

Evidence for Two Chain Growth Probabilities on Iron Catalysts in the Fischer-Tropsch Synthesis

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New data and reexamination of several previous studies in either fixed bed or slurry liquid reactors with iron catalysts show that the products frequently may be characterized as the sum of two Flory carbon number distributions. In many cases the dominating distribution shifts at about C_{10} . At higher carbon numbers hydrocarbons are produced with a much higher probability of chain growth than for lower carbon numbers. Results are interpreted in terms of a two-site catalyst structure.

Considerable uncertainties remain as to whether or under what circumstances the Fischer-Tropsch products from an iron catalyst may be characterized by a single value of the chain growth probability, α , in the Flory distribution, rather than by two or more values. In a very recent paper, König and Gaube (1) reported that on a precipitated iron catalyst without addition of potassium the carbon number distribution from about C_3 to C_{20} was well represented by a single value of $\alpha = 0.65$ whereas with a precipitated iron catalyst containing 2 wt% K_2CO_3 , the carbon number distribution was represented by two values of α , equal to 0.57 and 0.87. With the first catalyst a slight deviation in the product distribution above C_{12} from a single value of α was attributed to traces of potassium and sodium impurity, detected by SIMS surface analysis. They concluded that pure iron would exhibit a single α and they postulated that the catalyst to which potassium had been added had two kinds of sites, with and without potassium.

In contrast Dyer *et al.* (2), working in a slurry reactor with a reduced fused ammonia synthesis catalyst containing 0.5% K_2O and 0.7% CaO , recently reported that the product distribution, measured from C_1 to about C_{25} to C_{30} corresponded to a single

value of α when the (H_2/CO) ratio in the feed gas was 2.0 or 0.71 but corresponded to two values of α , shifting at about C_{10} , when the (H_2/CO) feed ratio was 0.36.

Schulz *et al.* (3) report data on a "modified" iron catalyst that shows an essentially constant value of α from C_3 to C_{15} , but on a precipitated and supported iron catalyst containing 0.5 parts K_2CO_3 per 100 parts Fe, a slight increase in α was noted at about C_{10} to C_{13} .

We present here new data and reexamination of previous studies, including our own, to show that the existence of two values of α may be found with many iron catalysts, even when potassium is not added in their formulation.

With two values of α , on a Flory plot the data fall on two straight lines, as illustrated in Fig. 1. Plots of this sort first appeared in the data from the 1943 Schwarzheide tests in Germany (see, e.g., Shultz *et al.* (4), Anderson (5)). The product distribution from iron catalysts supplied by six different German companies all showed two straight lines intersecting at about C_{10} , with a marked decrease in slope for the $C_{10} +$ products. Data from a later study by the Standard Oil Company of New Jersey (now Exxon), using an iron catalyst in a fluidized bed reactor, showed a mild break at about

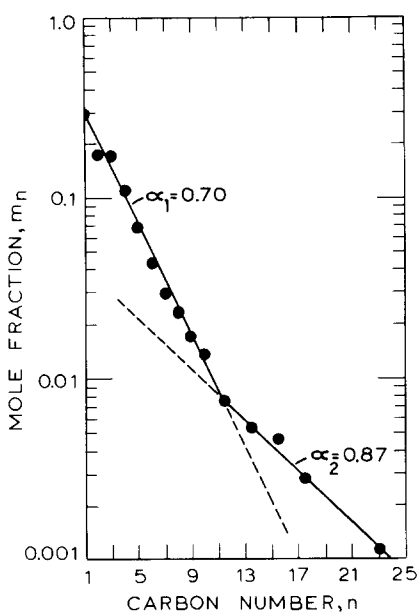


FIG. 1. Application of Flory distribution to industrial Fischer-Tropsch data (calculated from data of Weingaertner (6)). Iron catalyst in a fixed bed reactor, 224°C, 1 MPa, and H_2/CO feed ratio = 1.3.

