit. This carbonaceous layer is sufficiently thick to obscure completely the iron Auger signal (703 eV) which has an escape depth of at least 20 Å. The formation of this multilayer carbon mass occurs within the same time regime in which chain growth is terminated and the methanation rate at 300°C falls to a turnover number of 0.38 from its initial value of 1.9. Repeated experiments verified that the presence of iron in the surface is a necessary condition for chain growth and for a high methanation rate. It should be noted that under no circumstance was any oxygen-containing species observed on the surface while using reactant mixtures in the range of 1:1 to 11:1, H_2:CO.

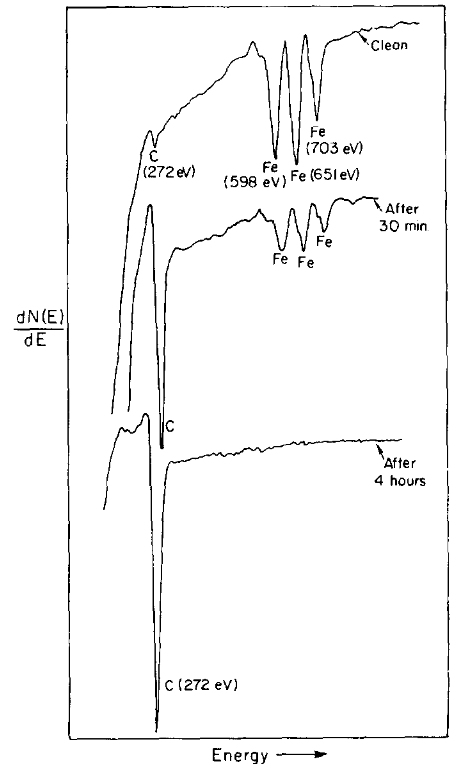

FIG. 4. Auger spectra of the iron foil before, after 30 min, and after 4 hr of reaction (6 atm, 3:1 H_2:CO, 300°C).

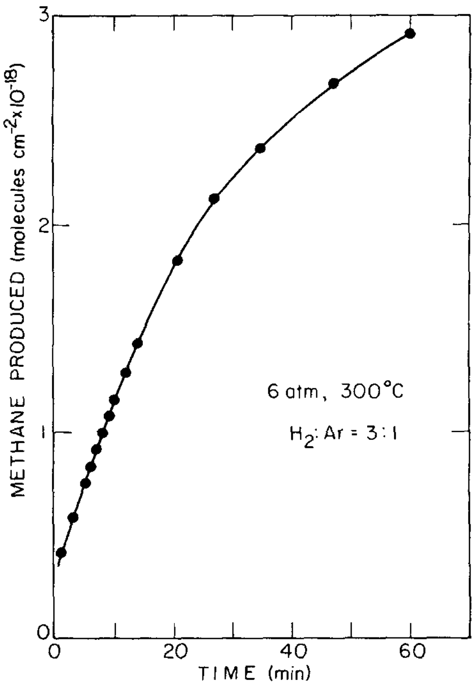

FIG. 5. Methane produced by direct hydrogenation of the carbon multilayer deposit.

To investigate further the methanation reaction which occurs when only carbon is present on the surface, the activation energy for the reaction was evaluated after 4 hr of reaction. The results of these measurements indicated that the activation energy was 12 ± 2 kcal $mole^{-1}$. This lower activation energy that nevertheless accompanies a markedly lower rate of methanation on the carbonaceous layer suggests that the mechanism of methanation on the carbon layer

