

The Role of Readsorption in Determining the Product Distribution during CO Hydrogenation over Fe Single Crystals

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The H₂/CO reaction has been investigated over well-characterized iron(111) single crystal surfaces. Under the reaction conditions (6 atm, 3:1 H₂:CO, 300°C) the dominant product was methane (85 mole%) with small amounts of ethylene (11 mole%) and propylene (3 mole%). Due to the low surface area of our catalyst (1 cm²) the total conversion was less than 1%. The addition of ethylene or propylene in small concentrations (0.04 to 2.7 mole%) to the reactant stream resulted in a product distribution more typical of high conversion reactors (dominant product C₅⁺). These results suggest that readsorption and secondary reaction of the initially produced α -olefins is an important pathway leading to the formation of large molecular weight hydrocarbons during Fischer-Tropsch synthesis.

I. INTRODUCTION

Using a high pressure isolation cell attached to a standard LEED (low energy electron diffraction)-Auger UHV system, we have determined the rates and hydrocarbon product distribution during the reaction of CO and H₂ (1). Our catalyst was a polycrystalline iron foil of approximately 1-cm² surface area and the reaction was carried out at 6 atm, 3:1 H₂:CO ratio, and at 300°C. There are two important observations that distinguish our results from those observed over typical Fischer-Tropsch iron catalysts. (i) At low conversions (<1%) obtained under our conditions the products are primarily methane and ethylene with trace amounts of other α -olefins up to C₅. This product distribution is compared to that obtained from pilot plant studies (2) under industrial conditions

and at high conversions (85%) in Fig. 1 that yield higher molecular weight paraffins in large concentrations. (ii) The clean or oxidized iron foils in our experiments rapidly poison by deposition of multi-layers of carbon while commercial catalysts have a much longer lifetime.

In this paper we attempt to verify the reasons for the differences in product distribution in the two types of experiments. We show that readsorption of ethylene and propylene, the initial olefinic products of CO and H₂ over iron, initiates secondary reactions which lead to the production of higher molecular weight hydrocarbons. The reasons for the observed rapid poisoning of our catalyst will be addressed in a subsequent paper. Potassium and other surface additives as well as compositional change in the gas stream at high conversion that adjusts the surface composition of the catalyst play important roles in preventing poisoning.

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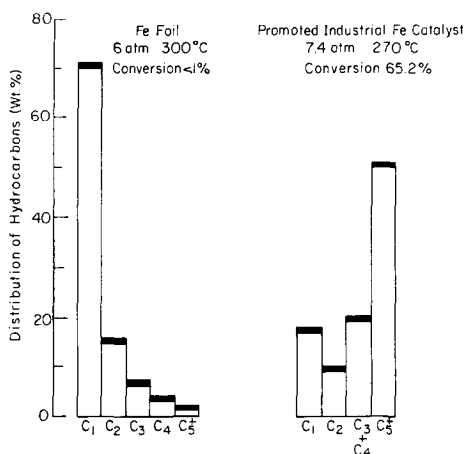


Fig. 1. Comparison between the product distribution obtained at low conversion from Ref. (1) with that obtained at high conversions [Ref. (2)].

II. EXPERIMENTAL

The apparatus used in the present study has been described in detail elsewhere (1, 3, 4). It consists of a diffusion pumped ultra high vacuum bell jar equipped with a retarding grid LEED-Auger system, a quadrupole mass spectrometer, and a 2-keV ion sputter gun. The vacuum system is fitted with an internal sample isolation cell which allows high pressure (20 atm) catalytic reactions to be carried out while maintaining UHV in the bell jar.

The sample isolation cell is attached to an external gas recirculation line, a gas chromatograph sampling valve, and a gas manifold. The gas recirculation system is driven by a high pressure metal bellows pump. The total internal volume of the pump, recirculation line, and cell is approximately 165 cc. Products generated in the cell are analyzed with a gas chromatograph equipped with a flame ionization detector. A chromasorb 102 column (6', 30 ml min⁻¹ N₂, 120°C) was used to separate the reaction products.

