

#### **IV. The Effect of 1-Alkene Addition on Hydrocarbon Product Distribution on a Cobalt Catalyst**

##### **Abstract**

The cobalt-catalyzed reactions of  $C_2H_4$ ,  $C_3H_6$ , or  $1-C_4H_8$  added to synthesis gas in concentrations ranging from 0.5 to 1.2 mol.% of total feed were studied at 220°C, and 0.45 to 1.48 MPa.  $H_2/CO$  feed ratios were varied between 1.45 to 2.25 and  $H_2 + CO$  conversions between 5 and 30% were observed.

1-Alkenes incorporate into growing chains on the catalyst surface, probably by initiating and/or terminating the chain growth process. Only ethene may propagate chain growth significantly. The propensity of the 1-alkenes to incorporate decreases with increasing carbon number of the 1-alkene and is affected by the extent of competitive reactions, notably hydrogenation to the alkene and isomerization to the 2-alkene. Incorporation is most evident in products above about  $C_{10}+$ .

The double- $\alpha$  behavior exhibited by most Fischer-Tropsch catalysts can be interpreted as the sum of two growth processes, one a stepwise single-carbon growth process and the other a 1-alkene incorporation process. Many of the effects of process variables on the hydrocarbon selectivity of Fischer-Tropsch catalysts are consistent with this theory.

#### IV. A. Introduction

Section III describes the effect of process variables on the product composition and carbon number distribution of a cobalt catalyst. The sensitivity of the hydrocarbon distribution to process variables seems to be greater than that encountered with iron catalysts. Therefore, secondary reactions of 1-alkenes formed by the primary synthesis may be important in determining the final product composition. These reactions are primarily chain incorporation, hydrogenation, and isomerization of a 1-alkene to the 2-alkene. The objective of this part of the study was to develop a more fundamental understanding of the role of 1-alkenes in the hydrocarbon chain growth process on Fischer-Tropsch catalysts.

A large number of studies have been published on the effects observed upon addition of 1-alkenes to synthesis gas in contact with iron catalysts, but relatively little on effects observed on cobalt. Summaries of the literature, focussing on iron, have been published recently.<sup>2-5</sup> In most cases, with either iron or cobalt catalysts, the possibility of chain incorporation has been examined with respect to light hydrocarbon products. There is general agreement that ethene is much more reactive than propylene or butene, but the extent of incorporation is dependent on many variables. Incorporation into light products on iron typically appears to be minor.

Our two previous studies with reduced fused magnetite catalysts in which we added light 1-alkenes to synthesis gas indicated that chain incorporation could be observed but was minor in amount. Then we were focussing on carbon products mostly of C<sub>10</sub> and less. A new feature from our present study is the observation that effects are much more noticeable for higher molecular weight products. In agreement with earlier

work, we conclude that incorporation occurs more readily on cobalt than on iron catalysts. The following summarizes the literature on cobalt.

In early work, Gibson and Clarke<sup>6</sup> fed 5.1 mol.% labelled  $^{14}\text{C}$ CO, 49.1 mol.%  $\text{C}_2\text{H}_4$ , and 45.8 mol.%  $\text{H}_2$  to a 100Co:5ThO<sub>2</sub>:8MgO:200kieselguhr catalyst. Operating conditions of their fixed-bed reactor were 185°C, 0.1 MPa, and they achieved about 50%  $\text{C}_2\text{H}_4$  conversion. The average radioactivity at each carbon atom within the  $\text{C}_6$  and  $\text{C}_7$  1-alkenes was determined. Because the radioactivity was significantly lower nearer the end of the  $\text{C}_6$  and  $\text{C}_7$  chains, they concluded that ethene both initiates and terminates the chain growth process. They were unable to determine if ethene propagates chain growth.