C_{10} but the decrease in slope was much less pronounced (5). The data in Fig. 1 are from Rheinpreussen A.G. as reported by Weingaertner (6) on an iron catalyst promoted with copper and potassium, in which oxygenated compounds are included with hydrocarbons.

Other studies on iron catalysts under well-controlled conditions in which adequate data are available likewise show results which fit a Flory plot with two straight lines. Atwood and Bennett (7) studied a nitrated reduced fused iron catalyst in a gradientless reactor. The catalyst contained K_2O (0.4 to 0.8 wt%) and SiO_2 (less than 0.4 wt%). Their published results for hydrocarbons are recalculated in the form of a Flory plot in Fig. 2. Some product in the range C_9 – C_{12} appears to have been lost but two values of α , of about 0.69 and 0.81, are needed to fit the overall distribution, with a discontinuity at about C_9 .

More recently, Caldwell (8) correlated data published by Wender for a SASOL fixed bed reactor packed with an iron cata-

lyst. There was a break in the C_1 -to- C_{30} Flory plot at about C_5 ; the two lines corresponded to values of α of 0.87 and 0.90. Madon and Taylor (9), working with an alkali-promoted iron-copper catalyst in a fixed bed reactor reported data for C_{10} to about C_{40} on a Flory plot which showed a break at about C_{20} .

In an earlier paper (10) we described a study with a reduced fused magnetite catalyst in a well-stirred slurry reactor. The focus of our attention at that time was to show that if oxygenates were included with hydrocarbons, the product distribution on a total carbon number basis could be represented by one value of α on a Flory plot. Analysis was based on products volatilized from the slurry and the focus of attention was on lighter products. Slight deviations at higher carbon numbers were attributed to experimental artifacts caused by inaccuracies in product trapping and analysis. Although runs lasted for as much as 100–200 h, we subsequently determined that for many cases longer runs were required to collect sufficiently representative quantities of the higher molecular weight products to determine the existence of two values of α .

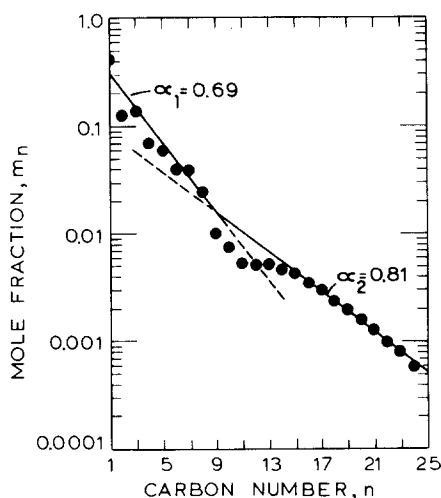


FIG. 2. Flory distribution for a nitrated fused-iron catalyst (after Atwood and Bennett (7)). Vapor-phase reactor at 250°C, 2.0 MPa, and H_2/CO feed ratio = 2.0, 33% conversion.

EXPERIMENTAL

The apparatus is described in detail elsewhere (11). Synthesis gas was passed continuously into a 1-liter, mechanically-stirred autoclave about half-filled with an essentially nonvolatile and inert liquid, *n*-octacosane (C₂₈) of greater than 99% purity in which the catalyst was suspended. The contents were well mixed so the reactor behaved as a C.S.T.R. Volatile products were removed overhead continuously while the inert liquid remained mostly in the reactor for the duration of a run. After an initial period, steady-state operation with regard to catalytic activity and selectivity was obtained over the entire run.

Most of the studies were with a fused magnetite catalyst (from United Catalysts, Inc., and designated C-73) that contained 2.0–3.0% Al₂O₃, 0.5–0.8% K₂O, 0.7–1.2% CaO, and <0.4 SiO₂, on an unreduced weight basis, and is the same that we used previously. About 75 g of crushed catalyst was prerduced in a separate vessel with hydrogen at a space velocity of 10,000 h⁻¹, 400°C, and atmospheric pressure. It was then slurried with *n*-octacosane to produce a 15 wt% suspension (unreduced basis).

