5.4.3 Proposed Reaction Networks for Hydrogenation and Chain Growth
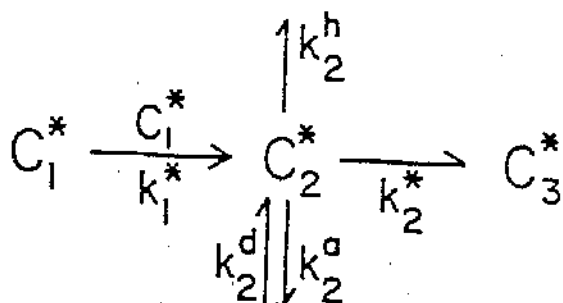   Intermediates:

In many of the proposed FT reaction schemes (33,87,16) the
chain building reactions are envisioned as a series of reactions
involving the insertion of a single carbon containing monomer into a
growing chain. This reaction network is useful describing the
conformity of the product distribution to the Schulz Flory
polymerization scheme and is presented in such discussions in sections
4.6 and 5.3. However, the kinetic model based on this simple reaction
scheme may not readily account for the influence of secondary reactions
such as hydrogenation, isomerization and olefin incorporation on the
hydrocarbon product distribution.

The results presented in section 5.4.1 indicate that a common site
may be responsible for both the chain growth and secondary reactions but
there is experimental evidence indicating that different intermediates
are involved in these reactions. In section 5.4.2.1 these reaction
sequence involving a common chain growth/secondary reaction intermediate
is compared to the experimental results obtained with both the ethylene
containing and pure CO/H_2 mixtures. The inconsistancies found with this
model lead to the development of the reaction sequence involving
seperate surface intermediates for the chain growth and secondary
reactions.

In the last two sections (5.4.2.3 and 5.4.2.4) the experimental
results obtained with the 1-pentene CO/H_2 feed are presented and found
to be consistent with this mechanism.

5.4.3.1 Common Intermediate for Hydrogenation and Chain Growth

The series reaction sequence presented in section 4.6, given below, is now discussed in terms of the secondary reactions of ethylene hydrogenation and chain initiation.

$$C_1^* \xrightarrow[k_1^*]{C_1^*} C_2^* \xrightarrow[k_2^*]{} C_3^* \qquad\qquad 4.6.5$$

(with k_2^h above and k_2^d, k_2^a below C_2^*)

In this reaction model the two carbon surface intermediate C_2^* can either react to form C_3^*, desorb as ethylene, or hydrogenate to ethane. Ethylene in the feed gas can adsorb and form C_2^*. The presence of relatively high concentrations of ethylene in the feed gas enhances the surface concentrations of C_2^*. Ethane results from the direct hydrogenation of C_2^*. The enhanced C_3 yields obtained with the ethylene/CO/H_2 feed are due to the increase in the overall rate of the $C_2^* \rightarrow C_3^*$ reaction since the surface concentration of C_2^* is enhanced. For this reaction sequence the ratio of the hydrogenation rate (r_H) to the chain growth (propagation) rate (r_p) is given by

$$\frac{r_H}{r_p} = \frac{k_2^h \, C_2^*}{k_2 C_2^* C_1^*} \qquad\qquad 5.4.3$$

where k_2^h includes the functional dependence of hydrogen.

If one assumes that the monomer concentration C_1^* is relatively constant and equal for both the ethylene and pure CO/H_2 feeds one can rewrite this ratio as

$$\frac{r_H}{r_p} = \frac{k^h}{k'} \qquad\qquad 5.4.4$$

where $k_2' = k_2 C_1^*$

The ratio of the ethylene hydrogenation rate to the ethylene propagation rate is constant and dependent only on the surface reaction rate constants. Therefore any increase in the C_2^* surface concentration should result in a proportional increase in both the ethane and $C_{n>2}$ product yields if the reaction network given by equation 4.6.5 is valid. However the results presented in sections 5.2 and 5.3 indicate otherwise.

Table 5.4.2 contains four numbered columns. Columns #1 and #2 are tabulated data taken from the previous two sections. The fraction of ethylene consumed using the ethylene/CO/H_2 mixture at the conditions indicated in the table are listed in column #1. Column #2 gives the fraction of feed ethylene hydrogenated at these conditions. In all cases the amount of feed ethylene hydrogenated is at least 15 times greater than the amount consumed in chain growth reactions. This is an important point to remember once the meaning of the values in columns #3 and #4 is made evident.