Schulz et al.<sup>7</sup> performed the most complete study of the effects of adding selected labelled compounds during synthesis on cobalt. They added ethene ( $^{14}\text{C}$ ), propene (1- $^{14}\text{C}$  and 2- $^{14}\text{C}$ ), butane (1- $^{14}\text{C}$ ), 2-methylpentadecane (15- $^{14}\text{C}$ ), and 1-hexadecene (1- $^{14}\text{C}$ ) at concentrations ranging from 0.10 to 0.78 vol.% of total synthesis gas feed. They ran their fixed-bed reactor at 185-190°C, 0.1 MPa, with  $\text{H}_2/\text{CO}=2$  synthesis gas at a space velocity of 75 NI/min/liter of catalyst (unreduced basis). For the 1-alkenes studied, hydrogenation to alkanes was the predominant reaction, with 67 mol.% of the added ethene hydrogenated, 51 mol.% of the propene, and 79 mol.% of the 1-hexadecene. Of the added 1-alkene which was not hydrogenated, they found that 88 mol.% of the ethene was incorporated into growing chains, 63 mol.% of the propene, and 31 mol.% of the 1-hexadecene, thus producing higher molecular weight products.

Schulz and coworkers also examined the radioactivity of products at carbon numbers greater than the added component and noted two different behaviors, one for ethene and one for both propene and 1-hexadecene. Adding ethene, products at even

carbon numbers had higher radioactivity than those at odd carbon numbers, indicating that ethene can propagate growing hydrocarbon chains; the levels of radioactivity at odd carbon numbers were consistent with the hypothesis that ethene can terminate and/or initiate growing chains. In contrast, propene was found to propagate growing chains only slightly, producing monomethyl branched compounds. Schulz and coworkers conclude that  $C_3+$  1-alkenes must be involved predominantly in chain termination and initiation. The added alkanes underwent negligible reaction at the process conditions studied. No data on the effect of process variables on the rate of incorporation were presented.

In a report to the German government, Schulz<sup>7a</sup> reported the results of extensive studies on five cobalt catalysts, all containing  $ThO_2$  on aerosil (a silica gel). Three contained MgO in addition. Reaction conditions were 175 to 185°C and 9 bar. The compositions containing MgO showed a much more pronounced double  $\alpha$  than those without and gave a considerably higher fraction of  $C_{10}+$ . In the presence of MgO, the  $C_2H_4$  in the product was substantially less than when MgO was absent. Although this was not commented on by the author, this seems to be additional evidence that  $C_2H_4$  was being incorporated into  $C_{10}+$  product and by a mechanism influenced by MgO.

Kibby et al.<sup>8</sup> co-fed ethene or propene at 10 vol.% with a  $(H_2/CO)_{in}$  of 1 and 2 to a reduced 30 wt.% Co, 5 wt.%  $ThO_2$ , on 65 wt.%  $Al_2O_3$  catalyst in an internal recycle reactor operated at 195°C and 0.79 MPa. To calculate yields to various product classes, Kibby et al. measured the composition of the light gases ( $C_1-C_4$ ) and determined the yield to  $C_5+$  as the difference between the CO consumption and the  $C_1-C_4$  yield. Present analysis of their data at  $(H_2/CO)_{in}=2$  indicates that the wt.% of  $C_5+$  hydrocarbons increased to 62.5 wt.% with ethene addition and 54.7 wt.% with propene

addition, as compared with 44.6 wt.% with no added 1-alkenes. With ethene addition the wt.% of C<sub>5</sub>+ hydrocarbons increased to 85.4 wt.% at (H<sub>2</sub>/CO)<sub>in</sub> = 1 from 62.5 wt.% at (H<sub>2</sub>/CO)<sub>in</sub> = 2. This effect of decreasing incorporation with increasing H<sub>2</sub>/CO ratio is consistent with a set of reaction pathways for alkenes in which hydrogenation and incorporation both consume alkenes competitively; thus, at higher H<sub>2</sub>/CO, more alkenes are hydrogenated and consequently less are incorporated in growing chains. In separate experiments at feed conditions similar to Gibson and Clarke,<sup>7</sup> Kibby et al. also observed "hydropolymerization" of ethene, propene, and 1-butene.