The results reported here on this catalyst were all obtained on one charge that was on stream for a total of 680 h during which time a variety of conditions were studied. Pressure was varied from 445 to 1480 kPa, temperature from 232 to 263°C. The H₂/CO feed ratio was 0.90 for the first 237 h, 1.81 from 236 to 425 h, and 0.55 from 425 to 680 h. On a freshly reduced catalyst, steady-state activity was attained within about 24 h and results reported here were those for the steady-state conditions. We also report on limited studies with a precipitated Cu-K promoted iron catalyst and with a MnO/Fe catalyst.

The overhead products were analyzed by capillary gas chromatography (12). They were grouped into four categories at each carbon number—oxygenates, *n*-paraffins, *n*-1-olefins, and branched hydrocarbons

(which included paraffins and olefins). The products were characterized by carbon number on a total organic basis, based on the volatile products collected overhead of the reactor.

As carbon number increases, an increasing fraction of the product is retained in the liquid both because of its decreasing volatility and because it is produced in lesser amounts. To obtain overhead representative products for a substantial range of carbon numbers requires extended runs. As a guide to expected behavior we use calculated plots of the form of Fig. 3 which show the time required for a specified percentage of hydrocarbon product of carbon number *n* to have appeared overhead. This is a function of numerous variables, including catalyst activity, pressure, temperature, space velocity, and composition of liquid in the reactor initially. Figure 3 is for the set of conditions under which the results of Fig. 5 were obtained. It illustrates, for example, that with a 600-h run, 90% or more of the product formed up to about C₂₁ will have

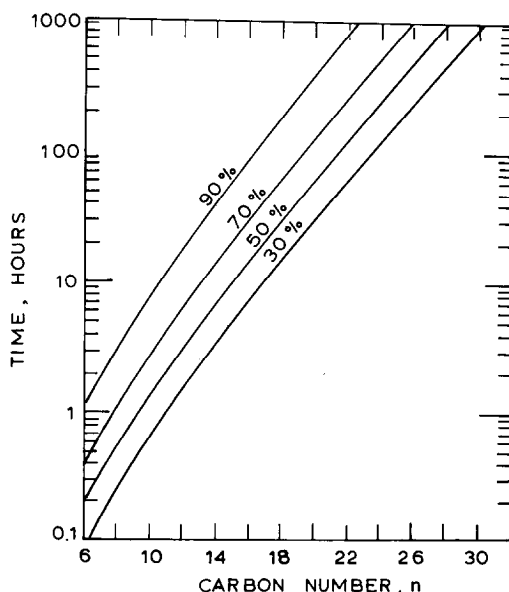


FIG. 3. Time required for specified percentage of paraffin product of carbon number *n* to have appeared overhead. Reaction conditions of Fig. 5. Liquid initially pure *n*-octacosane.

been recovered overhead but only 30% of the C_{29} product. Such a guide is only approximate, since in fact reaction conditions may be deliberately changed during the course of a long run.

Figure 4 shows a typical Flory plot of products formed when operating so as to collect representative quantities of products in the higher molecular weight range. A clean break in the Flory plot occurs at about C_9 - C_{10} , and a second straight line is obtained which eventually drops off because of accumulation of heavy products in the reactor liquid. In this run the H_2/CO feed ratio was relatively high, which reduces the value of α_1 (0.62) and makes the break with α_2 more pronounced. The occurrence of the double α is not some artifact associated with a slurry liquid reactor system. The same catalyst studied in a "vapor phase" fixed bed reactor under identical reaction conditions again showed a double α

distribution with similar values to those obtained in the slurry reactor (13).