The catalyst used in the present experiments was a 1-cm² iron single crystal wafer with both sides oriented and polished parallel to the (111) plane. The crystal was mounted on the ends of two tantalum sup-

port rods in the vacuum chamber such that it could be resistively heated. A chromel-alumel thermocouple was spot welded to the bottom edge of the crystal to monitor its temperature. Before each experiment a two-step catalyst cleaning procedure was followed. Surface carbon was removed by cycling the crystal between room temperature and 800°C in 8×10^{-7} Torr of O₂. The cycling was continued until CO no longer evolved from the surface during heating. Residual sulfur and oxygen impurities on the surface were then removed by ion sputtering (2 keV, Ar⁺, 30 μ A cm⁻²) for ≈ 3 min followed by annealing at 800°C for 2 min. This procedure generally produced a well-ordered (111) surface which contained only trace levels of carbon as a surface impurity. The clean iron Auger spectra and diffraction patterns are shown in Fig. 2.

Synthesis gas (3:1 H₂:CO) was prepared from research grade carbon monoxide and hydrogen by mixing in the gas manifold prior to expansion into the closed isolation cell. Research grade ethylene and propylene were added to the synthesis gas in the manifold for those experiments requiring these additives. Mass spectroscopic analysis and gas chromatographic analysis indicated that H₂O at approximately 100 ppm was the major impurity in the synthesis gas. Small amounts of methane (20 ppm) were detected in those gas mixtures containing propylene or ethylene.

Once the desired surface was prepared in vacuum, the isolation cell was closed and the synthesis gas mixture expanded into the cell at a total pressure of 6 atm. The crystal temperature was then raised to 300°C and G-C sampling of the reaction products was commenced. At any point in the reaction the crystal could be cooled, the cell evacuated, and the surface inspected by Auger electron spectroscopy. The pump-down from 6 atm to 5×10^{-8} Torr took approximately 1 min.

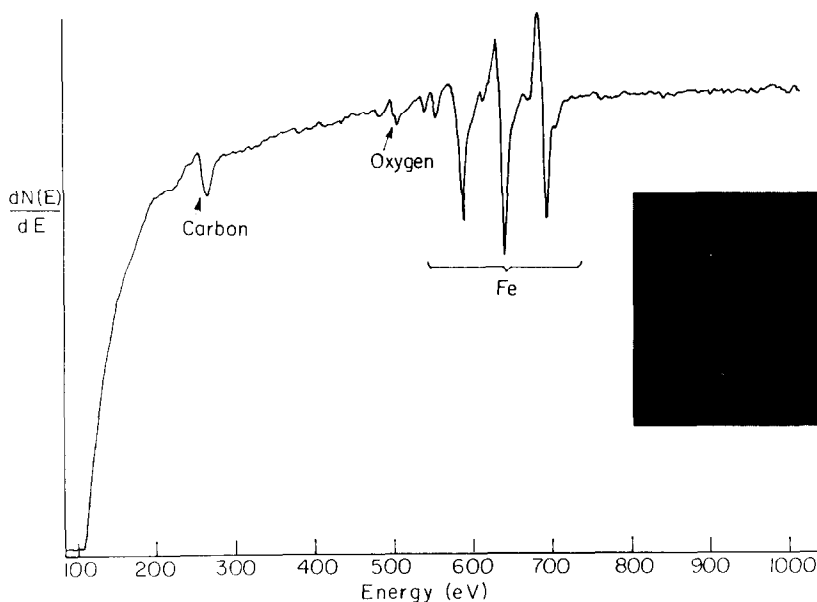


FIG. 2. Auger electron spectrum and low energy electron diffraction pattern of the "clean" Fe(111) crystal face.

III. RESULTS

The H₂/CO Reaction on Initially Clean Fe(111)

The H₂/CO reaction was investigated under the reaction conditions: 6 atm 3:1 H₂:CO, 300°C. Under these conditions the Fe(111) surface behaved in a manner similar to the previously investigated polycrystalline iron surface. The predominant product is methane (85%) with decreasing amounts of chain products up to C₅. The chain products were mostly α -olefins: ethylene, propylene, 1-butene, and 1-pentene. The corresponding straight chain alkanes were also observed with an olefin to paraffin ratio of about 4:1. No branched products were detected. The product distribution is given in Fig. 4. Due to the very small number of surface sites present in our experiments the total CO conversion is <1%.