Most alkene addition studies on cobalt by various researchers were performed in conjunction with a more extensive study of feed additions to iron catalysts; as a result, cobalt catalysts were studied at only a few different process conditions. Although 1-alkenes appear to be incorporated into growing chains on cobalt, there is little agreement as to the extent to which incorporation affects the product distribution; further, no studies exist which cover a wide range of process conditions, for example only Kibby and co-workers performed experiments at above atmospheric pressure.

#### IV. B. Experimental Procedure

Catalyst composition, reduction procedure and experimental methods are described in previous sections. After reduction, the catalyst was allowed to achieve stable activity and selectivity. Process variables were then manipulated to provide data over a broad operating range, during the course of a single run that lasted over several hundred hours. Data were obtained at 220° C, 0.45 to 1.48 MPa and synthesis gas flow rate between 0.015 and 0.030 NI/gcat/min with inlet H<sub>2</sub>/CO ratios of 1.45 to 2.25 yielding H<sub>2</sub> + CO conversions between 5 and 30%.

The 1-alkenes were co-fed with the synthesis gas feed in about 2 mol.% of a single 1-alkene in CP Grade CO (Matheson and MedTech Gases, Inc.); each of three 1-alkenes, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>6</sub>, and 1-C<sub>4</sub>H<sub>8</sub>, were added in quantities to comprise from 0.5 to 1.2 mol.% of total feed. At these feed rates, the added 1-alkenes are present in concentrations ranging from 2 to 10 times those observed during normal synthesis. These light 1-alkenes were chosen because they are not condensed to any significant extent in either our hot or cold traps<sup>10,11</sup> and, therefore, analysis of these light 1-alkenes is less subject to error. 15 material balances were performed adding C<sub>2</sub>H<sub>4</sub>, six adding C<sub>3</sub>H<sub>6</sub>, and eight adding C<sub>4</sub>H<sub>8</sub>.

For each material balance in which 1-alkenes were added, a material balance was performed at similar process conditions without 1-alkenes added, so that comparison of hydrocarbon selectivity with and without alkene addition could be made directly.

#### IV. C. Evidence for Incorporation on Cobalt

Figures IV-1a, IV-1b, and IV-1c show Schulz-Flory diagrams comparing ethene, propene, and 1-butene additions to material balances at similar process conditions without added alkenes. To avoid presenting dilution effects in these results, data are normalized to remove the "added" carbon number, according to equation 1:

$$\text{Normalized}(M_n) = \frac{\text{Observed}(M_n)}{(1 - \text{Observed}(M_{\text{added}}))} \quad (1)$$

In equation 1, Observed(M<sub>n</sub>) are the actual mole fraction data and the Observed(M<sub>added</sub>) is the mole fraction at the carbon number added. Thus, for Figure IV-1a, the actual mole fraction data are divided by (1-M<sub>2</sub>); the normalized M<sub>2</sub> are removed from the plot

and thus the normalized data, the first 20 carbon numbers of which are shown on the plot, sum to unity. The figures show that 1-alkenes incorporate into growing chains on the catalyst surface, as evidenced by the increase in products at higher carbon numbers. This increase in products predominantly in the  $\alpha_2$  region of the Schulz-Flory plot will be discussed in detail below.

A measure of the extent to which the  $C_n$  added alkene incorporated was determined by comparing the  $C_{n+1}/C_{n-1}$  of the material balance with added alkene to the base case material balance. If  $C_n$  alkene incorporates, then the  $C_{n+1}$  hydrocarbon is affected most dramatically, while the  $C_{n-1}$  hydrocarbon yield remains unchanged, assuming negligible cracking. Thus, the higher this  $C_{n+1}/C_{n-1}$  ratio is relative to the base case, the more the  $C_n$  alkene can be inferred to incorporate.

Figures IV-2a through IV-2c show the ratio of  $C_{n+1}/C_{n-1}$  for the  $C_n$  addition material balance divided by the  $C_{n+1}/C_{n-1}$  for the base case versus  $P_{H_2}/P_{CO}$  for ethene, propene, and 1-butene additions respectively. Although the data scatter, ethene can be inferred to incorporate more than propene, which incorporates more than 1-butene. Similar trends upon co-feeding 1-alkenes with synthesis gas were reported on cobalt<sup>7,8</sup> and on iron.<sup>7</sup> Increasing  $H_2/CO$  ratio decreases incorporation, seen most readily in Fig. IV-2a. This is consistent with the observation that the rate of hydrogenation of alkenes is approximately proportional to the  $H_2/CO$  ratio.<sup>1</sup> In using the  $C_{n+1}/C_{n-1}$  criterion with respect to ethylene addition, it should be recalled that methane formation occurs by a mechanism that does not involve a carbon species polymerization.

