corresponds to the value obtained with the pure CO/H_2 mixture over the $C_{n>3}$ carbon range.

5.3.3 SF Parameterization for the FeCo catalyst

The growth probability, α, for the alloy catalyst is not affected by the presence of either the ethylene of 1-pentene in the feed gas at 1 and 7.8 atmospheres. Figure 5.3.10 presents some typical SF plots for the ethylene/CO/H_2 mixture at one atmosphere. The α value is approximately 0.47 for this feed corresponding to the same value obtained with the pure CO/H_2 feed. At 7.8 atmospheres there again is no change in α (Figure 5.3.11) however the $\ln(Y_{C_3})$ increased to a value corresponding to the straight line determined by the $\ln(Y_{C_i})$ for the $C_{n>4}$ products. This behavior is identical to that observed for iron and discussed in the next section. Figures 5.3.12 and 5.3.13 present the SF plots for the 1-pentene/CO/H_2 feed over the FeCo catalyst at 1 and 7.8 atmosheres respectively. There again is no change in the value of α compared to that obtained with the pure feed.

5.3.4 Mechanistic Implications of Schulz Flory Distributions Using the Olefin Enhanced Feeds

The growth probability, α, is a ratio of two reaction rates shown below to be

$$\alpha = \frac{r_{propagation}}{r_{propagation} + r_{termination}} \qquad 5.3.1$$
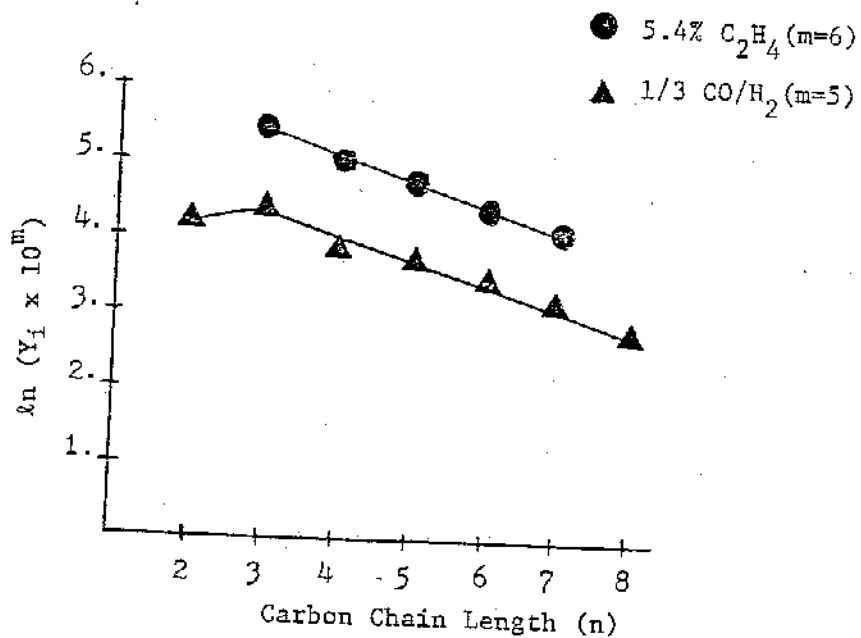
Figure 5.3.9 Schulz Flory plot for the Co
catalyst using the ethylene containing and pure
1/3 CO/H_2 feed at 7.8 atm and 250°C. Nominal
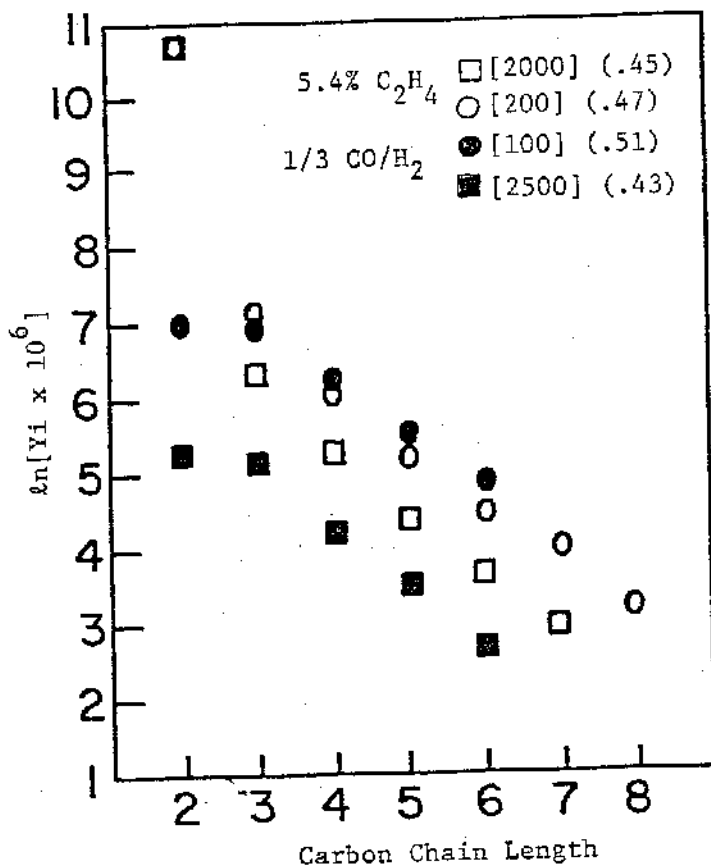$\alpha=0.77$ GHSV $\simeq$ 1000 hr^{-1}.