The SF product distribution plots (sections 4.5 and 5.3) for all catalysts and conditions studied consistently show the C_2 product yield

Table 5.4.2 Ethylene Fractions Consumed via Secondary Reactions

Catalyst	GHSV (hr^{-1})	Pressure atm	Feed Fraction Consumed in Chain Growth Reactions (1)	Feed Fraction Hydrogenated $C_2H_4/CO/H_2$ (2)	$\dfrac{x_{C_2}}{x_C\ SF}$ CO/H_2	Fraction deviation from ideal SF yield $(1-\eta corp)$
Fe	5100	1.0	.032S	.37	.25	.62
	825 (2)	1.0	.03	.43	.3	.77
	4443	7.8	.02	.3	.15	.37
	526	7.8	.02	.6	.226	.58
FeCo	4381	1.0	.01	.2	.1	.52
	494 (2)	1.0	.025	.4	.216	.44
	2758	7.8	.01	.36	.1	.75
	467	7.8	.025	.6	.28	.65
Co	24100	1.0	.03	.12	.12	.44
	15700	1.0	.04	.23	.1	.5
	1368	7.8	.005	.13	.214	.62
	142	7.8	.015	.64	.23	.66

(1) Based on calculating the C_2 yield required for SF behavior (Y_{C_2SF} subtracting the observed C_2 yield Y_{C_2Obs} from this value, and dividing the difference by Y_{SFC_2}.

(2) GHSV values in brackets correspond to comparable ethylene molar flux rates.

(3) Ethane mole fraction divided by ideal SF C_2 product yeild.

(4) Total C_2 mole fraction divided by ideal SF C_2 product yield.

$(\ln(Y_{C2}))$ lies below the straight line established through the $C_{n>3}$ products. In other words, the C_2^* reaction intermediate does not obey ideal Shulz Flory polymerization kinetics. A probable reason for this deviation may be due to the relatively high propagation rate associated with the C_2^* intermediate compared to the rate of longer chain intermediates. Since the production of all $C_{n>2}$ hydrocarbon chains must at one time exist as a C_2^* intermediate this is a reasonable assumption. If one extrapolates the linear portion of the SF distribution to the two carbon chain ($n = 2$), the ideal SF C_2 product yield ($Y_{C_2}SF$) can be obtained. This represents the total amount of C_2 produced if ideal SF behavior existed for this product. The fractional amount of C_2 consumed ($X_{C_2}SF$) in chain growth reactions can then be calculated by the following equation

$$X_{C_2}SF = \frac{Y_{C_2}SF - Y_{C_2}}{Y_{C_2}SF}$$

where $X_{C_2}SF$ is fraction of C_2 consumed via chain growth

reactions assuming ideal SF behavior for C_2 products

Y_{C_2} measured C_2 product yield

$Y_{C_2}SF$ ideal C_2 product yield

This calculation is performed at the conditions indicated using the CO/H_2 mixture. The corresponding values are listed in column #4. The fraction of ethane produced is determined as follows

$$X_{ethane} = \frac{Y_{ethane}}{Y_{C_2}SF}$$

The ethane fractions are listed in column #3.

Now some qualatitative arguments involving the nature of the C_2 hydrogenation and chain growth intermediate can be made. Comparing the tabulated values in columns 3 and 4, one sees that the fractional deviation (X_{SF}) from the ideal SF C_2 yield typically is between 0.4 and 0.7. If one assumes that Y_{C_2SF} corresponds to the total C_2 products produced, than these fractions (X_{SF}) represent the total amount of C_2 consumed via chain growth reactions. The X_{SF} fractions are at least an order of magnitude greater than the fraction of feed ethylene consumed in chain growth reactions (column #1 in Table 5.4.2). This comparison suggest that ethylene produced via the FT synthesis is more readily available for seconedary chain growth reactions compared to gas phase feed ethylene. It appears that gas phase ethylene does not readily adsorb as a C_2^* chain growth intermediate. Results presented in section 5.4.1 suggest that the hydrogenation and chain growth reactions share a common site but as illustrated in Table 5.4.2 not a common intermediate.

5.4.3.2 A Reaction sequence based on different surface intermediates for hydrogenation and chain growth
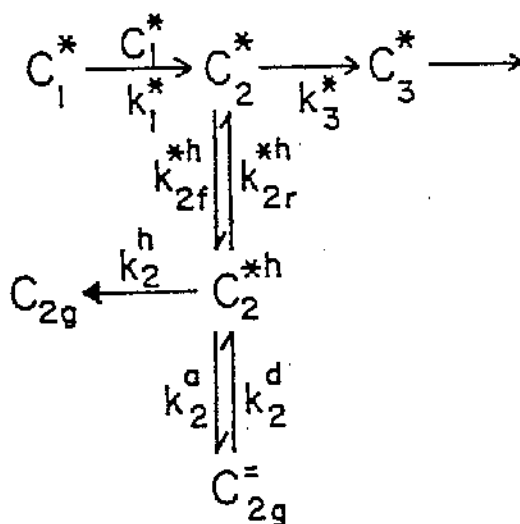
The results presented in the previous section (5.4.2.1) indicate that adsorbed ethylene can react to form possibly more than one C_2 reaction intermediate. This is shown below

$$C_{2g}^= \; - \; C_2^*H \; - \; C_2^*$$
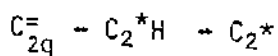
<div align="right">5.4.5</div>

Upon readsorption the gas phase ethylene ($C_2^=g$) undergoes one or more surface reactions to become a surface reaction intermediate for hydrogenation (C_2^{*h}). This intermediate may convert to the FT chain growth intermediate (C_2^*) via subsequent surface reaction possibly on the same catalytic site. The specific nature of the surface intermediates is not needed for the present discussion and in section 6.4 the possible chemical structure of the C_2^* and C_2^{*h} intermediates are discussed.