Figure 5 shows a typical carbon number distribution for categories of products based on material volatilized from the reactor. In this case $(H_2/CO)_{in} = 0.55$ and $\alpha_1 = 0.68$. A break in the Flory curve again occurs at about C_{10} for 1-olefins, n -paraffins, and branched hydrocarbons, but not for oxygenates.

After termination of this run, that lasted 680 h, a sample of the liquid carrier that remained in the autoclave was analyzed at the Exxon Corporate Research Laboratories, Linden, New Jersey by a gas chromatographic technique, utilizing a conventional 10-ft by $\frac{1}{8}$ -in. o.d. stainless-steel column packed with SP 2100 coated on Supelcoport. Results, shown on Fig. 6, on a C_{28} -free basis, correspond to $\alpha_2 = 0.93$. Another sample of the same material was analyzed by Stenger (14) using a different high

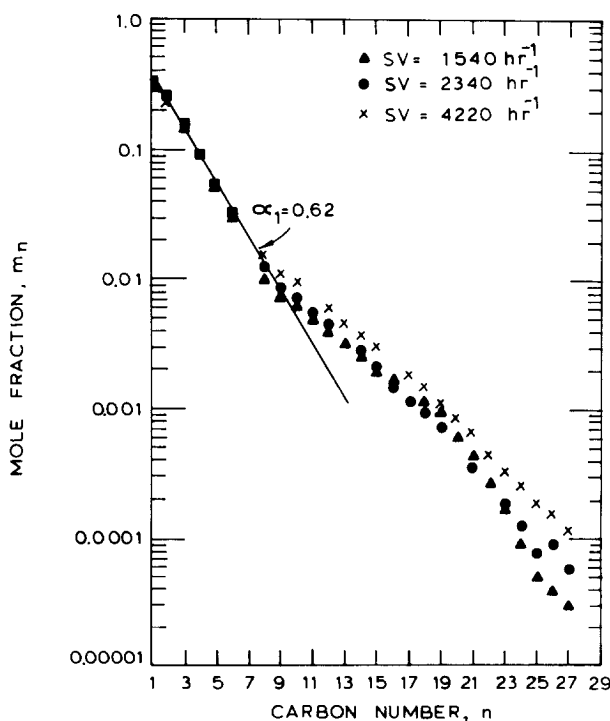


FIG. 4. Carbon number distribution. Reduced fused magnetite catalyst; 248°C, $(H_2/CO)_{in} = 1.81$, 790 kPa.

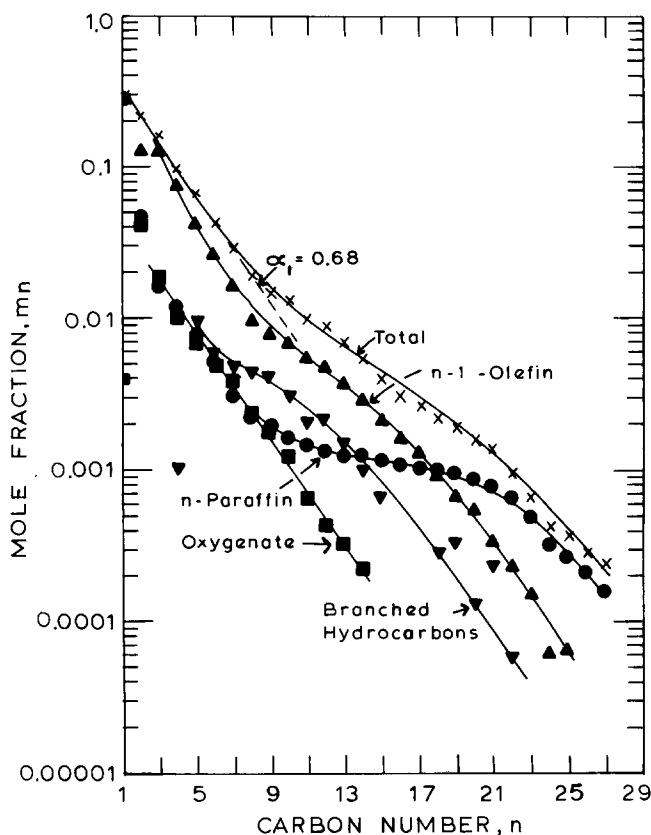


FIG. 5. Flory distribution by organic class. Reduced fused magnetite catalyst; 263°C, 790 kPa total pressure, H_2/CO feed ratio = 0.55, space velocity of 2320 h^{-1} .