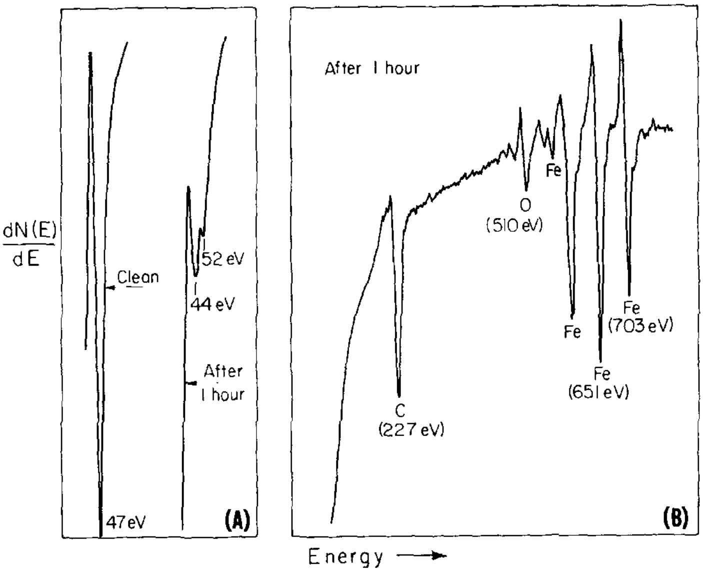

FIG. 6. Auger spectra of iron foil after 1 hr at 6 atm, 3:1 H_2:CO_2, 300°C. (A) Low-energy iron Auger peak showing characteristic oxide doublet. (B) Standard Auger scan showing carbon and oxygen present on the surface.

is different from that initially observed at short reaction times. Additional information concerning the methanation mechanism on this thick carbon deposit was obtained from the following experiment. A usual reaction (6 atm, 3:1 H_2:CO, 300°C) was run for 4 hr until the carbon deposit was well established. The reaction was then terminated and the presence of the thick carbon layer was verified by AES. The carbon-covered foil was then sealed in the cell and a 3:1 H_2:Ar mixture was admitted. Upon heating the foil to 300°C methane was produced as shown in Fig. 5. In addition, the initial rate of methanation was identical to that seen just prior to termination of the H_2/CO reaction. AES measurements revealed that surface carbon was removed by the hydrogen treatment. However, carbon remained on the iron surface even after 24 hr of hydrogen treatment, suggesting that the carbon on the iron surface cannot be totally removed by hydrogen at this temperature. It was also found that the removal of the thick carbonaceous deposit by hydrogen treatment reactivated the iron foil, and chain growth was observed when a H_2/CO mixture was reintroduced.

B. *H_2/CO_2 Reaction on the Initially Clean Iron Surface*

The H_2/CO_2 reaction was studied employing conditions identical to those used for the H_2/CO reactions: 6 atm, 3:1 H_2:CO_2, 300°C. The results, however, were dramatically different from those for the H_2/CO reaction. The H_2/CO_2 reaction produces almost exclusively methane (97% by mole). The only other detectable product was ethane with little or no ethylene. In addition to the change in product distribution there is a marked increase in the methanation rate when compared to the rate obtained for the CO/H_2 reaction as shown in Fig. 2. The initial specific rate was 10.9 which is about fivefold greater than the rate for the H_2/CO reaction.

The activity of the foil decreases as a function of time in the H_2/CO_2 reaction and the methanation rate drops to a level comparable to that in the H_2/CO reaction

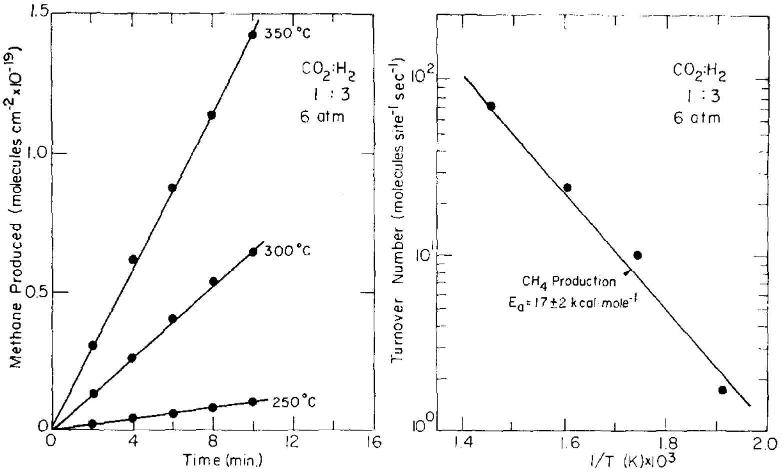

FIG. 7. The influence of temperature on the methanation rate for the H_2/CO_2 reaction. The corresponding Arrhenius plot is also shown.

after approximately 4 hr. It is interesting to note that the deactivation of the iron foil occurs at about the same rate in the CO_2 reaction as in the CO reaction.