The series reaction sequence discussed in previous sections can now be written (up to C_3^*) to include the hydrogenation reaction intermediate C_2^{*h}.

$$C_1^* \xrightarrow[k_1^*]{C_1^*} C_2^* \xrightarrow{k_3^*} C_3^* \longrightarrow$$

$$k_{2f}^{*h} \Big\updownarrow k_{2r}^{*h}$$

$$C_{2g} \xleftarrow{k_2^h} C_2^{*h}$$

$$k_2^a \Big\updownarrow k_2^d$$

$$C_{2g}^=$$

5.4.6

where C_{2g}, $c_{2g}^=$ represents gas phase ethane and ethylene respectively

k_2^h rate for C_2^{*h} hydrogenation

k_2a, k_2d are the rate constants for ethylene adsorption and desorption respectively

$k_{2_f}^{*h}$ rate constant for the reaction of C_2^* to C_2^{*h}

$k_{2_f}^{*h}$ rate constant for the reaction of C_2^{*h} to C_2^*

The reaction network depicted in equation 5.4.6 omits the explicit

reaction steps involving adsorption and desorption of the gas phase products and the functional dependency of adsorbed hydrogen. The rates corresponding to these reactions can be considered to be included in the overall reaction rates given in the model.

. The results obtained with the ethylene/CO/H_2 mixture appear to be consistent with the reaction sequence proposed in equation 5.4.6. If one accepts the assumption that the C_2 product yield deviations from SF kinetics are due to enhanced C_2^* propagation rates, then this reaction sequence can readily explain why the feed ethylene predominantly hydrogenates rather than reacts to form longer chain products. With the pure CO/H_2 feed, a large fraction of the ideal SF C_2 yield undergoes chain growth (column #4 in Table 5.4.2). In terms of the proposed reaction sequence this would indicate that the propagation rate constant (k_3^*) is greater than the rate constant associated with the conversion of the chain growth intermediate into the surface reaction intermediate for hydrogenation to ethane.

$$k_3^* \; > \; k_{2_f}^{*h} \qquad\qquad\qquad 5.4.7a$$

The presence of high ethylene partial pressures (such as in the ethylene feed increases the fractional coverage of C_2^{*h} thereby increasing the C_2^* concentration and enhancing the yields of longer chain products. The fact that a much larger fraction of the gas phase ethylene hydrogenates rather than enters into chain growth reactions suggests that

$$k_2^h \; > \; k_{2_r}^{*h} \qquad\qquad\qquad 5.4.7b$$

The presence of the hydrogenation intermediate C_2^{*h} is supported by the radioactive ethylene studies of Hall, Kokes and Emmett (54). They observed a decrease in the amount of ethylene consumed in chain growth reactions with increasing pressure. The surface concentration of C_2^{*h} would increase at higher pressures since it involves an adsorption process which is enhanced by increasing the ethylene partial pressure. However, the surface concentration of the chain growth intermediate (C_2^*) would not show a proportional increase at higher pressures, since the production of C_2^* does not involve any gas phase reactants. The C_2^{*h} hydrogenation rate depends upon the partial pressure of hydrogen and is expected to increase with increasing pressure. The surface reaction rate for conversion of the hydrogenation intermediate (C_2^{*h}) into the chain growth intermediate (C_2^*) may not be as favored at higher pressures. Supporting evidence is presented in Section 5.2 where data is presented which shows that the influence of gas phase ethylene on the longer chain ($C_{n>3}$) product yields diminishes with both increasing pressure and decreasing GHSV. Both of these changes result in an increase in the fraction of feed ethylene hydrogenated and are compatable with a larger increase in C_2^{*h} surface concentration relative to the C_2^* concentration.

The fact that the $X_{C_2^=}/X_{C_2}$ ratios are comparable for both the ethylene containing and pure CO/H_2 feeds (Section 5.4.1) indicates that the ethylene adsorption rate ($k_2{}^a[C_{2g}^=]$) is not a rate-limiting step with respect to the reactions involving C^*h. If the adsorption kinetics were relatively slow one would expect much higher $X_{C_2^=}/X_{C_2}$ values for the ethylene/CO/H_2 mixture compared to the pure CO/H_2 feed since the ethylene feed concentration is at least fifty times higher than the corresponding
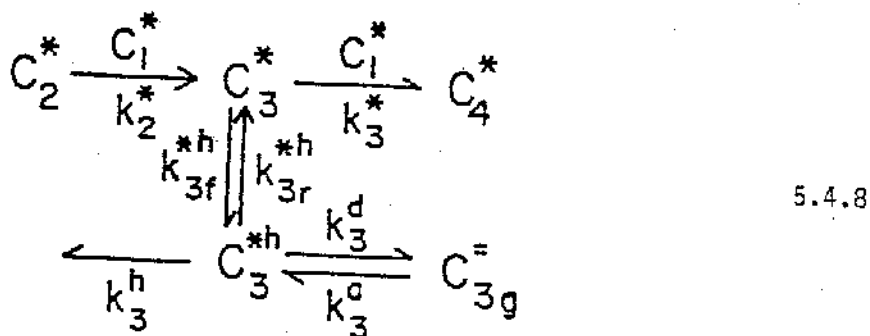
concentrations obtained with the pure feed under the reaction conditions employed. These results suggest that