temperature gas chromatographic procedure which utilized a glass-lined stainless-steel column filled with 60/80 mesh dimethyl silicone (PermaBond) packing and a flame ionization detector. Results were very similar and the calculated value of $\alpha_2 = 0.90$.

DISCUSSION

The drop in products having carbon numbers greater than about 20 to 25 shown on Figs. 4 and 5, is attributed to significant accumulation in the liquid carrier. Although the liquid carrier was initially pure *n*-octacosane, after 680 h on stream it contained more than 14 wt% C_{50} + hydrocarbons and less than 56 wt% *n*-octacosane (C_{28}). The liquid analysis shows that a maximum was reached at C_{24} (Fig. 6), above which most of the product remains in the liquid

carrier. This peak corresponds to about the same carbon number at which products collected overhead begin to tail off.

At a carbon number of about 10 in Fig. 5, there is a marked change in product selectivity. Below C_{10} , the slope of each organic group is approximately the same. The total organic curve from C_1 to C_9 can be fitted by a straight line with an α value of 0.68 from the Flory equation:

$$m_n = (1 - \alpha)\alpha^{n-1} \quad (1)$$

Since the cumulative C_1 -to- C_9 fraction comprises about 95 mol% of the organic collected for this run, the error in neglecting the C_{10+} material is small; hence the same α value is calculated from either the slope or the intercept by the Flory equation. Above C_{10} , the slope for normal paraffins becomes much lower than those for the

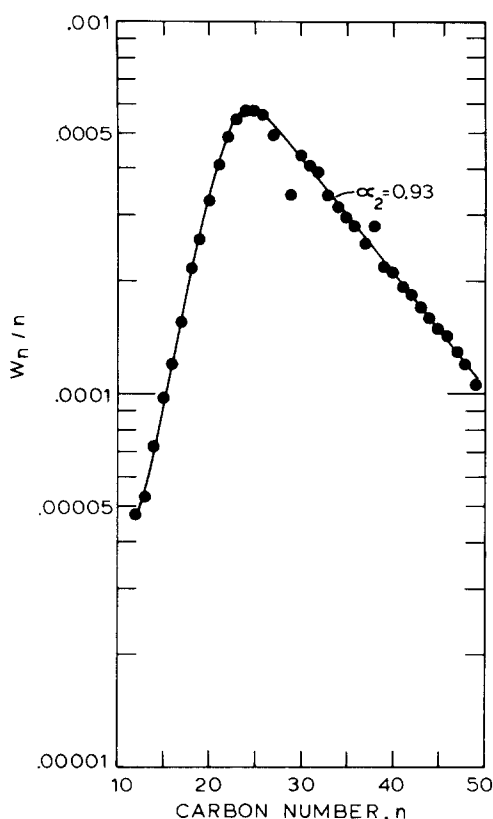


FIG. 6. Flory distribution of liquid in reactor, excluding octacosane.

other hydrocarbons. The oxygenate slope remains constant.

The C_{20+} portion of the total product can be inferred from the data of Fig. 5 by linear extrapolation of the C_{11} to C_{20} portion, which assumes no further irregularities in the carbon number distribution. Below C_9 , the α value for the total product was 0.68 for this set of conditions. The linear paraffins above C_{11} correspond to the same value of α obtained by the analyses of the liquid carrier. They become the major product at carbon numbers greater than about 20.