The initial methanation rate was determined by evaluating the slope of the accumulated methane versus time curve then dividing this value by the total num-

ber of surface sites (1.22×10^{15} cm²). The initial methanation rate for Fe(111) was 1.35 molecules site⁻¹ sec⁻¹. This rate is comparable to that previously measured for the polycrystalline surface (1.9 molecules site⁻¹ sec⁻¹) (1). The comparable rates for the two surfaces suggest that surface imperfections play only a minor role in catalyzing the methanation reaction. It is also likely that the annealed polycrystalline surface contains a large fraction of (111) type surfaces.

As was the case for the polycrystalline foil, the Fe(111) surface was unstable under the present conditions and excessive carbon deposition occurred. The reaction could be divided into regimes. The first regime is characterized by rapid methanation and Fischer-Tropsch (F-T) activity. The second regime occurs after approximately 2 hr and is characterized by the lack of F-T activity and slow methanation (0.35 molecules site⁻¹ sec⁻¹). It was shown in the previous study (1) that the deactivation is due to the buildup of a multi-layer carbon deposit on the surface which eventually

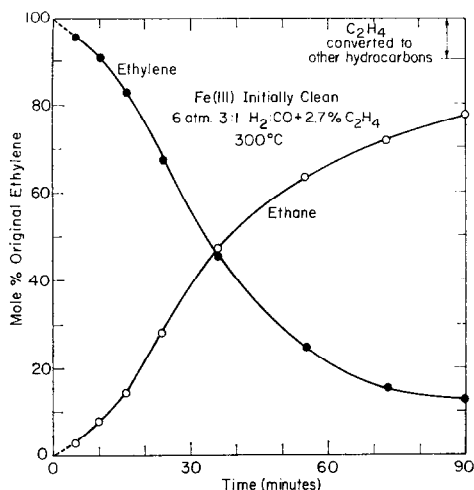


FIG. 3. The conversion of 2.7 mole% added ethylene to ethane as a function of time. Note that some of the ethylene is converted to other hydrocarbons.

blocks iron sites necessary for F-T activity. The final slow methanation reaction is due to the direct hydrogenation of the multi-layer carbon deposit. It is thought that this carbon deposit is sustained by CO which diffuses through the carbon layer and dissociates at the iron carbon interface.

The Effect of Added Ethylene

An experiment was performed in which a small partial pressure of ethylene was

added to the synthesis gas. The fate of the ethylene was then followed as a function of reaction time under our standard conditions (6 atm, 3:1 $H_2:CO$, $300^\circ C$). Under these conditions, 80 to 90% of the ethylene reacted. The majority of the ethylene was hydrogenated to ethane as shown in Fig. 3. In this particular experiment a partial pressure of 74.2 Torr ethylene was added to the synthesis gas. After 90 min of reaction 16.25 mole% of the original ethylene remained in the cell, 75.6 mole% was converted to ethane, and the 8.15 mole% was converted to other hydrocarbons. The conversion of ethylene to other hydrocarbons had a significant impact on the product distribution of the CO- H_2 reaction as shown in Fig. 4. The relative amount of C_3-C_5 hydrocarbons increased due to the presence of ethylene in the synthesis gas. A detailed analysis of the mass distribution revealed that the total mass of ethylene consumed in the reaction that does not hydrogenate to form ethane is almost equal to the C_3-C_5 mass. Assuming that all of the original ethylene unaccounted for in the C_2H_4 or C_2H_6 fractions is found in the C_3-C_5 fractions, then four out of five carbon atoms in the C_3-C_5 fraction had their origin in the original ethylene