In most previous studies with olefin addition, either radioactive tracers were used or relatively high concentrations of olefin were added, e.g., 5 to 10 mol% of the synthesis

gas feed, to magnify reaction effects and make possible overall material balances to search for the fate of the added olefin. The approach here was to use much lower added olefin concentrations that were closer to those formed by the normal synthesis, so that the results might be more representative of ordinary practice. This gain was purchased at the loss of being able to make useful material balances on the added component.

To verify that added alkenes were not undergoing cracking to any significant extent, Figure IV-3 shows that the rate expression for the rate of production of methane<sup>9</sup> fits the data collected here, even when alkenes are added to the feed. There are reports from studies on iron that added ethene may have an inhibiting effect on methanation, but these seem to have occurred only with much higher ethene concentrations. Adesima et al.<sup>5</sup> in a study on a cobalt catalyst at 0.11 MPa and 200°C report that methane production rates were unchanged upon addition of 1 to 2% ethene. Figure IV-4 shows a Schulz-Flory diagram for two material balances performed without added alkene and 1850 hours-on-stream apart. Within the scatter of the data, the hydrocarbon selectivity is unchanged with time.



#### IV. D. Mathematical Modelling of Incorporation

To develop a fundamental understanding of the effect of incorporation on product distributions, mathematical models for incorporation were developed. These models are complex, but their mathematical behavior closely parallels that of a single- $\alpha$  distribution. The double- $\alpha$  is postulated to be the sum of two growth processes, one a stepwise single-carbon growth process, represented by  $\alpha_1$ , and the other a 1-alkene incorporation process, represented by  $\alpha_2$ .

Alkene incorporation adds mathematical complexity to the mathematical models of the chain growth process and introduces a number of adjustable parameters. Alkenes can be assumed to either initiate and terminate hydrocarbon chains only or initiate, terminate, and propagate chains. These two behaviors are treated separately below.

All formulations for alkene incorporation are somewhat complex, have a large number of parameters, and require knowledge of relative rates of surface reaction that cannot be measured directly. To develop a useful model, the limiting behavior of these different models is shown to match that of a most probable, single- $\alpha$  distribution, except at very low carbon numbers. This single- $\alpha$  chain growth probability is therefore essentially a lumped parameter which accounts for contributions to the chain growth process from the incorporation reactions of the entire series of alkenes.

**IV. D. 1. Initiation and Termination by 1-Alkenes.** If 1-alkenes initiate and terminate growing chains, then the mole fraction of products observed at a given carbon number ( $M_n$ ) depends not only on the mole fraction one carbon number before it ( $M_{n-1}$ ), but also on the mole fractions of all the carbon numbers before it, ( $M_{n-2}$ ,  $M_{n-3}$ , etc.).

Equation 2 shows how the simple, no-incorporation chain growth process represents the dependence of mole fraction at carbon number  $n$  on the mole fraction at carbon number  $n-1$ , as

$$M_n = p_1 M_{(n-1)} \quad (2)$$

In equation 2,  $p_1$  is analogous to a Schulz-Flory chain growth probability,  $\alpha$ .

To develop an equation for 1-alkene incorporation, only ethene and propene are assumed to initiate and terminate alkenes, for the purposes of illustration. This analysis can be easily extended by analogy to include initiation or termination by any number of alkenes; however, for simplicity, only this model is presented.

If ethene and propene can initiate or terminate growing chains, then the mole fraction for  $C_4+$  is given by:

$$M_{n>3} = p_1 M_{(n-1)} + p_2 M_{(n-2)} + p_3 M_{(n-3)} \quad (3)$$

In equation 3,  $p_1$  is the probability of  $C_1$  addition,  $p_2$  is the probability of  $C_2$  initiation or termination, and  $p_3$  is the probability of  $C_3$  initiation or termination.