$$k_2 h > k_{2_r} {}^* h$$

5.4.7c

The fact that the $X_{C_2^=}/X_{C_2}$ values obtained with the ethylene containing feed agree with the $X_{C_2^=}/X_{C_2}$ ratios obtained with the pure CO/H_2 feed at comparable GHSV values, implies that the ethylene adsorption rate is not the limiting step in the secondary hydrogenation reaction. This can be written as

$$k_2 {}^d > k_2 {}^h$$

5.4.7d

The higher propylene/propane ratios observed with the ethylene CO/H_2 feed as compared to the pure CO/H_2 feed can be due to the different relative rates of the surface reaction. Consider the proposed reaction network for the C_3 products shown below

$$C_2^* \xrightarrow[k_2^*]{C_1^*} C_3^* \xrightarrow[k_3^*]{C_1^*} C_4^*$$

$$k_{3f}^{*h} \Uparrow\Downarrow k_{3r}^{*h}$$

$$\xleftarrow[k_3^h]{} C_3^{*h} \underset{k_3^a}{\overset{k_3^d}{\rightleftharpoons}} C_{3g}^=$$

5.4.8

Since propylene is the principal C_3 product, it is reasonable to assume that

$$k_3 {}^d > k_3 {}^h$$

5.4.9

When ethylene is present in the feed gas, there is an increase in C_3^{*h} due to secondary insertion. The corresponding increase in the $N_{C_3^=}/N_{C_3}$

compared to the pure CO/H_2 feed conditions can be due to a higher rate of desorption relative to the adsorption rate. The relationship among the rate constants involved with the C_3^{*h} intermediate can be

$$k_3^d > k_3^a > k_3^h \qquad\qquad 5.4.10$$

5.4.4 Reaction studies using the 1-pentene/CO/H_2 Feed

The selectivity data contained in section 5.4.3.1 are based on the yield data presented in section 5.2, where 1-pentene hydrocracking and chain insertion reactions are discussed. The present discussion is aimed at providing supporting evidence for the reaction sequence proposed in the previous section. The 1-pentene secondary reactions of hydrogenation and olefin isomerization are treated in section 5.4.3.2 while the reaction sequence for the C_5 intermediates is discussed in section 5.4.3.3.

5.4.4.1 Olefin/paraffin Selectivities for the C_2 and C_3 products

The presence of 0.5 mole % 1-pentene in the 1/3 CO/N_C feed only marginally affects the $N_{C_2^=}/N_{C_2}$ and $N_{C_3^=}/N_{C_3}$ selectivities for the Fe catalyst at one atmosphere (Figure 5.4.9). The low molecular weight product yields ($C_{n<4}$) are lower in this feed as compared to the pure CO/H_2 feed for a given GHSV (Section 5.2). If these diminished yields are due to a supression in the CO activity due to site inhibition by the feed 1-pentene one would expect higher olefin/paraffin selectivities for the olefin containing feed since these ratios increase with decreasing CO conversion (Section 4.3). On the other hand, if significant 1-pentene hydrocracking is occuring the C_2 and C_3 olefin/paraffin selectivities would most probably be lower in the 1-pentene containing feed since
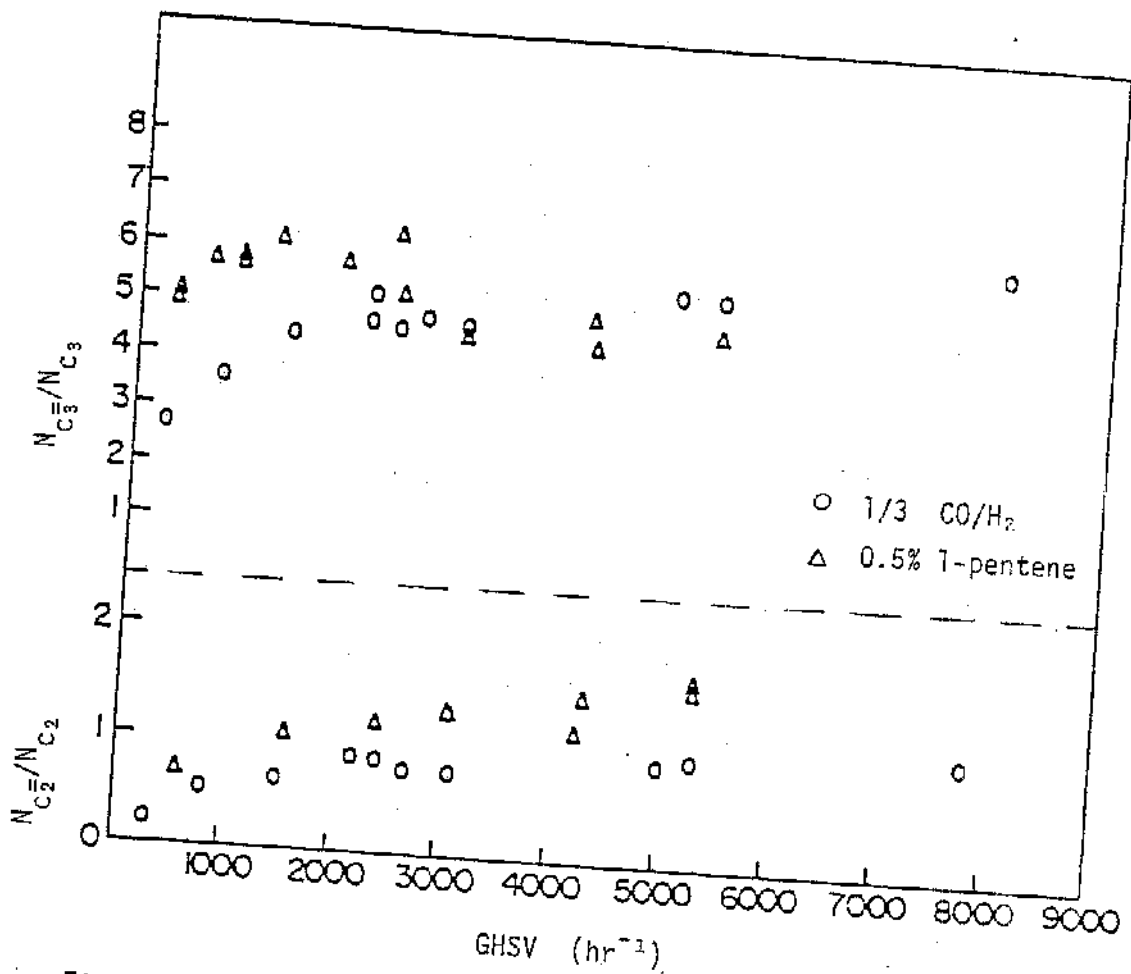
Figure 5.4.9 Ethylene/ethane (bottom) and propylene/propane (top) selectivities versus GHSV for the Fe catalyst using the 1-pentene containing and pure 1/3 CO/H_2 feed at 1 atm. and 250°C.