Figure 5.3.10 Schulz Flory plot for the FeCo catalyst using the ethylene containing and pure 1/3 CO/H_2 feed at 1 atm. and 250°C. Number in brackets refers to the GHSV [hr^{-1}]. Number in parenthesis refers to α.
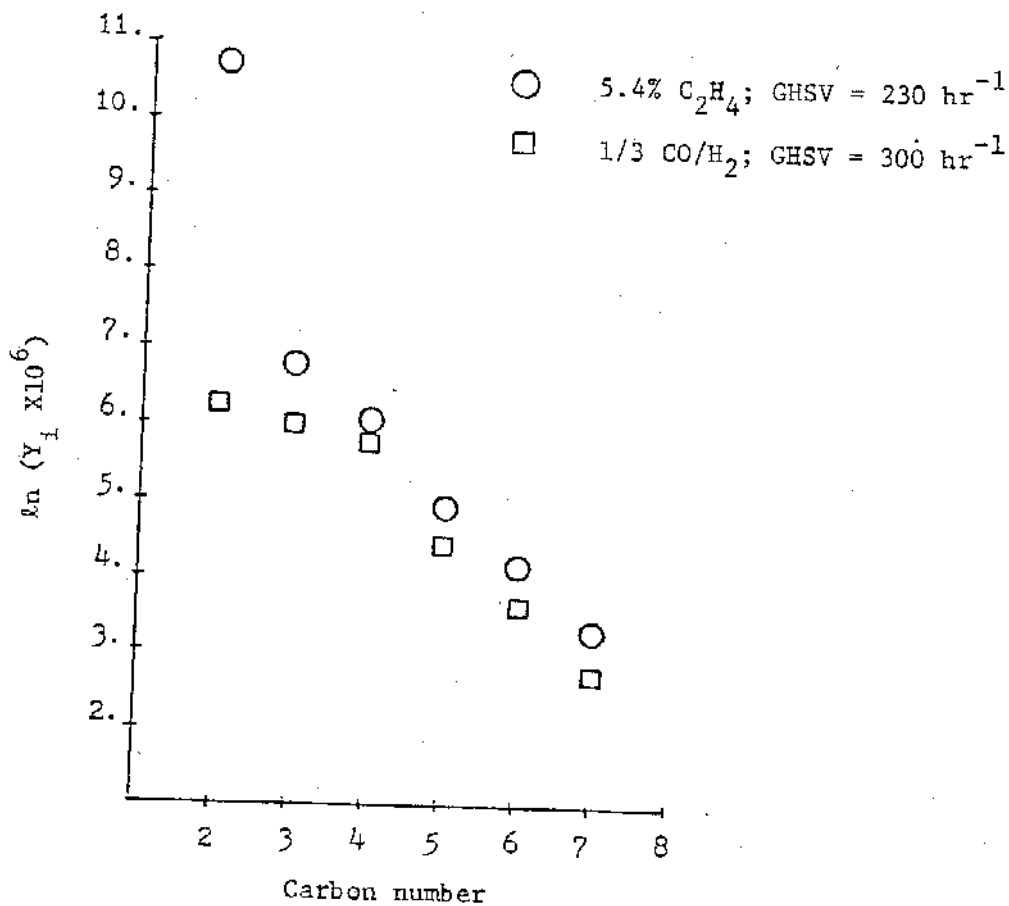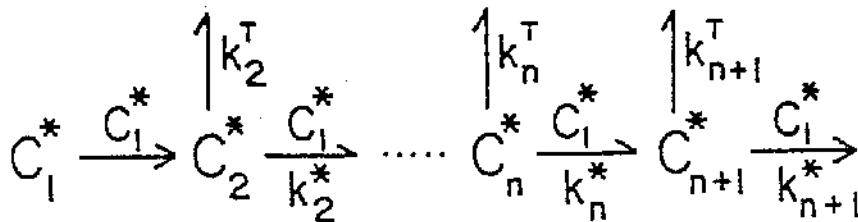
Figure 5.3.11 Schulz Flory plot for the FeCo catalyst using the ethylene containing and pure 1/3 CO/H_2 feed at 7.8 atm. and $250^{\circ}C$. Nominal value of $\alpha = 0.45$.