To develop a closed-form expression for the mole fraction at all carbon numbers, it is noted that, since only initiation or termination can occur, a  $C_n$  can only be formed by either all  $C_1$  growth (like equation 2), all  $C_1$  growth except for having incorporated one  $C_2$ , or all  $C_1$  growth except for having incorporated one  $C_3$ . Thus, the mole fractions of all components can be expressed in terms of an arbitrary constant,  $M_0$ .  $M_0$  can be thought of as the hypothetical mole fraction at carbon number zero. Equations 4-7 show the mole fraction in terms of this arbitrary constant,  $M_0$ .

In equation 7, the first term is the stepwise growth process adding  $C_1$  units one-at-a-time,

$$M_1 = p_1(1-p_1) M_0 \quad (4)$$

$$M_2 = p_1^2(1-p_1) M_0 \quad (5)$$

$$M_3 = p_1^3(1-p_1) M_0 + p_2 p_1(1-p_1) M_0$$

$$M_{n > 3} = p_1^n(1-p_1) M_0 + p_2 p_1^{(n-2)}(1-p_1) M_0 + p_3 p_1^{(n-3)}(1-p_1) M_0 \quad (7)$$

the second term accounts for  $C_2$  initiation or termination, and the last term accounts for  $C_3$  initiation or termination.

To remove the arbitrary constant, the mole fractions are summed from  $n=1$  to  $\infty$  and equated to 1. Thus, the constant is found to be,

$$M_0 = \frac{1}{p_1(1 + p_2 + p_3)} \quad (8)$$

Substituting equation 8 into equations 4-7, the complete distribution can be described in terms of  $p_1$ ,  $p_2$ , and  $p_3$ , by the following equations:

$$M_1 = \frac{(1 - p_1)}{(1 + p_2 + p_3)} \quad (9)$$

$$M_2 = \frac{p_1(1 - p_1)}{(1 + p_2 + p_3)} \quad (10)$$

$$M_3 = \frac{(p_1^2(1 - p_1) + p_2(1 - p_1))}{(1 + p_2 + p_3)} \quad (11)$$

$$M_{n > 3} = \frac{(p_1^{(n-1)}(1-p_1) + p_2 p_1^{(n-3)}(1-p_1) + p_3 p_1^{(n-4)}(1-p_1))}{(1 + p_2 + p_3)} \quad (12)$$

Figure IV-5 shows a theoretical product distribution for  $p_1=0.7$ ,  $p_2=0.3$ , and  $p_3=0.1$ .  $p_2 > p_3$  matches the experimental evidence, presented in Figures IV-2a through IV-2c, which show that ethene incorporates more than propene. The multiparameter initiation and termination model appears to be very similar to a single- $\alpha$  model at carbon numbers above 3.  $C_2$  and  $C_3$  hydrocarbons are produced in lower quantities than would be observed by a Schulz-Flory mechanism; this behavior of  $C_2$  lying below the line predicted by Schulz-Flory mathematics has been observed previously on a number of catalysts operated over a wide range of conditions.<sup>12</sup>

**IV. D. 2. Initiation, Termination, and Propagation by 1-Alkenes.** The above model for the hydrocarbon products of the Fischer-Tropsch synthesis describes the product distribution if only initiation or termination by alkenes occurs; however, on cobalt catalysts, Schulz et al.<sup>7</sup> have observed propagation by ethene and, to a lesser extent, propene.