paraffins would be the predominant products due to the high partial pressure of hydrogen. The comparable selectivities obtained with both mixtures support the arguments against independent hydrogenation sites on the catalytic surface. If such sites existed, the presence of feed 1-pentene would probably inhibit the adsorption of primary FT products (α-olefins) on the hydrogenation sites and higher selectivity ratios in the olefin feed would be observed.

Figure 5.4.10 presents the $N_{C_2^=}/N_{C_2}$ and $N_{C_3^=}/N_{C_3}$ selectivities for the Fe catalyst at 7.8 atmospheres for both feeds. The C_2 selectivity is essentially identical for both feed mixtures indicating that neither hydrocracking nor site inhibition are affecting these products. The $N_{C_3^=}/N_{C_3}$ selectivity is only marginally higher for the 1-pentene containing feed, again suggesting the common site model.

Similar results are obtained with the alloy catalyst at 1 and 7.8 atmospheres. The $N_{C_2^=}/N_{C_2}$, $N_{C_3^=}/N_{C_3}$ and $N_{C_4^=}/N_{C_4}$ selectivities are unaffected by the presence of the feed 1-pentene (Figures 5.4.11 and 5.4.12). Figure 5.4.13 presents the C_2 and C_3 selectivities for the Co catalyst at one atmosphere. Again it appears that 1-pentene hydrocracking and site inhibition are not present at these conditions. At 7.8 atmospheres the Co catalyst exhibits lower $N_{C_2^=}/N_{C_2}$ selectivities with the 1-pentene feed (Figure 5.4.14). There is evidence of significant 1-pentene hydrocracking at