If one assumes a series of insertion reaction to occur on the surface (Section 4.6) involving a monomer containing one carbon atom, the surface reactions can be written as shown below

$$
C_1^* \xrightarrow{C_1^*} C_2^* \xrightarrow[k_2^*]{C_1^*} \overset{\displaystyle\uparrow k_2^T}{} \ldots\ldots C_n^* \xrightarrow[k_n^*]{C_1^*} \overset{\displaystyle\uparrow k_n^T}{} C_{n+1}^* \xrightarrow[k_{n+1}^*]{C_1^*} \overset{\displaystyle\uparrow k_{n+1}^T}{}
$$

5.3.2

where c_1^* is the single carbon insertion monomer

c_n^* surface intermediate containing n carbon atoms

k_i^* rate constant for insertion reaction of intermediate C_i^*

k_i^T rate constant for termination reaction of intermediate C_i^*

The growth probability can be written in terms of the individual reaction rates of surface intermediate C_i^* as shown below

$$
\text{growth probability} = \alpha = \frac{k_i^* C_i^* C_i^*}{k_i^* C_i^* C_i^* + k_T C_i^* C_i^*} \qquad 5.3.3A
$$

$$
= \frac{k_i^*}{k_i^* + k_T} \qquad 5.3.3B
$$

assuming c_i^* can be treated as a constant and lumped into k_i^* α. In this reaction scheme the termination reaction which include hydrogenation,
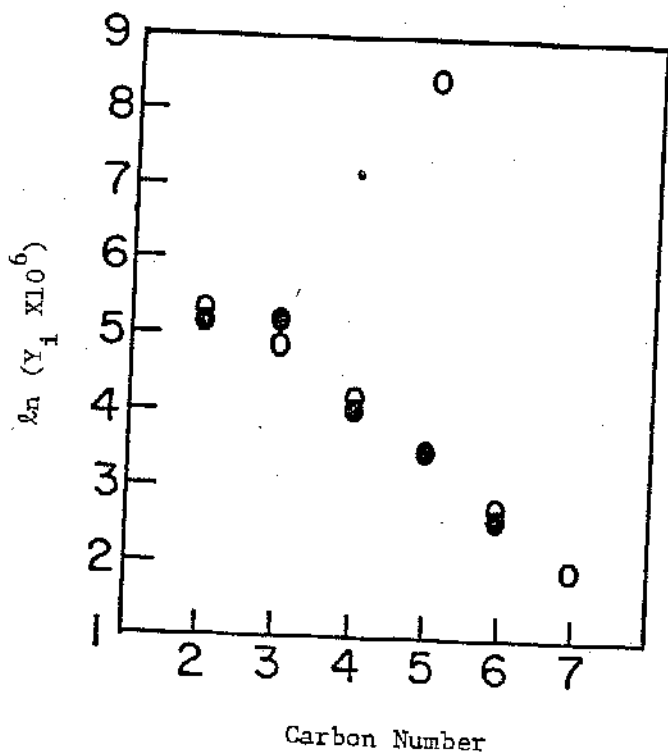
Figure 5.3.12 Schulz Flory plot for the FeCo catalyst using the 1-pentene containing and pure 1/3 CO/H_2 feed at 1 atm. and 250°C. Nominal α value = 0.45 .