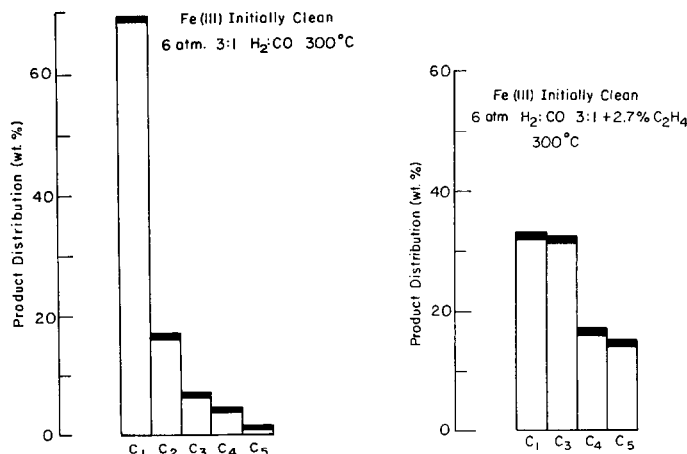


FIG. 4. Comparison between the product distribution obtained from initially clean Fe(III) with and without added ethylene. Ethylene concentration is in mole%.

This estimate is somewhat uncertain since ethylene can also be lost through decomposition to methane or remain on the catalyst surface. Auger analysis reveals that extensive carbon deposition occurs on the catalyst during the reaction.

The influence of ethylene concentration on the product distribution was investigated by varying the ethylene partial pressure between 2 and 150 Torr while the $H_2:CO$ ratio was held constant at 3:1 and the total pressure at 6 atm. Each experiment started with a clean surface and the crystal temperature was $300^\circ C$. The results of these experiments are summarized in Fig. 5 where the product distribution is given as a function of ethylene partial pressure. It is seen that as the initial ethylene partial pressure is increased in the reactor the *relative* amount of C_1 in the product distribution decreased although the amount of methane formed remains largely unchanged. The C_5^+ fraction on the other hand, increases with increasing ethylene in an almost linear fashion. The C_3 and C_4 fractions increase to limiting values of 30 and 21 wt%, respectively, at approximately 80 Torr initial ethylene partial pressure. In each experiment the initial methanation rate was measured to determine any influence of ethylene on methanation. The methanation rate had only a weak dependence on ethylene partial pressure. At low concentrations of ethylene the rate was $1.35 \text{ molecules site}^{-1} \text{ sec}^{-1}$, identical to that measured when using pure H_2-CO . The rate decreased somewhat at higher partial pressures of ethylene ($0.73 \text{ molecules site}^{-1} \text{ sec}^{-1}$ at 150 Torr). Due to the errors in determining the methanation rate it is hard to judge whether this drop (less than a factor of 2) is significant but the trend does seem to indicate a slight inhibition of methanation at high ethylene partial pressures.

Poisoning of the surface due to excessive carbon deposition was still a problem during the ethylene experiments. In all experi-

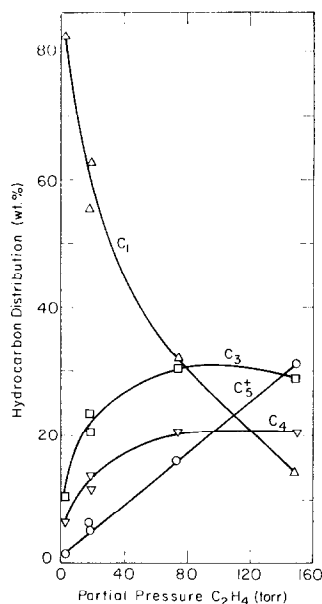


FIG. 5. Product distribution for fixed reaction conditions (6 atm, 3:1 $H_2:CO$, $300^\circ C$) as a function of added ethylene.

ments the F-T activity lasted approximately 3 hr. An attempt was made to adjust the operating parameters to extend the catalyst lifetime. In previous work on iron foils (1) it was found that preoxidized iron surfaces are considerably more active (10-fold increase in overall rate) than the initially clean surface. Experiments were, therefore, performed in which the clean Fe(111) surface was oxidized in 800 Torr O_2 at $300^\circ C$ for 20 min. This procedure resulted in the formation of an amorphous surface oxide in excess of 100 \AA thick. When exposed to the CO/H_2 mixture with added ethylene the enhanced catalytic activity previously reported was again observed. However at $300^\circ C$ the oxide is rapidly reduced (within 15 min) and the activity falls to the level observed from the initially clean surface. Lowering the reaction temperature extended the period of enhanced reactivity. The lower temperatures also increased the C_5^+ fraction. The product distribution from one experiment performed on a preoxidized surface at $235^\circ C$