Novak et al.<sup>13</sup> developed a model to predict carbon number distribution by  $C_1$  chain growth combined with independent  $C_2$  addition. Their model has four parameters,  $\alpha$  (a stepwise chain growth probability),  $\Gamma$  (a reactivity ratio of  $C_2$  to  $C_1$  addition processes),  $\theta_1$  (the mole fraction of  $C_1$ ), and  $\theta_2$  (the mole fraction of  $C_2$ ). The product distribution is derived to be:

$$M_{n > 2} = \frac{(\Theta_2 - \Theta_1 f_2) f_1^{(n-1)} + (\Theta_1 f_1 - \Theta_2) f_2^{(n-1)}}{(f_1 - f_2)} \quad (13)$$

$$\text{where } f_{1,2} = \frac{\alpha}{2(1+\Gamma\alpha)} \pm \left[ \left( \frac{\alpha}{2(1+\Gamma\alpha)} \right)^2 + \frac{\Gamma\alpha}{(1+\Gamma\alpha)} \right]^{1/2} \quad (14)$$

$f_{1,2}$  are the roots of the quadratic equation;  $M_1$  is the same as  $\Theta_1$ , and  $M_2$  is the same as  $\Theta_2$ .

Equation 13 appears qualitatively similar to the double- $\alpha$  formulation typically used to describe Fischer-Tropsch product distributions; however,  $f_2$  in equation 13 is negative (see equation 14), causing oscillation of the product distribution. Schulz et al.<sup>7</sup> present data from ethene additions to cobalt which show oscillating levels of radioactivity, with even carbon numbers higher than odd carbon numbers; such behavior is consistent with this type of formulation.

Oscillations are not observed in experimental carbon number distributions for at least two reasons. First, if the ratio of  $C_2$  propagation to  $C_1$  is low (i.e.  $\Gamma$  is almost zero), then the oscillations are observed at only very low carbon numbers. Second, there can be a great deal of "scatter" in experimentally-obtained hydrocarbon distributions which causes subtleties, such as minor oscillations, to be masked.

Figure IV-6 shows a theoretical product distribution based on ethene both initiating, terminating, and propagating chains on the catalyst surface, for  $\Theta_1=0.5$ ,  $\Theta_2=0.1$ ,  $\alpha=0.62$ , and  $\Gamma=0.2$ . As with the model which accounts for only initiation and termination, the model is similar to a single- $\alpha$  distribution at high carbon numbers.

Thus, in summary, both multiparameter incorporation behaviors can be well represented by a lumped parameter, single- $\alpha$  chain growth process, shown in equation 2.

This lumped parameter is the probability that a  $C_n$  hydrocarbon will become a  $C_{n+1}$  hydrocarbon by any alkene incorporation process and, therefore, represents the sum of all alkene incorporation processes.

Using sophisticated models that account for a large number of surface processes is inappropriate, because experimentally-obtained hydrocarbon data do not provide the resolution necessary to determine these models' parameters accurately. For example, accounting for  $C_1$ ,  $C_2$ , and  $C_3$  initiation and termination and  $C_1$  and  $C_2$  propagation, all of which have been observed experimentally, requires a model with at least seven adjustable parameters; this many adjustable parameters should not be estimated from Fischer-Tropsch product distribution data.

#### IV. E. A Model for the Double- $\alpha$ Distribution

A double- $\alpha$  model has been developed to describe the mole fraction of products at carbon number  $n$  for the  $C_3+$  products.<sup>12</sup> This can be expressed as<sup>9,14</sup>:

$$M_n = x_1(1-\alpha_1)\alpha_1^{(n-1)} + (1-x_1)(1-\alpha_2)\alpha_2^{(n-1)} \quad (15)$$

In equation 15,  $x_1$  can be visualized as the mole fraction of products synthesized by the " $\alpha_1$ " mechanism; therefore,  $(1-x_1)$  is the mole fraction of products synthesized by the " $\alpha_2$ " mechanism.

In Figures IV-1a through IV-1c, the difference in the Schulz-Flory diagrams between alkene addition runs and base case runs is most notable at higher carbon numbers. Based on this observation, the " $\alpha_1$ " site is postulated to be the site on which normal stepwise addition of  $C_1$  units occurs and the " $\alpha_2$ " process is assumed to be the site which accounts for the incorporation processes. As discussed above, the sum of all

incorporation processes can be approximated by a single chain growth probability, in this case  $\alpha_2$ . In this theory,  $x_1$  represents the mole fraction of products synthesized by the simple stepwise growth process of  $C_1$  units and  $(1-x_1)$  is the mole fraction of products synthesized by the sum of all incorporation processes.