AES measurements as a function of reaction time reveal that both carbon and oxygen accumulate on the surface initially during the H_2/CO_2 reaction. A typical Auger spectra taken after a 1-hr reaction period is shown in Fig. 6. The appearance of a split $M_{2,3}M_{4,5}M_{4,5}$ iron Auger line in Fig. 6 is of particular importance. The $M_{2,3}M_{4,5}M_{4,5}$ iron Auger transition involves the iron *d* orbitals and is often sensitive to the chemical environment of the iron atom. A splitting of the type shown in Fig. 6 is characteristic of iron oxide (*8*). This split iron peak and the intense oxygen Auger signal are therefore taken as evidence for the presence of surface oxide.

Auger spectra taken after 2 hr of reaction indicate that carbon deposition occurs on the oxide surface. Eventually a carbonaceous multilayer deposit similar to that encountered in the H_2/CO reaction is built upon the surface. Once again it appears that the loss of catalytic activity can be associated with deposition of excess surface carbon.

The variation of the H_2/CO_2 methanation rate with temperature is shown in Fig. 7. The corresponding Arrhenius plot yields an activation energy of 17 ± 2 kcal mole^{-1}.

C. H_2/CO Reaction on the Preoxidized Surface

Iron Fischer–Tropsch catalysts are known to contain both iron carbides and oxides in addition to α-iron (*1–4*). To investigate the influence of oxide surfaces on the H_2/CO reaction, a series of experiments was performed on preoxidized iron foils. The oxidation was carried out by heating the foil to 300°C in 4 atm of dry oxygen for 20 min. This treatment resulted in a relatively homogeneous surface oxide as judged by AES and uniform discoloration of the foil. Reactions were performed on this oxide under the usual conditions: 6 atm 3:1 H_2:CO, 300°C.

The major product of the iron oxide-catalyzed reaction was again methane (76%), with a slight shift in the product distribution toward the higher molecular weight products as shown in Table 1. The accumulation of methane as a function of time is compared to that of the H_2/CO and H_2/CO_2 reactions starting with the clean

TABLE 1

Product Distribution of H_2/CO and H_2/CO_2 Reactions

Reaction	Foil condition	Product (%)					Methanation rate (molecules $site^{-1}$ sec^{-1})
		C_1	C_2	C_3	C_4	C_5	
H_2/CO 3:1 6 atm, 300°C	Initially clean	85	11	3	1.5	0.5	1.9
H_2/CO_2 3:1 6 atm, 300°C	Initially clean	97	3	—	—	—	10.9
H_2/CO 3:1 6 atm, 300°C	Thick carbonaceous layer	100	—	—	—	—	0.38
H_2/CO 3:1 6 atm, 300°C	Initially oxidized	76	17	4.5	1.75	0.75	18.7

surface in Fig. 2. The most striking feature of the methanation kinetics on the preoxidized foil is a tenfold increase in the initial rate. In forming other products, the preoxidized foil behaves in a manner similar to the clean iron foil. The activity of the surface oxide decreases with time and chain growth ceases after approximately 2 hr. The methanation rate after 2 hr becomes comparable to the rates obtained from the untreated foil after a similar reaction time.

Auger spectra recorded at various stages of the reaction supply important insights into the reaction on the preoxidized foil. These Auger measurements show that the surface oxide is unstable under the reaction conditions and is rapidly reduced. This fact is evident from the spectra displayed in Fig. 5. The oxygen Auger signal is attenuated during the reaction until it is no longer detectable after 25 min. Simultaneously, carbon is deposited on the surface such that the Auger spectra generated after 25 min are identical to those obtained from the initially clean surface after short reaction times. Depth profiling by ion sputtering indicated that the oxide is truly reduced and not simply covered by a multilayer deposit of carbon.