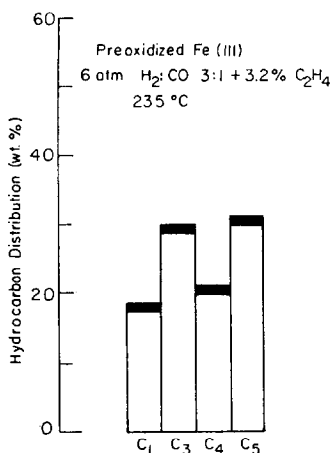


FIG. 6. Product distribution obtained over the oxidized iron crystal surface at 235°C.

is given in Fig. 6. Comparing Fig. 6 with Fig. 4 it is seen that the combined influence of lower temperature and surface oxide is to increase the C₅⁺ fraction.

The Effect of Added Propylene

Experiments in which propylene was added to the synthesis gas produced results similar to the ethylene experiments. Adjusting the propylene concentration in the gas stream had a marked effect on the observed product distribution. Partial pressures of propylene as small as 2 Torr increased the amount of C₃⁺ produced

during the reaction. Unfortunately the G-C column used in the experiments did not sufficiently resolve propylene and propane peaks to permit us to perform a detailed analysis of the amount of propylene which is incorporated into the higher molecular weight hydrocarbons. Based on relative yields of C₃-C₅ fractions it would appear that propylene is somewhat less likely to be incorporated into the growing hydrocarbon chains than ethylene. Propylene did, however, seem to produce larger molecules than the corresponding ethylene experiments. This is demonstrated in Fig. 7 which contains the product distribution obtained from a preoxidized surface (3:1 H₂:CO + 2.2% C₃H₆, 300°C). In this experiment substantial amounts of C₆ and C₇ and even trace amounts of C₈ hydrocarbons were observed. The product distribution of this experiment is compared with a distribution typical of high conversion experiments in Fig. 8. The similarity of the distributions is apparent and indicates that by adding small concentrations of propylene it is possible to obtain the product distribution found under high conversion conditions.

DISCUSSION

The formation of hydrocarbons from CO and H₂ can be divided into several steps:

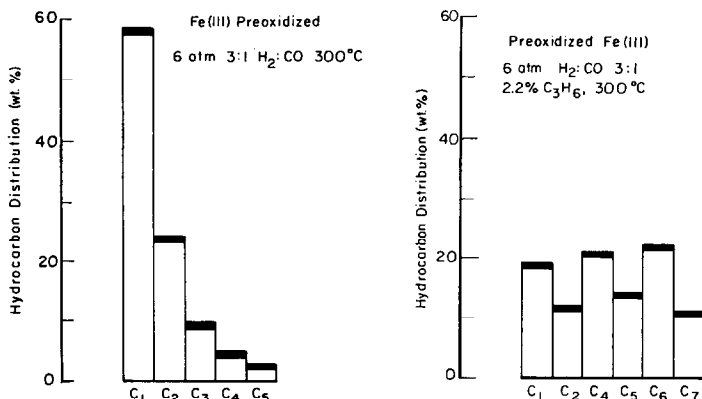


FIG. 7. Product distribution obtained over the oxidized iron crystal surface in the presence of propylene.

(i) adsorption (both molecular and dissociative), (ii) the hydrogenation of carbon containing surface species, (iii) the insertion of single carbon units into growing hydrocarbon chains (5). Each step is complex and is likely to have several branches. There is evidence, for example, that methanation proceeds via direct hydrogenation of surface carbon, i.e., dissociated CO or via hydrogenation/dehydration of molecular bound CO. The insertion mechanism leading to chain growth is likely to be even more complex. In the present experiments we have demonstrated that olefin readsorption accelerates this insertion step. The product distribution obtained at low conversion (<1%) during CO hydrogenation over iron or oxidized iron single crystal catalysts was predominantly methane, ethylene, and propylene, while liquid hydrocarbons predominated in conventional Fischer-Tropsch studies. When the olefinic products (C_2H_4 or C_3H_6) are added to our reactant stream in small concentrations, the product distribution over iron crystals approaches or becomes identical to that obtained from commercial iron catalysts. While this effect is pronounced under our reaction conditions it is probably only one of several mechanistic pathways leading to the formation of higher molecular weight hydrocarbons.