○ 5.4% $1-C_5^=$/1/3 CO/H_2 feed; GHSV = 1800
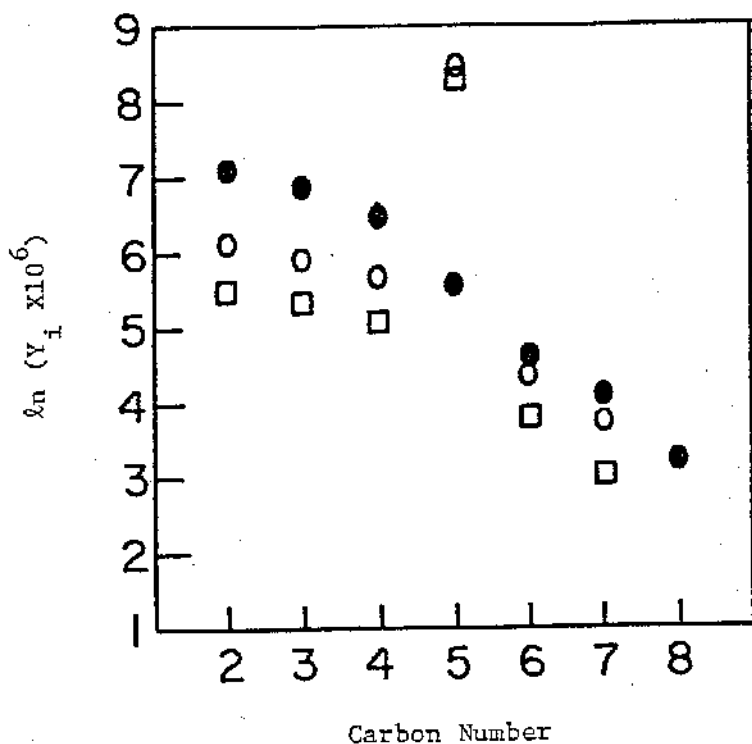
● 1/3 CO/H_2 feed; GHSV = 1800

Figure 5.3.13 Schulz Flory plot for the FeCo
catalyst using the 1-pentene
containing and pure 1/3 CO/H_2
feed at 7.8 atm. and 250°C.
Nominal α value is 0.5 .

● 1/3 CO/H_2 feed; GHSV = 300 hr^{-1}

○ 1-$C_5^=$/CO/H_2 feed; GHSV = 460 hr^{-1}

□ 1-$C_5^=$/CO/H_2 feed; GHSV = 1300

olefin desorption, and olefin isomerization are lumped into one effective rate constant $k_i{}^T$.

The presence of high olefin concentrations in the feed stream should increase (at least) the concentrations $C^*{}_x$ where x is the carbon number corresponding to the feed olefin. Rearranging equation 5.3.3 one obtained

$$1/\alpha = 1 + \frac{k_i{}^T}{k_i{}^*}$$

The value of α is independent of the surface concentrations of the growth reaction intermediates ($[C_i{}^*]$) in the carbon range complying with SF kinetics. Consequently any enhancement in $[C_i{}^*]$ should result in an increase in the observed product yield and the slope determined by $\ln (Y_{i+1}) - (\ln Y_i)$ should remain unchanged at steady state conditions. Indeed this is observed for the $C_{n>4}$ products for the iron based catalyst at all conditions studied and the Co catalyst at 7.8 atmospheres. However, there are two observable departures from this behavior which warrant further discussion.

For both iron containing catalyst the increased in the C_3 product yields associated with the ethylene/CO/H_2 feed brought the $\ln(Y_{C_3})$

values in agreement with the straight line established by the longer chain products. This increase can be fortuitous due to the ethylene feed composition chosen or due to a mechanistic limitation based the monomer concentration available on the surface for reaction, or a change in the termination rate relative to the propagation rate. Consider the surface kinetics of the ethylene insertion reaction shown below

$$C_{2\ gas}^{\equiv} \leftrightarrow C_2^* \qquad\qquad 5.3.5a$$

$$C_2^* + C_1^* \xrightarrow{\ k_2^*\ } C_3^* \qquad\qquad 5.3.5b$$

The steady state production rate of C_3^* depends upon the C_2^* and C_1^* surface concentration. It is shown in section 5.4 that at least 30% of gas phase ethylene reacts on the surface to form ethane. It is reasonable to assume that a certain fraction of the gas phase ethylene reacts on the surface for form C_2^* surface concentrations and indeed these yield increase typically several hundred percent (Tables 5.2.1 and 5.2.2). However, if the increase in the C_2^* surface concentration is great enough one would expct the C_1^* concentration to become limiting according to the surface kinetic relationship

$$r_{C_3}{}^* = k_2^* C_2^* C_1^* - k_3^* C_3^* C_1^* - k_T C_3^* \qquad\qquad 5.3.6$$

where $r_{C_3}{}^*$ is the production rate of C_3^* and

c_i^* is the surface concentration of intermediate i.