The poisoning of chain growth at long reaction times was again correlated with a buildup of excess surface carbon. The response of the preoxidized surface is, therefore, directly analogous to that of the clean foil except for the enhanced methanation activity over the first 25 min. This enhanced activity is apparently linked to the reduction of the surface oxide. It is possible that the reduction process produces metallic iron clusters which are initially very active. Further reduction produces a carbon-covered surface which displays activity similar to that observed in the clean foil experiments.

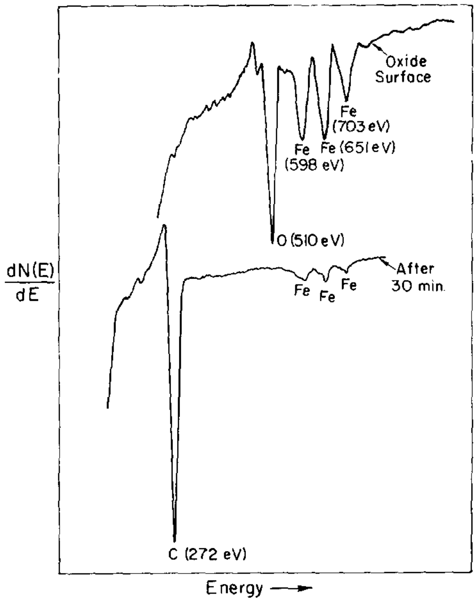

FIG. 8. Auger spectra demonstrating the reduction of the preoxidized surface under high-pressure reaction conditions (6 atm, 3:1 H_2:CO, 300°C).

IV. DISCUSSION

The hydrogenation of CO and CO_2 over iron foils has been investigated under highly controlled conditions (3:1 H_2:CO, 300°C, 6 atm). The product distribution, rates, activation energies for methanation, as well as the surface composition at various stages of the reaction have been measured. These data have revealed several important features of these surface reactions. It appears that the metallic iron surface is not stable under our reaction conditions. In the H_2/CO and H_2/CO_2 reactions the iron surface is covered with a carbonaceous monolayer or an oxide–carbon layer, respectively. These surfaces which display considerable catalytic activity are also unstable under the present reaction conditions and are eventually poisoned by the deposition of multilayers of carbon.

The CO/H_2 methanation reaction proceeds through at least two mechanisms. One mechanism predominates at short reaction times and occurs concurrent with chain growth. This reaction is characterized by high activity (turnover number 1.9) and an activation energy of 23 ± 2 kcal $mole^{-1}$.

Auger spectra show that this reaction occurs on a carbonaceous deposit of approximately monolayer coverage. The second mechanism which proceeds at a slower rate (turnover number 0.38) and lower activation energy (12 kcal $mole^{-1}$) dominates after 2 hr of reaction. This second mechanism is apparently the direct hydrogenation of the multilayer carbon deposit. The evidence for the hydrogenation mechanism is fairly conclusive. Auger spectra reveal that only carbon is present on the surface at this stage of the reaction and that surface carbon can be removed as methane by a H_2/Ar mixture, at the same rate as in the H_2/CO mixture after 4 hr of reaction. An important observation concerning the hydrogenation of this carbon deposit is that no chain products were observed (100 mole% CH_4), i.e., there is no CO insertion activity. This fact suggests that the direct hydrogenation of surface carbon does not contribute to the formation of chain products in the H_2/CO reaction.

CO is known to dissociate on iron as indicated by chemisorption studies using single crystal surfaces (*9*). Thus, we are justified to write the reaction

$$CO + Fe_{(s)} \rightarrow Fe_{(s)}\text{-}C + Fe_{(s)}\text{-}O, \quad (1)$$

which must take place initially on the clean iron foil. This reaction, of course, does not exclude the simultaneous presence of molecular CO on the iron surface as evidenced by chemisorption studies. Since no surface oxygen is detected in the H_2/CO reaction oxygen must be removed by one or both of the following reactions:

$$Fe_{(s)}\text{-}O + CO \rightarrow CO_2 + Fe_{(s)}, \quad (2)$$

$$Fe_{(s)}\text{-}O + H_2 \rightarrow H_2O + Fe_{(s)}. \quad (3)$$

Rapid methanation and chain growth occur when both $Fe_{(s)}$ and $Fe_{(s)}$–C sites are present on the surface. If only the $Fe_{(s)}$ site participates in the insertion of CO and the subsequent hydrogenation, it must be an exceedingly active site since the surface is covered with carbon in near monolayer quantity. If the $Fe_{(s)}$–C site is active for insertion and hydrogenation this activity competes with the catalyzed reduction of CO on these sites which eventually positions the reaction by the formation of a multilayer carbon deposit. The poisoning reaction may be written as

$$C_{(s)}+CO+H_2 \rightarrow C_{(s)}-C_{(s)}+H_2O \quad (4)$$

or

$$C_{(s)}+2CO \rightarrow C_{(s)}-C_{(s)}+CO_2 \quad (5)$$

In these circumstances increased partial pressures of CO_2 or H_2O in the reactant stream should slow down or inhibit the poisoning reaction.

The H_2/CO_2 reaction results initially in the formation of a surface oxide on the catalyst. This oxide is unstable with respect to the formation on an active carbon monolayer which is unstable, and finally a multilayer carbon deposit forms. It should be noted that within our experimental sensitivity no change in the product distribution can be observed as the surface composition changes from an oxide to an active carbon monolayer. The oxidation of the iron surface is not surprising since CO_2 is expected to be a mild oxidant and reactions of the type,

$$3Fe + 4CO_2 \rightarrow Fe_3O_4 + 2CO, \quad (6)$$

are thermodynamically feasible at 300°C.

The H_2/CO_2 reaction was very selective toward methane (97% by mole) with the only other detectable product being ethane. This product distribution is what one would expect from a hydrogen-rich H_2/CO reaction. A high hydrogen partial pressure in the H_2/CO reaction shifts the product distribution toward methane and results in saturated chain products. The similarity between the H_2/CO_2 and a hydrogen-rich H_2/CO reaction suggests the following mechanism for the H_2/CO_2 reaction. First the water-gas shift reaction is catalyzed by the surface oxide:

$$CO_2 + H_2 \rightleftarrows H_2O + CO. \quad (7)$$

The carbon monoxide is then hydrogenated to methane in a very hydrogen-rich environment:

$$3H_2 + CO \rightarrow CH_4 + H_2O. \quad (8)$$

Vannice (7) found that the rate of methanation from H_2/CO mixtures varies directly with the hydrogen partial pressure, whereas it has an inverse relationship to the CO partial pressure. The rapid initial rate of methanation observed in the present H_2/CO_2 reaction is, therefore, consistent with the water/gas shift mechanism which proposes a large hydrogen to carbon monoxide ratio.

Experiments that utilized preoxidized iron surfaces as a catalyst for H_2/CO reaction have demonstrated that, under the present reaction conditions, the oxide surface is unstable and is rapidly reduced. During the early stage in the reaction, while the oxide is being reduced, high methanation and Fischer–Tropsch activities were observed. This enhancement of the surface reaction rates may be due to the formation of highly active iron atoms or clusters on the surface during the reduction process. If this explanation is correct then it suggests that the iron sites are the active centers for the Fischer–Tropsch reaction. The carbonaceous layer observed during the H_2/CO reaction on the initially clean surface may in fact be inactive with respect to the Fischer–Tropsch reaction. A small concentration of highly active clean iron sites could be responsible for the observed chain growth on the carbonaceous monolayer.

The product distribution observed in our study is very different from those obtained using promoted iron catalysts. Also, the initially clean iron foil poisons rapidly as compared to the iron Fischer–Tropsch catalysts. It appears that clean iron is certainly *not* the catalytic surface that produces alcohols and higher molecular weight hydrocarbons, by more efficient insertion reactions and that resists poisoning by carbon buildup. The influence of additives that increase the surface concentration of oxygen (potassium, for example) and the presence of iron compounds (carbides or oxycarbides) on the product distribution, reaction rates, and catalyst stability is presently being investigated.

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