these conditions (Section 5.2.2) and this may indeed by the cause for the lower C_2 selectivities. The $N_{C_3^=}/N_{C_3}$ selectivities for this catalyst at 7.8 atmospheres were not obtained with the pure CO/H_2 feed since the GHSV values employed at these conditions were too high and measurable amounts of propane were not
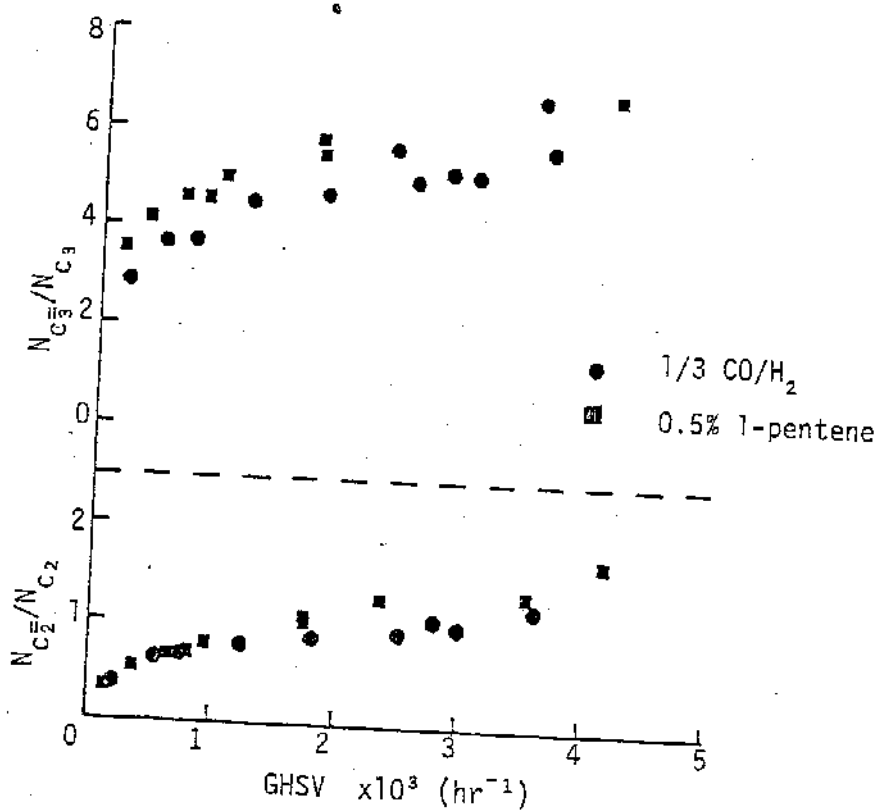
Figure 5.4.10 Ethylene/ethane (bottom) and propylene/propane (top) selectivities versus GHSV for the Fe catalyst using the 0.5% 1-pentene containing and pure 1/3 CO/H_2 feed at 7.8 atm. and 250°C.
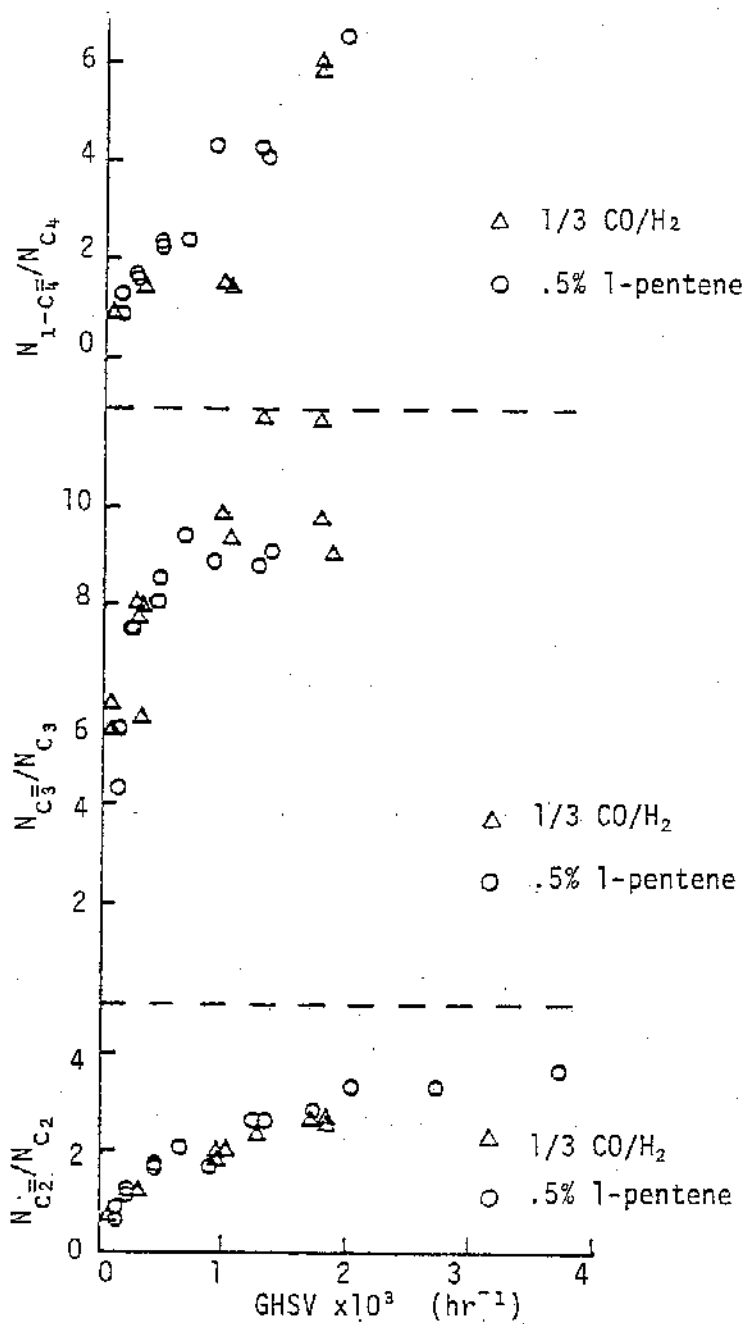
Figure 5.4.11 Ethylene/ethane(Bottom), propylene/propane (middle), and Butene/ butane (top) selectivity for the FeCo catalyst using the 0.5% 1-pentene containing and pure 1/3 CO/H_2 feed at 1 atm. and 250°C.