This reasoning also requires the C_1^* to be the rate limiting reactant for all surface reactants involving longer chain intermediates. It is possible that the reverse reaction.

$$C_3^* \rightarrow C_2^* + C_1^*$$

<div align="right">5.3.7</div>
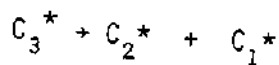
is occuring on the surface however one would imagine this unlikely due to the high concentration of ethylene in the gas phase and the absence of significant cracking. Additionally this reaction most probably involves some type of dehydrogenation step which would not be favored due to the high partial pressure of hydrogen present under the low conversion reactor conditions.

The deviations in the C_2 and C_3 product yields with respect to ideal SF behavior may be due to changes in the overall termination and propagation due to changes in surface concentration. At 7.8 atmospheres the iron catalyst exhibits these deviations in the pure CO/H_2 feed (Figure 5.3.3). One can envision that the C_3^* propagation rate is much faster relative to that of the longer chain products. However when ethylene is present in the CO/H_2 feed the enhanced C_3^* surface concentration appears to undergo termination (hydrogenation) more readily than the propagation. The resultant ratio in these investigations agrees with the value obtained with the longer chain products suggesting that the maximum value α is independent of gas phase olefin concentrations,

since the slope between $\ell n(Y_{C3})$ and $\ell n(Y_{C4})$ agrees with the slope throughout the entire carbon range. Similar arguments hold for the alloy catalyst at 7.8 atmospheres.

The Co catalyst at one atmosphere exhibits an increase in α due to the feed ethylene. In section 4.5 it is shown that the growth probability increases with increasing total pressure. This is most probably due to some type of product desorption/readsorption effect either increasing the rate of propagation or decreasing the termination rate. A similar effect can be occurring at one atmosphere due to the presence of the relatively high concentration of the feed ethylene.

5.4   Selectivity Studies and Secondary Reactions

5.4.1 Olefin/paraffin Selectivities for C_2 and C_3 products using the Ethylene Enhanced Feed

5.4.1.1 Fe Catalyst

The mole fraction ratio of ethylene to ethane $(X_{C_2^=}/X_{C_2})$ is plotted as a function of the GHSV in Figure 5.4.1 for both the pure and ethylene containing feed at 1 and 7.8 atmospheres. This ratio is approximately two times higher for the olefin feed at one atmosphere and at the higher pressure $X_{C_2^=}/X_{C_2}$ ratios appear to be equal at lower GHSV values for both feeds. These results indicate that a significant fraction of the feed ethylene is undergoing hydrogenation. At one atmosphere and a nominal CO conversion of 1% (GHSV $\pm$ 5000), approximately 30% of the ethylene hydrogenates. As the GHSV is decreased it appear that the hydrogenation of feed ethylene is more pronounced than the ethylene produced via the FT synthesis since the decrease in $X_{C_2^=}/X_{C_2}$ for the ethylene feed is more
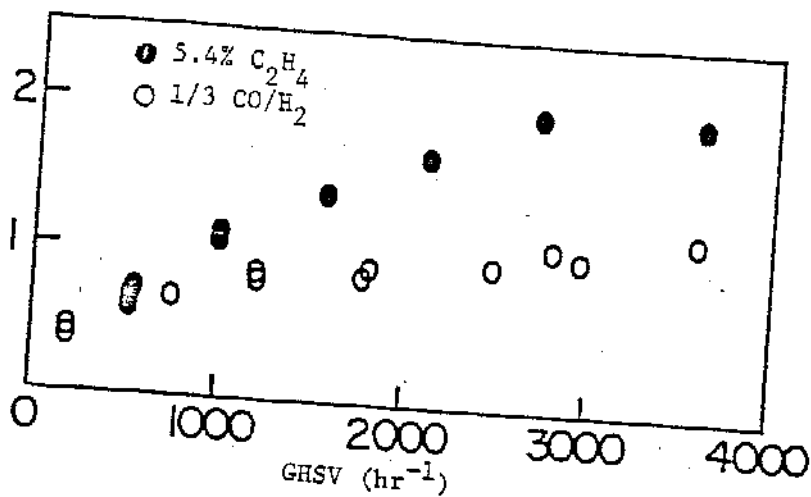
Figure 5.4.1B Ethylene to ethane mole fraction ratio versus the GHSV for the Fe catalyst with the ethylene containing and pure 1/3 CO/H₂ feeds at 7.8 atm. and 250°C.
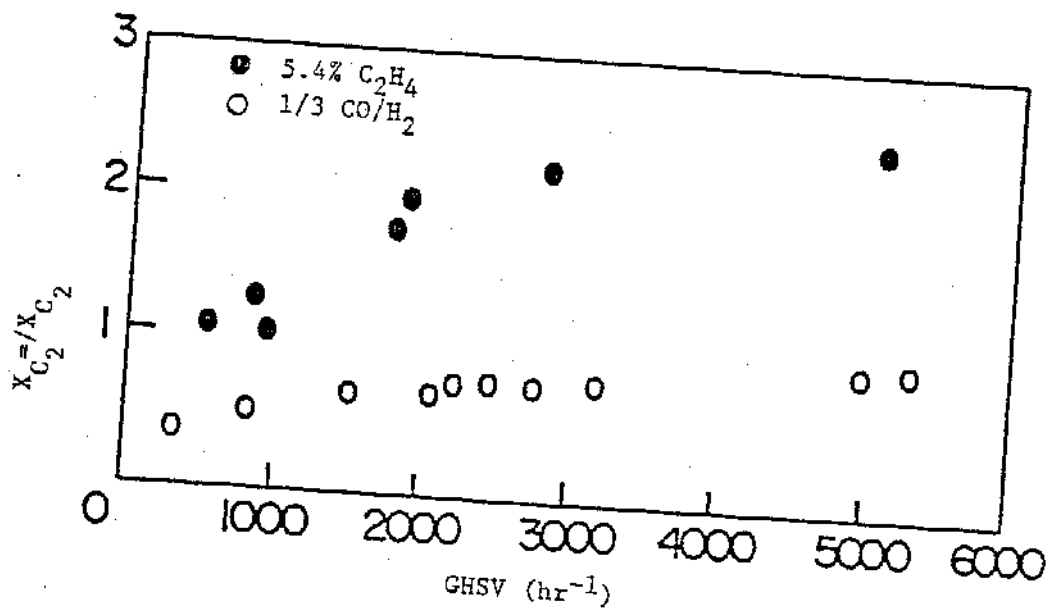