This model is not catalyst-specific, and the results of the alkene addition experiments can be well interpreted in its terms. When alkenes are added to the feed, only the mole fraction of products synthesized by alkene incorporation should change relative to the base case material balance without alkenes added; thus, adding alkenes should decrease  $x_1$ , while  $\alpha_1$  and  $\alpha_2$  should remain constant.

Figure IV-7 shows the Schulz-Flory diagrams of the ethene addition and base case material balances. The solid line is the fit of the double- $\alpha$  model to the base-case data. To fit the data from the ethene addition studies, the values of  $\alpha_1$  and  $\alpha_2$  are retained, and only the value of  $x_1$  is changed. The resulting fit is shown as the dashed line. More heavy products are produced by alkene incorporation processes when alkenes are added to the feed; thus, the value of  $x_1$  decreases.

Figure IV-8 shows the ratio of products with ethene addition to the ratio of products from base case material balances. The change in the normalized mole fractions is well predicted by the model.

#### **IV. F. Explanations of Selectivity Trends**

**IV. F. 1. Cobalt.** Process variable effects observed during normal synthesis<sup>1</sup> can be explained by the effects of the process variables on the concentration of 1-alkenes and

thus on the rate of incorporation. Table IV-1 shows the observed process variable effect on selectivity and the postulated explanation, based on incorporation being an important mechanism for chain growth. Figure IV-9 shows the effect of space velocity on the yield of  $C_1$  (undesired) and  $C_{10+}$  (desired). Data labels show the *in situ* ethene to ethane ratio. At higher space velocities (lower total conversions) less hydrogenation of alkenes occurs, as indicated by the increase in ethene to ethane ratio; thus, more high molecular weight products are synthesized via the " $\alpha_2$ " mechanism. Figure IV-10 shows the effect of *in situ*  $H_2/CO$  on the yield of  $C_{10+}$ . Data labels show the *in situ* ethene to ethane ratio. At higher  $H_2/CO$  ratios, a greater fraction of ethene is hydrogenated, reducing the fraction of products synthesized by the " $\alpha_2$ " mechanism. Figures IV-9 and IV-10 provide experimental evidence that the theory is consistent with actual behavior of a cobalt catalyst.



**IV. F. 2. Iron.** Many of the effects of process variables on the product distribution on iron catalysts can be interpreted in terms of their effects on the concentration of 1-alkenes and their degree of adsorption onto the catalyst, and thus on the degree of their incorporation into the product. Thus increased potassium loading increases the yield of heavy products, but it also decreases secondary hydrogenation and isomerization, thereby increasing 1-alkene concentration and the probability of chain incorporation. Increasing the  $H_2/CO$  ratio decreases the yield of heavy products by increasing the hydrogenation of 1-alkenes and thereby decreasing incorporation.

Sorting out these and other effects in detail is complex since most data available are from fixed bed reactors in which composition varies with position. For example, competitive adsorption between 1-alkenes and CO can cause markedly different effects at low and high degrees of conversion with  $H_2$ -rich gas, and these effects are integrated in the exit product. Further, pressure and temperature can affect competing reactions differently.

#### **IV. G. Conclusions**

The cobalt-catalyzed reactions of light 1-alkenes added to synthesis gas feed have been studied. Reaction conditions were 220°C, 0.45 to 1.48 MPa utilizing a synthesis gas flow rate between 0.015 and 0.030 NI/gcat/min, with  $H_2/CO$  ratios of 1.45 to 2.25.  $C_2H_4$ ,  $C_3H_6$ , and 1- $C_4H_8$  were added to the synthesis gas feed in concentrations ranging from 0.5 to 1.2 mol.% of total feed. For each material balance in which 1-alkenes were added, a "base case" material balance was performed at similar process conditions without 1-alkenes added. Material balances without added 1-alkenes were also repeated

to verify catalyst selectivity stability.

1-Alkenes are found to incorporate into growing chains on the catalyst surface and are thought to initiate and terminate the chain growth process. The relative reactivity of the 1-alkenes decreases with increasing carbon number. On the basis of data in the literature, only ethene is believed to propagate chain growth.