Other studies on this same catalyst show that secondary hydrogenation of olefins to paraffins under our reaction conditions was negligible except for that of ethylene. Thus no butene was hydrogenated when it was added to synthesis gas (15) and there was no effect of contact time on the olefin/paraf-

fin ratio for C_3 or C_7 species for constant hydrogen partial pressure (16). For other iron-based catalysts, however, such as MnO/Fe, secondary hydrogenation can be significant (17). Over the range we studied, pressure and space velocity (conversion) apparently had little effect on α , but α_1 decreased moderately with increasing H_2/CO feed ratio. Thus $\alpha_1 = 0.62$ with a $(H_2/CO)_{in}$ of 1.81 (Fig. 4) and $\alpha_1 = 0.68$ with $(H_2/CO)_{in} = 0.55$ (Fig. 5).

OTHER CATALYSTS

Precipitated Cu-K Promoted Iron

This catalyst had the composition 100 Fe:22 Cu:1 K_2CO_3 and was a sample of the same catalyst on which results have been reported in a fixed bed reactor by Madon and Taylor (9). It was studied (18) at 250°C and 0.987 MPa and 225°C and 1.132 MPa with an inlet H_2/CO ratio of 1.42, each run of 30 h duration. Figure 7 is a Flory plot of the distribution of total organic products volatilized overhead at the two temperatures. The heavier product distribution drops more noticeably at 225°C than at 250°C because of greater accumulation of products in the reactor liquid, but clearly there is a break in the Flory plot at about C_8 . For the lighter fraction, $\alpha = 0.68$, the same as that for the reduced fused magnetite catalyst at a similar value of $(H_2/CO)_{in}$. From the 250°C run a value of $\alpha_2 = 0.86$ can be calculated but this may be slightly low since product accumulation in the slurry may have been significant. More details of this study appear elsewhere (18). With the same catalyst studied in a fixed bed reactor, Madon and Taylor also reported a break in the Flory plot, but it occurred at about $C_{20}-C_{25}$.

MnO/Fe Catalyst

A sample of this catalyst, prepared at the Technical University of Berlin, was studied at 283°C, 1.24 MPa with $(H_2/CO)_{in} = 1.19$ (17). The catalyst analyzed 8.1% Fe, 58% Mn, remainder oxygen. Figure 8 presents a

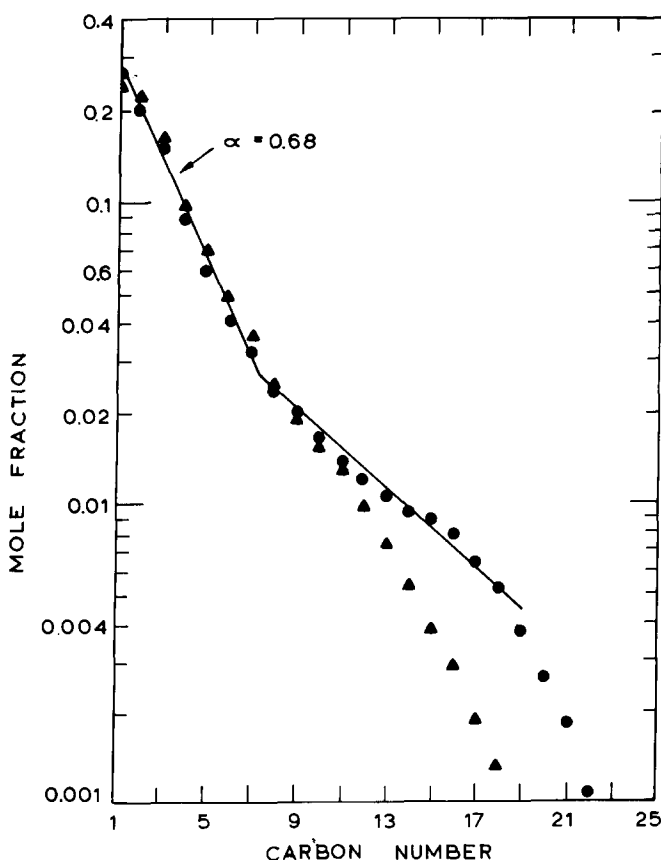


FIG. 7. Flory distribution for precipitated iron catalyst promoted with Cu and K. $(\text{H}_2/\text{CO})_{\text{in}} = 1.42$. 225°C (\blacktriangle) and 250°C (\bullet).