Figure 5.4.1A Ethylene to ethane mole fraction ratio versus the GHSV for the Fe catalyst with the ethylene containing and pure 1/3 CO/H₂ feeds at 1 atm. and 250°C.

rapid than the decrease in the C_2 mole fraction ratio obtained with the pure CO/H_2 feed. The kinetics of the ethylene hydrogenation and the mechanistic implications with regard to the FT process is discussed in section 5.4.2.

The propylene to propane mole fraction ratio ($X_{C_3^=}/X_{C_3}$) for the Fe catalyst is presented in Figure 5.4.2 for both the ethylene and pure CO/H_2 feed at 1 and 7.8 atmospheres. The ratio is significantly higher in the ethylene containing feed over the GHSV range studied, however at lower space velocities the ratios appear to be approaching comparable values. These results indicate that the primary product of ethylene initiation is propylene. Furthermore it appears that propylene initially desorbs from the initiation/growth site and that subsequent hydrogenation is due to readsorptions of propylene onto a site capable of inserting hydrogen into the olefin bond. The other possiblity is that direct hydrogenation of the C_3 surface intermediate occured after the ethylene initiation reaction. If this is the case then one would expect the $X_{C_3^=}/X_{C_3}$ ratio to be the same for both feeds since the hydrogenation activity of the C_3^* surface intermediate depends on the hydrogen partial pressure and catalytic surface which are essentially the same in both cases. This subject is discussed further in section 5.4.2 and 6.3.