A theory is presented which postulates that the double- $\alpha$  is the sum of two growth processes, one a stepwise single-carbon growth process (the  $\alpha_1$  mechanism) and the other the sum of the 1-alkene incorporation processes (the  $\alpha_2$  mechanism). Many of the effects of process variables on the hydrocarbon selectivity of Fischer-Tropsch catalysts are consistent with this model.

#### IV.H. Nomenclature

$f_{1,2}$  - parametric constants for ethene propagation model.

$M_{\text{added}}$  - mole fraction of products at carbon number of added alkene.

$M_0$  - constant, the mole fraction of products at carbon number "zero".

$M_n$  - mole fraction of products at carbon number n.

n - carbon number.

Normalized( $M_n$ ) - normalized mole fraction, with  $M_{\text{added}}$  removed.

Observed( $M_n$ ) - mole fraction data, observed experimentally.

$p_1$  - the probability of  $C_1$  addition.

$p_2$  - the probability of  $C_2$  initiation or termination.

$p_3$  - the probability of  $C_3$  initiation or termination.

$x_1$  - mole fraction of products produced by  $\alpha_1$  mechanism.

#### *Greek*

$\alpha$  - single chain growth probability.

$\alpha_1$  - chain growth probability for stepwise addition of  $C_1$ .

$\alpha_2$  - chain growth probability for incorporation of alkenes.

$\Gamma$  - ratio of reactivity of  $C_2/C_1$ .

$\Theta_1$  - mole fraction of  $C_1$ .

$\Theta_2$  - mole fraction of  $C_2$ .

#### IV.I. Literature Cited

- (1) Yates, I.C.; Satterfield, C.N. "Hydrocarbon Selectivity of Cobalt Fischer-Tropsch Catalysts," Energy & Fuels, submitted.
- (2) Snel, R.; Espinoza, R.L. J. Mol. Cat. 1987, **43**, 237.
- (3) Boelee, J.H.; Custers, J.M.G.; van der Wiele, K. Appl. Catal. 1989, **53**, 1.
- (4) Tau, L-M.; Dabbagh, H.A.; Davis, B.H. Energy & Fuels, 1990, **4**, 94.
- (5) Adesima, A.A.; Hudgins, R.R.; Silveston, P.L. Appl. Catal. 1990, **62**, 295.
- (6) Gibson, E.J.; Clarke, R.W. J. Appl. Chem. 1961, **11**, 293.
- (7) Schulz, H.; Rao, B.R.; Elstner, M. Erdol und Kohle 1970, **23**, 651.
- (7a) Schulz, H. Report to the Bundesministerium für Forschung und Technologie, "Katalysatoren und Selektivitätslenkung bei der Fischer-Tropsch Synthese," BMFT-FB-T80-124, November 1980.
- (8) Kibby, C.L.; Pannell, R.B.; Kobylinski, T.P. A.C.S. Pet. Chem. Preprints 1984, **29(4)**, 1113.
- (9) Yates, I.C. The Slurry-Phase Fischer-Tropsch Synthesis, Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, Massachusetts, 1990.
- (10) Hanlon, R.T.; Satterfield, C.N. Energy & Fuels, 1988, **2**, 196.
- (10a) Chanenchuk, C.A.; Yates, I.C.; Satterfield, C.N. Energy & Fuels, submitted.

- (11) Matsumoto, D.K., The Effects of Selected Process Variables on the Performance of an Iron Fischer-Tropsch Catalyst, Sc.D. Thesis, Massachusetts Institute of Technology, Cambridge, Mass., 1987.
- (12) Donnelly, T.J.; Yates, I.C.; Satterfield, C.N. Energy & Fuels 1988, 2, 734.
- (13) Novak, S.; Madon, R.T.; Suhl, H. J. Chem. Phys., 1981, 74, 6083.
- (14) Huff, G.A., Jr., Fischer-Tropsch Synthesis in a Slurry Reactor, Sc.D. Thesis, Massachusetts Institute of Technology, Cambridge, Mass., 1982.