Flory plot of paraffins, olefins, and oxygenates as separate groups. On a total organic product basis, the carbon number distribution is very similar to that with a reduced fused magnetite, breaking sharply at C_{11} . The two values of α are 0.55 and 0.75. Notably this occurred on a catalyst to which potassium was not added in its preparation.

DISCUSSION

Two values of α clearly suggest that two kinds of sites are present, as also proposed by Madon and Taylor and by König and Gaube. Likewise, the change in catalyst selectivity in the region of C_{10} suggests that product is synthesized over more than one type of catalytic site. One type of growing chains may be more weakly bound on one site and more readily desorbed to form

mostly lighter products; whereas a second type are more strongly adsorbed on a second kind of site to produce higher molecular weight products. If two kinds of sites exist between which growing chains do not interact, then the Flory expression (Eq. (1)) becomes:

$$m_n = x(1 - \alpha_1)\alpha_1^{n-1} + (1 - x)(1 - \alpha_2)\alpha_2^{n-1} \quad (2)$$

where m_n = total moles of carbon number n relative to the total moles of organic product, α_1, α_2 = chain growth probabilities for the two sites, and x = mole fraction of organic product synthesized on Site 1.

If it were possible to adjust the relative number and/or activities of the two kinds of sites, the consequences on the total organic distribution could be significant. As an ex-

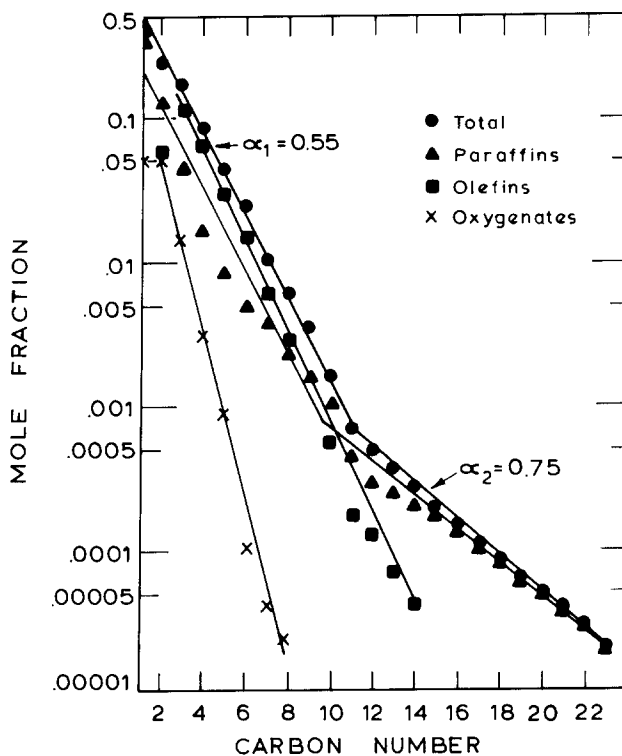


FIG. 8. Flory distribution for MnO/Fe catalyst; 283°C, 1.24 MPa, $(H_2/CO)_{in} = 1.19$.