5.4.1.2 Co Catalyst

Figure 5.4.3 presents the $X_{C_2^=}/X_{C_2}$ value for the Co catalyst at one atmosphere for both the pure and ethylene CO/H_2 mixture. At high GHSV values ($>20 \times 10^3 hr^{-1}$) the ethylene/ethane ratio is four to five times higher for ethylene containing feed as compared to the pure feed.
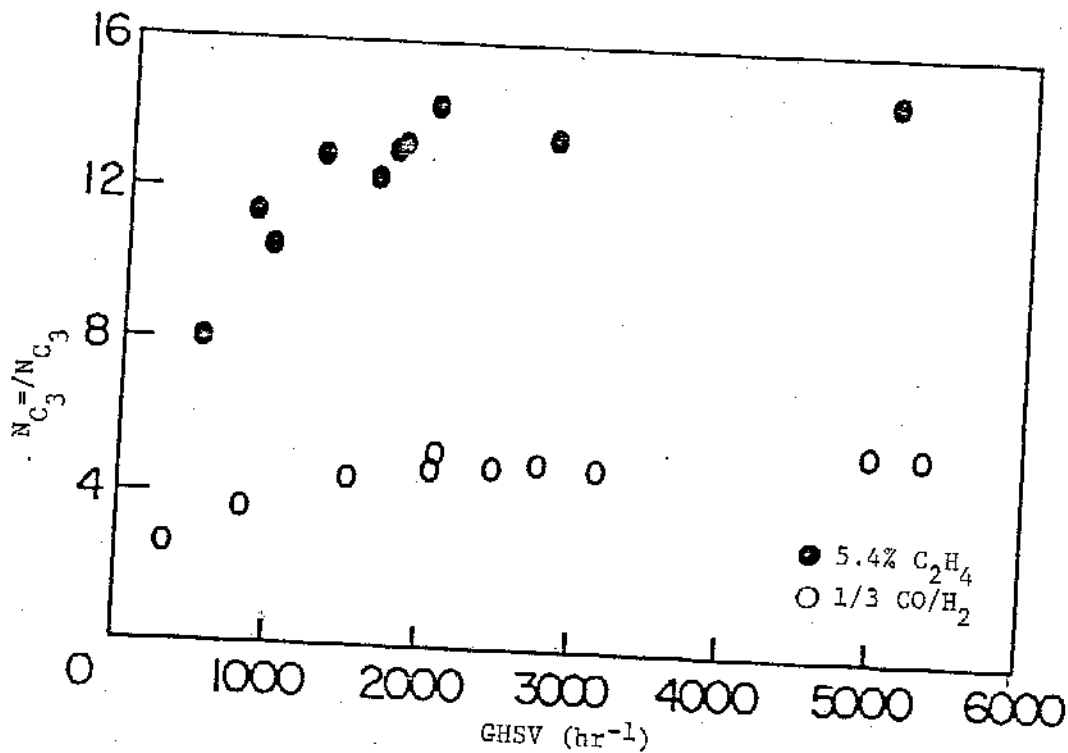
Figure 5.4.2A Propylene to propane mole fraction versus the GHSV for the Fe catalyst using the ethylene containing and pure 1/3 CO/H_2 feeds at 1 atm. and 250°C.