The chain growth mechanism during F-T synthesis is thought to involve the sequential addition of single carbon units as specified by Herington (6). This concept was later used by Friedel and Anderson (7) and Storch *et al.* (2) to predict the isomer distribution in F-T products. More recently, the distribution of F-T reaction products has been shown to follow a Schulz-Flory distribution (8). The Schulz-Flory distribution of molecular weights frequently encountered in polymerization processes is given by

$$Mp = (\ln^2 \alpha) P \alpha^p \quad (1)$$

where Mp is the weight fraction of hydrocarbon containing P carbon atoms. α is the

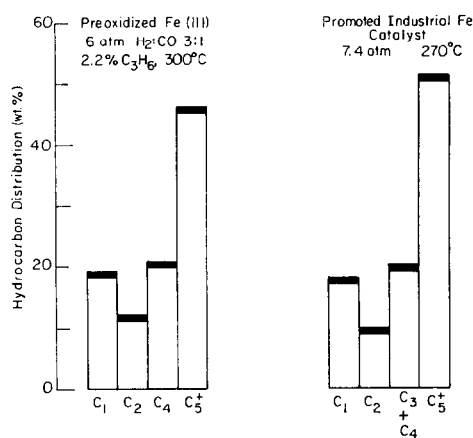


FIG. 8. Comparison between product distribution obtained by the addition of propylene to CO and H_2 in our low conversion experiments and that from high conversion experiments [Ref. (1)].

chain growth probability factor defined as

$$\alpha = r_p / (r_p + r_{tr}) \quad (2)$$

where r_p and r_{tr} are the rate of propagation and termination, respectively. Eq. (1) can be expressed in a logarithmic form

$$\log (M_p/P) = \log (\ln^2 \alpha) + P \log \alpha \quad (3)$$

A plot of $\log (M_p/P)$ versus P yields the value of α from either the slope or the ordinate intercept. Agreement between the slope and intercept is used as a criteria of the "goodness" of the Schulz-Flory fit.

The hydrocarbon distribution data evaluated for two different ethylene concentrations in the present experiments is presented in Fig. 9 according to Eq. (3). The chain growth parameter varies from 0.30 at 2 Torr ethylene to 0.56 at 125 Torr. Excellent agreement was obtained between the slope and intercept values of α (i.e., slope $\alpha = 0.303$, intercept $\alpha = 0.309$) confirming that our data follow a Schulz-Flory distribution. The increase in the chain growth probability with increasing ethylene partial pressure indicates that ethylene participates directly in the propagation step.

A Schulz-Flory plot of the hydrocarbon distribution observed during the propylene

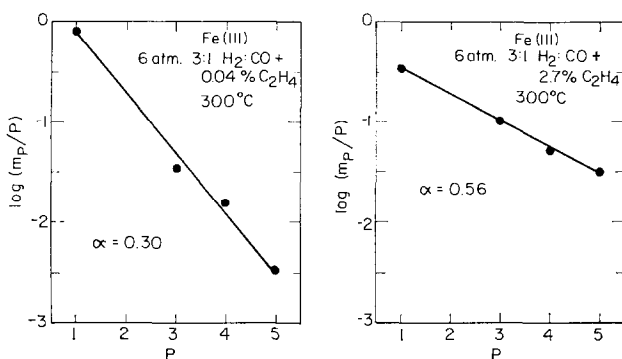


FIG. 9. Plot of the hydrocarbon distributions in the CO/H reaction over iron at two different partial pressures of added ethylene according to the Schulz-Flory distribution defined in Eq. (3). Note the increase in the chain growth parameter α at higher ethylene pressure.

experiment [100 Torr C₃H₆, preoxidized Fe(III)] is shown in Fig. 10. The slope and intercept yield a value of $\alpha = 0.70$. This value is the highest chain growth parameter observed in the present experiments and compares with the value 0.80 obtained from the high conversion data (8).