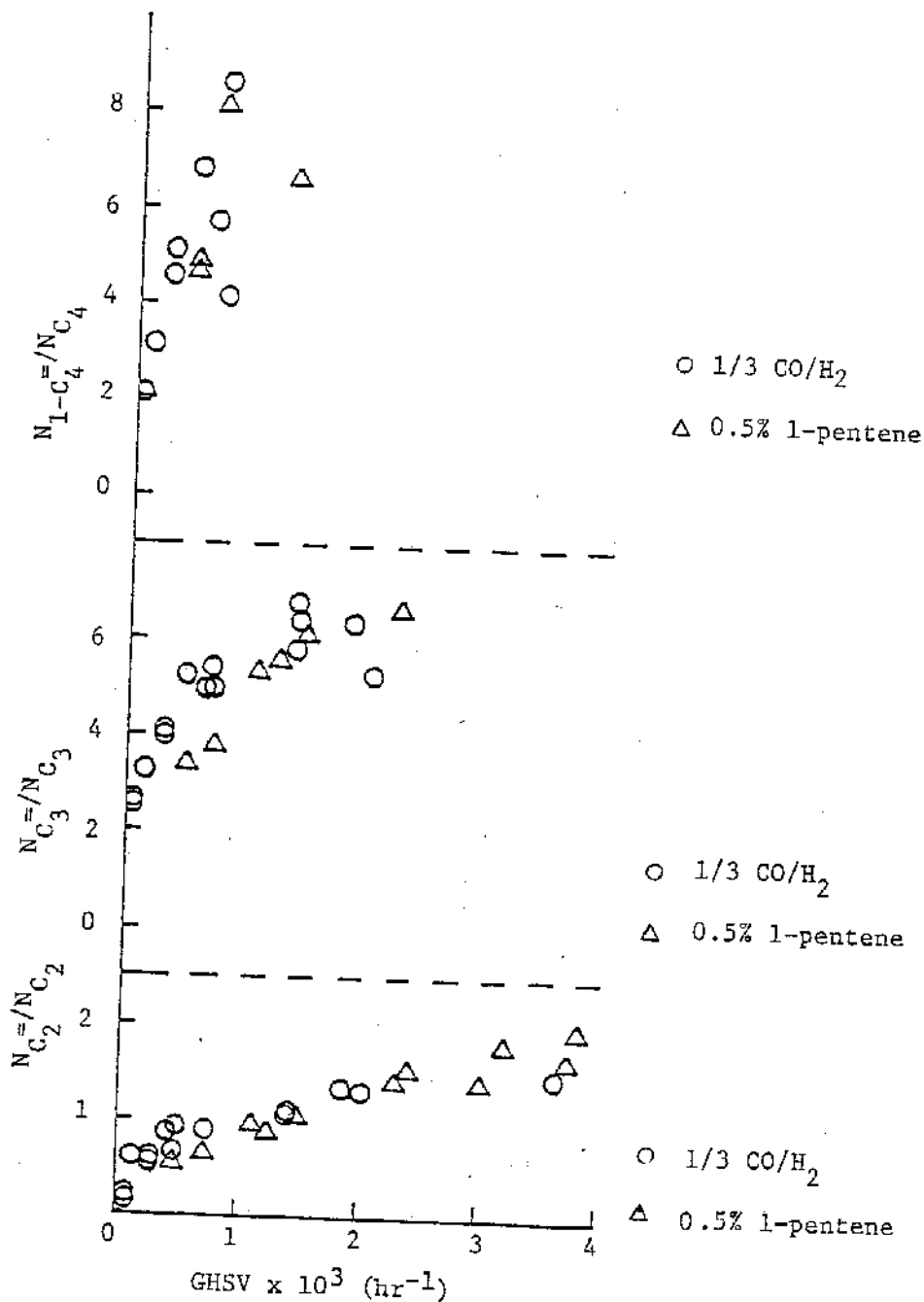
Figure 5.4.12 Ethylene/ethane (bottom), propylene/propane (middle), and 1-butene/n-butane (top) selectivities versus GHSV for the FeCo catalyst using the 0.5% 1-pentene and pure 1/3 CO/H$_2$ feed at 7.8 atm and 250°C.
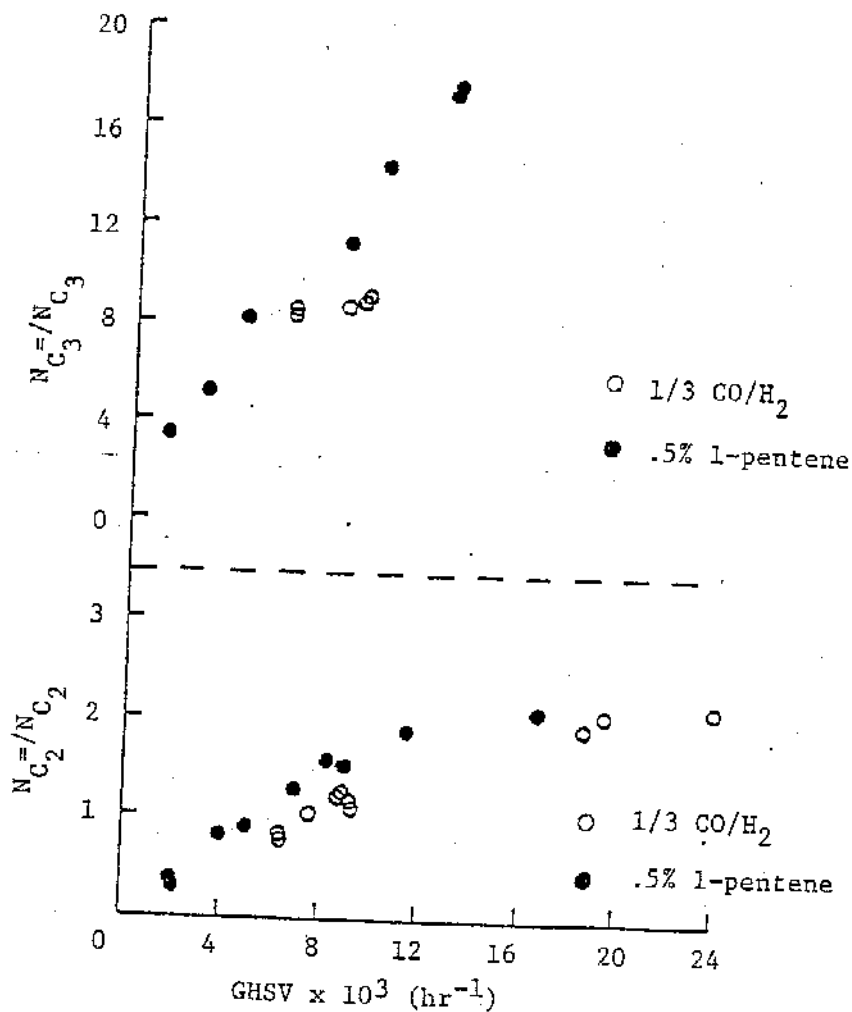
Figure 5.4.13 Olefin/paraffin selectivities for the C_2 (bottom) and C_3 (top) products versus the GHSV for the Co catalyst using the 1-pentene containing and pure 1/3 CO/H_2 feed at 1.0 atm and 250°C.
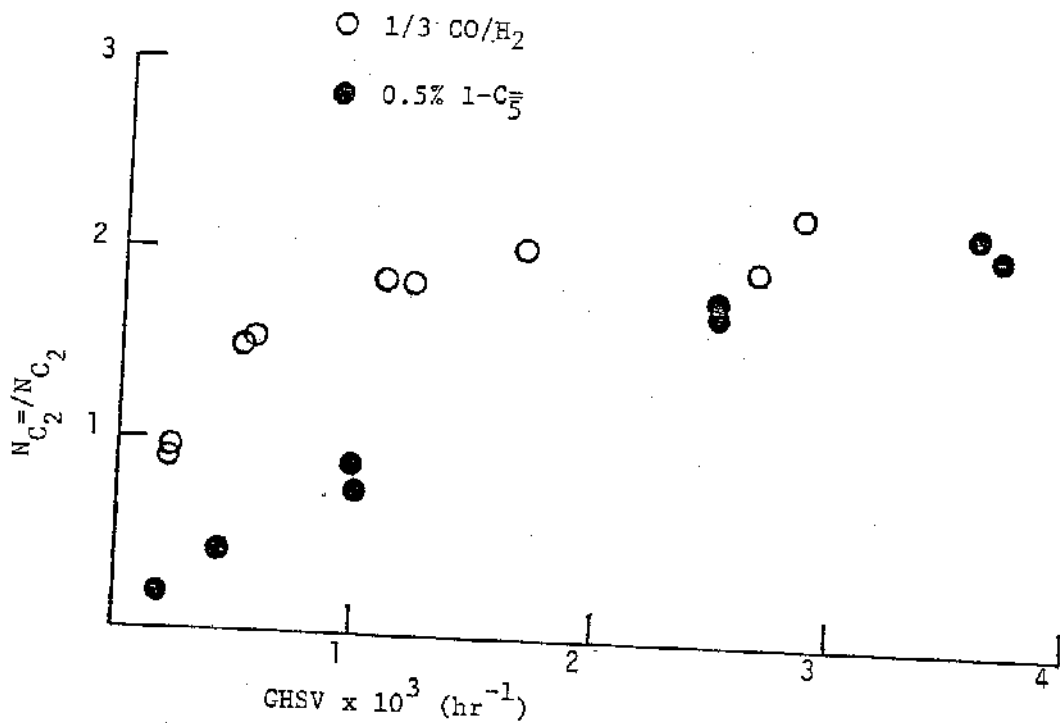
Figure 5.4.14 $N_{C_2^=}/N_{C_2}$ selectivity versus the GHSV for the Co catalyst using the 1-pentene containing and pure 1/3 CO/H$_2$ feed at 7.8 atm and 250°C.