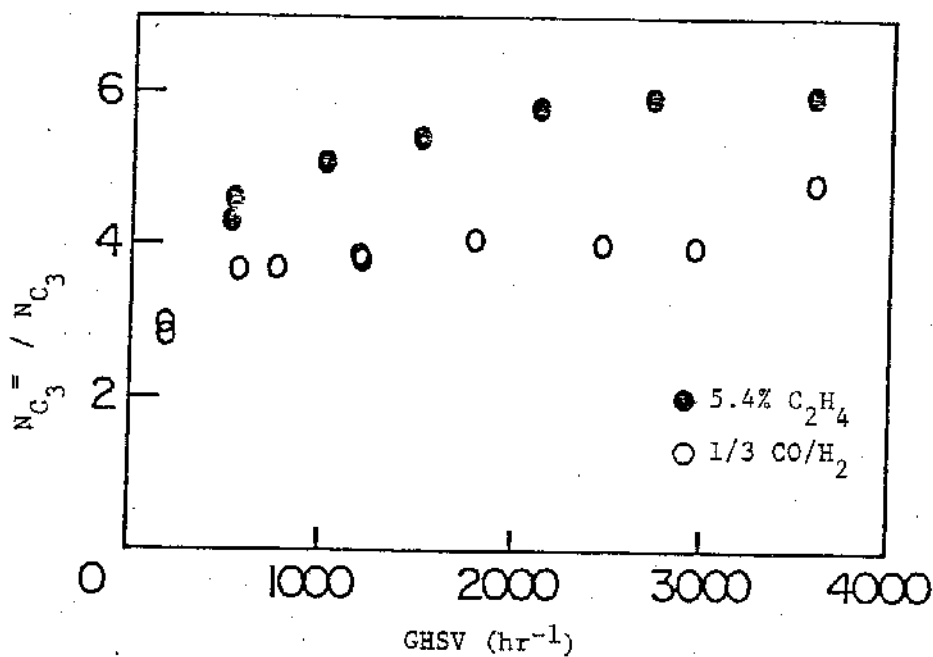
Figure 5.4.2B Propylene to propane product mole fraction ratio versus the GHSV for the Fe catalyst using the ethylene containing and pure 1/3 CO/H_2 feeds at 7.8 atm. and 250°C.
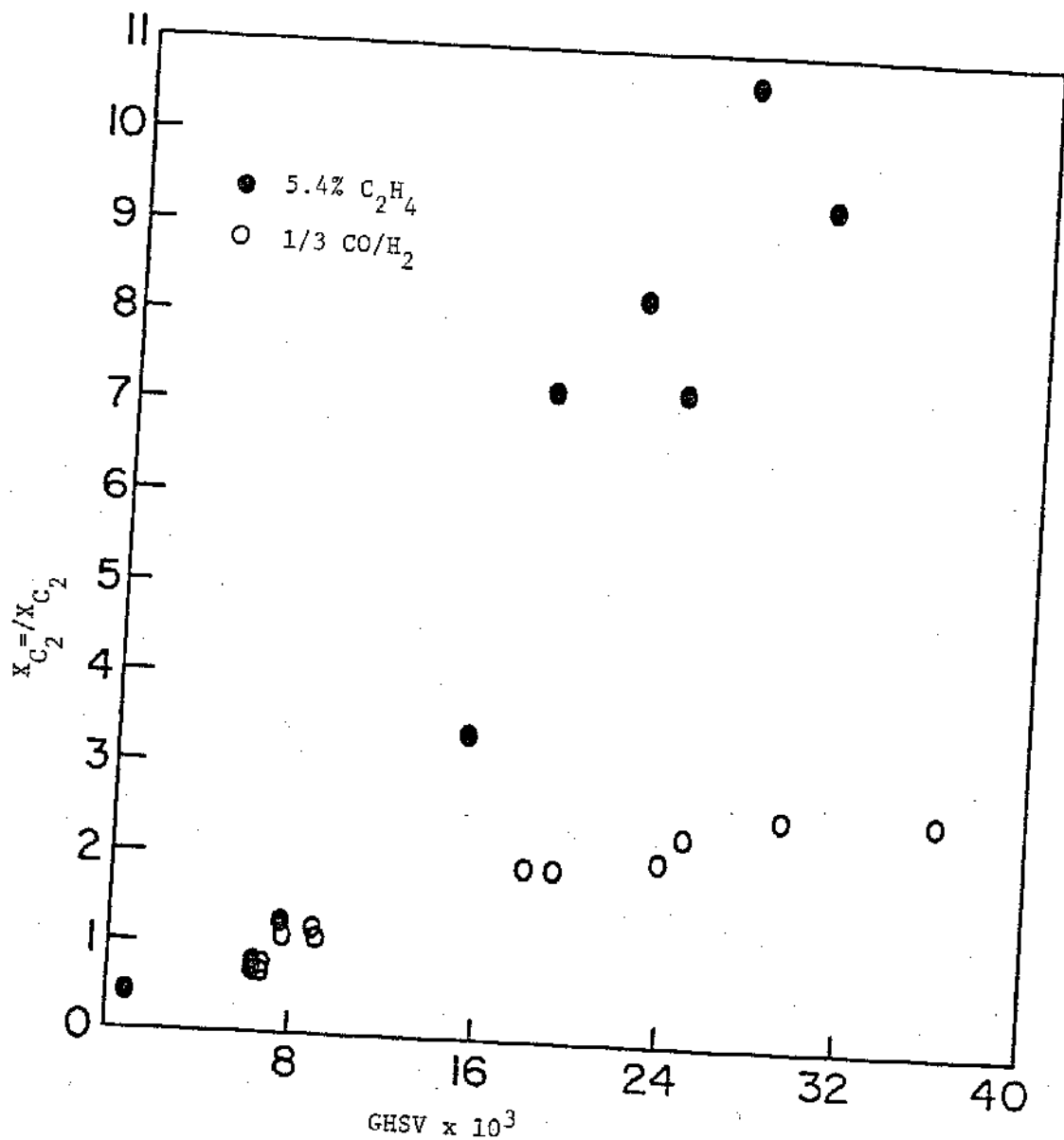
Figure 5.4.3 Ethylene to ethane ratio versus the GHSV for the Co
catalyst using the ethylene containing and pure 1/3 CO/H_2 feed at
1 atm. and 250°C.