Considerable work has been published concerning the incorporation of radiolabeled olefins into hydrocarbons during F-T reaction. The pioneering work of Kummer and Emmett (9) and Hall *et al.* (10) suggested that ethylene acted as a chain initiator over iron catalyst (1 atm, space velocity 288 hr⁻¹, 224°C, H₂:CO 1:1 + 1.5% C₂H₄). This conclusion was based on a constant molar radioactivity of the C₃-C₅ fractions. The

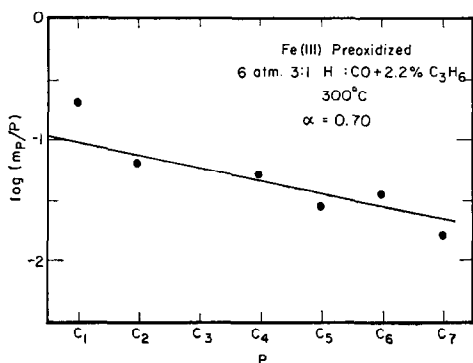


FIG. 10. Plot of the hydrocarbon distribution in the CO/H₂ reaction over iron obtained after the addition of propylene according to the Schultz-Flory distribution defined in Eq. (3).

same result was obtained over Co catalyst by Eidus and co-workers (11). Under their reaction conditions (CO:H₂ 1:1, 195°C + 1.48% C₂H₄) 25% of the ethylene was converted to higher hydrocarbons with constant molar radioactivity. The extent to which ethylene participated as a chain initiator increased in proportion to the amount of ethylene in the gas phase. It was suggested that ethylene is present in the initial surface complex responsible for chain growth.

The results of the present study indicate that ethylene acts not only as a chain initiator but also participates in chain propagation. This is based on the observation that the total amount of ethylene converted to hydrocarbons is approximately equal to the total mass of the C₃-C₅ fractions. If ethylene was a chain initiator then it would be expected that the mass of the C₃-C₅ fractions be significantly greater than the ethylene mass converted to hydrocarbons.

This result is in general agreement with the studies of Schulz, *et al.* (12). In their experiments ¹⁴C-labeled primary olefins, ethylene, propylene, 1-butene, and 1-hexadecene, were added to the synthesis gas over both Fe and Co catalyst. The products were analyzed by radio gas chromatography. They found that 90% of the added olefin reacted. The majority of

olefins were hydrogenated to alkane, but α -olefins were also incorporated into growing chains, initiated new chains, or were cracked to methane.

It has long been suspected that α -olefins are the primary products of F-T synthesis, although they are thermodynamically unstable under the reaction conditions (13). It has been shown that the concentration of α -olefins in the gas stream increases with increasing space velocity (14). At high space velocities ($>2000 \text{ hr}^{-1}$) the product distribution is shifted towards methane and the production of alkanes, β -olefins, and methyl paraffins are curtailed. These results indicate that readsorption and subsequent secondary reaction of α -olefins readily occur under F-T reaction conditions.

In the present experiments it has been shown that under extremely low conversion conditions the dominant product of the F-T synthesis is methane with trace amounts of α -olefins. However, by adding larger concentrations of ethylene or propylene (as low as 0.04 mole%) a product distribution consistent with traditional F-T studies is observed. It is suggested that readsorption and secondary reaction of α -olefins may be a major reaction pathway leading to the growth of hydrocarbon molecules during F-T synthesis. In standard flow reactors with high surface area catalysts it is expected that at the leading edge of the bed the product distribution will be similar to our low conversion measurements. As these initial reaction products proceed along the bed, they will be readsorbed and undergo secondary reactions leading to higher molecular weight products. As a result of the changing product distribution along the catalyst bed,

the surface composition of the catalyst is also likely to change.

The presence of readsorption as an important reaction step should permit one to devise new ways of controlling the product distribution. Various additives to the reactant mixture, changing the size and geometry of the catalyst bed and mixing of different catalysts are among the experimental variables that may be utilized in order to tailor the product distribution in the Fischer-Tropsch reaction.

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