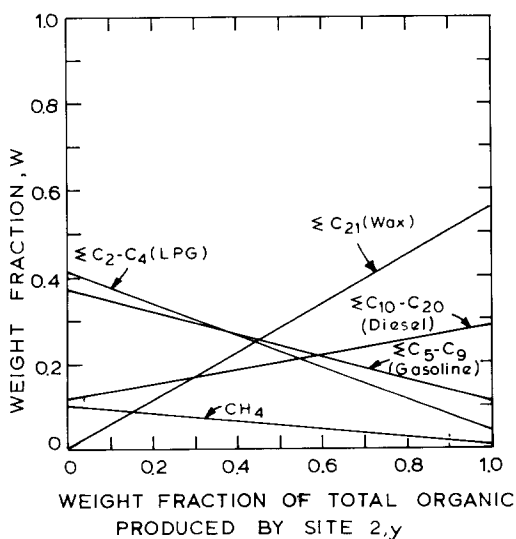


FIG. 9. Selectivity of selected hydrocarbon cuts in the Fischer-Tropsch synthesis predicted by Eq. (2) for $\alpha_1 = 0.68$ and $\alpha_2 = 0.93$.

ample, in Fig. 9, utilizing Eq. (2), the selectivity to various product cuts is predicted for $\alpha_1 = 0.68$ and $\alpha_2 = 0.93$ as a function of the total weight fraction of the organic product, W , formed on site 2, y . As seen in the figure, the C_{21+} weight fraction (wax) increases sharply and the C_9^- weight fraction decreases markedly. The C_{10} -to- C_{20} weight fraction (diesel oil) is only moderately increased as more product is formed over Site 2 than Site 1. The distributions at abscissa values of 0 and of 1 correspond to that for a single site model with $\alpha = 0.68$ or 0.93, respectively. (The values of W for wax at $y = 0$ and for CH_4 at $y = 1.0$ are finite.)

The product distribution calculated from the lighter products can give a highly misleading prediction of the fraction of heavier products formed if two α values typical of those observed here indeed apply. For example, for a single α of 0.68 ($y = 0$ in Fig. 9) the C_{10+} weight fraction is calculated to be

0.12. For the data in Fig. 5, with a double α of 0.68 and 0.93, the C_{10+} weight fraction becomes about 0.25. (This is consistent with a value of $x = 0.95$ in Eq. (2).)

Characteristics of the two sites are as follows:

(1) Site 1 dominates between C_1 and C_{10} , on which over 90 mol% of the organic product is synthesized. Values of α for all organic groups on this site are approximately the same.

(2) Site 2 dominates the formation of hydrocarbon product of C_{10+} .

(3) Oxygenates are not synthesized on Site 2, since there is no discontinuity in the slope at C_{10+} .

Until recently we were tempted to relate the two types of sites to differences in localized alkali content, as did König and Gaube, since all of the iron catalysts elsewhere on which this effect has been reported contain potassium and it is well documented that selectivity shifts toward heavier hydrocarbons with increasing alkali concentration. However, the fact that a sharp discontinuity on a Flory plot was also observed with a MnO/Fe catalyst to which K was not added in preparation suggests that other effects may also be involved. Conceivably the MnO/Fe catalyst may have been contaminated with a trace of alkali but the change in α at C_{11} is much more marked than that in the results of König and Gaube.

The observations of Dyer *et al.* of a single α with (H_2/CO) feed ratios of 2.0 to 0.71 on a reduced fused magnetite catalyst containing potassium also indicates that other effects are important. Their catalyst was very similar to ours and was prerduced in hydrogen in a separate vessel by a procedure very similar to ours. Yet they observed a single α under conditions where we observe a double α . This suggests that the effect is associated in a subtle way with certain changes in the structure of the iron which may occur with time or with procedures for bringing a reactor on stream.

SUMMARY

Our study of the Fischer-Tropsch synthesis on three different types of iron catalysts in a well-stirred slurry reactor shows a product distribution with a marked break at about C_{10} on a Flory plot in each case. At higher carbon numbers hydrocarbons are produced with a much higher probability of chain growth than for lower carbon numbers, but oxygenates are unaffected. The carbon number distribution is interpreted in terms of a dual site mechanism that can be described by an extended Flory equation which accounts for the fraction of product formed on each type of site.

ACKNOWLEDGMENTS

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