where k_i^h is the rate constant for the hydrogenation of surface intermediate C_i^*.

C_i is the paraffin produce containing i carbon atoms

$C_i^=$ is the primary olefin product containing i carbon atoms

The maximum in product yields obtained during the transient period using the 1/3 CO/H_2 feed may be due to the series reaction network involving hydrogenation since the high hydrogen partial pressure associated with this feed favors the formation of saturated hydrocarbon products. This subject is further discussed in Chapter 5 with respect to the overall FT mechanism.

4.6.5 Production of Carbon Dioxide and Methanol Through A Common Intermediate

4.6.5.1 Transient response of oxygenated products

Both the water gas shift reaction and the hydrogenation of CO into methanol are catalyzed by metal oxide surfaces and involve nondissociated chemisorbed CO as a reactant (72,83). In section 4.2 it is found that the shift activity (defined as N_{CO_2}/N_{H_2O} in Section 4.2) decreases while methanol production increases (Section 4.1) at higher total pressures. Ponec (95) suggests that the overall FT synthesis process consists of several reaction mechanisms occuring over surfaces that are carbidic, oxide and possibly metallic in nature. The present author is not aware of any investigations reporting a positive identification of multiple phases on the catalytic surface (i.e., carbide, oxide, etc.) over Fe catalyst however, some investigators report bulk phases consisting of a mixture of carbides, oxides and metal (92,91,6,84).

In many FT investigations the catalyst initially exists as an oxide phase or at least possesses an oxide surface. Prior to producing FT products the catalyst is either reduced in hydrogen or transformed into the active phase by the CO and H_2 reactants. It is not unreasonable to assume that a certain fraction of the initial oxide remains unchanged and can be catalytically active towards methanol and CO_2 production. Additionally, the presence of CO_2 and H_2O, formed during the synthesis, may oxidize a fraction of the reduced carbide surface. In conclusion it is very possible that oxides surfaces exist during the FT synthesis.

The reaction mechanism(s) involved in the production of CO_2 and methanol may not require an oxide surface in order to involve a common intermediate. Hall, Kokes, and Emmett (53) found that labeled methanol and formaldehyde readily decomposed to yield CO_2 and CO over a bulk iron catalyst. In fact formaldehyde decomposed to almost equilibrium concentrations of water and CO_2. The authors (53) report that very little CO_2 converted to CO or hydrocarbons. These results indicate that at least methanol can convert to CO_2 indicating a definite link between these two products. A brief review of the proposed mechanisms for the methanation and shift reactions over oxide surface is given to the next section to illustrate the possiblity that both CHOH and CH_3OH may be produced by a common reaction intermediate.

There appear to be some significant differences between the transient product yields obtained with the 1/1 and 1/3 CO/H_2 feeds. In Figure 4.6.9 the transient product yields of CO_2 and CH_3OH are shown at reactor pressures of 14 atmospheres with the 1/3 CO/H_2 feed. The CO_2 exhibits a maximum under these conditions. In the case of the 1/1 feed the CO_2 yield increased to a constant steady state value within forty five minutes after the flow changed. The different transient responses

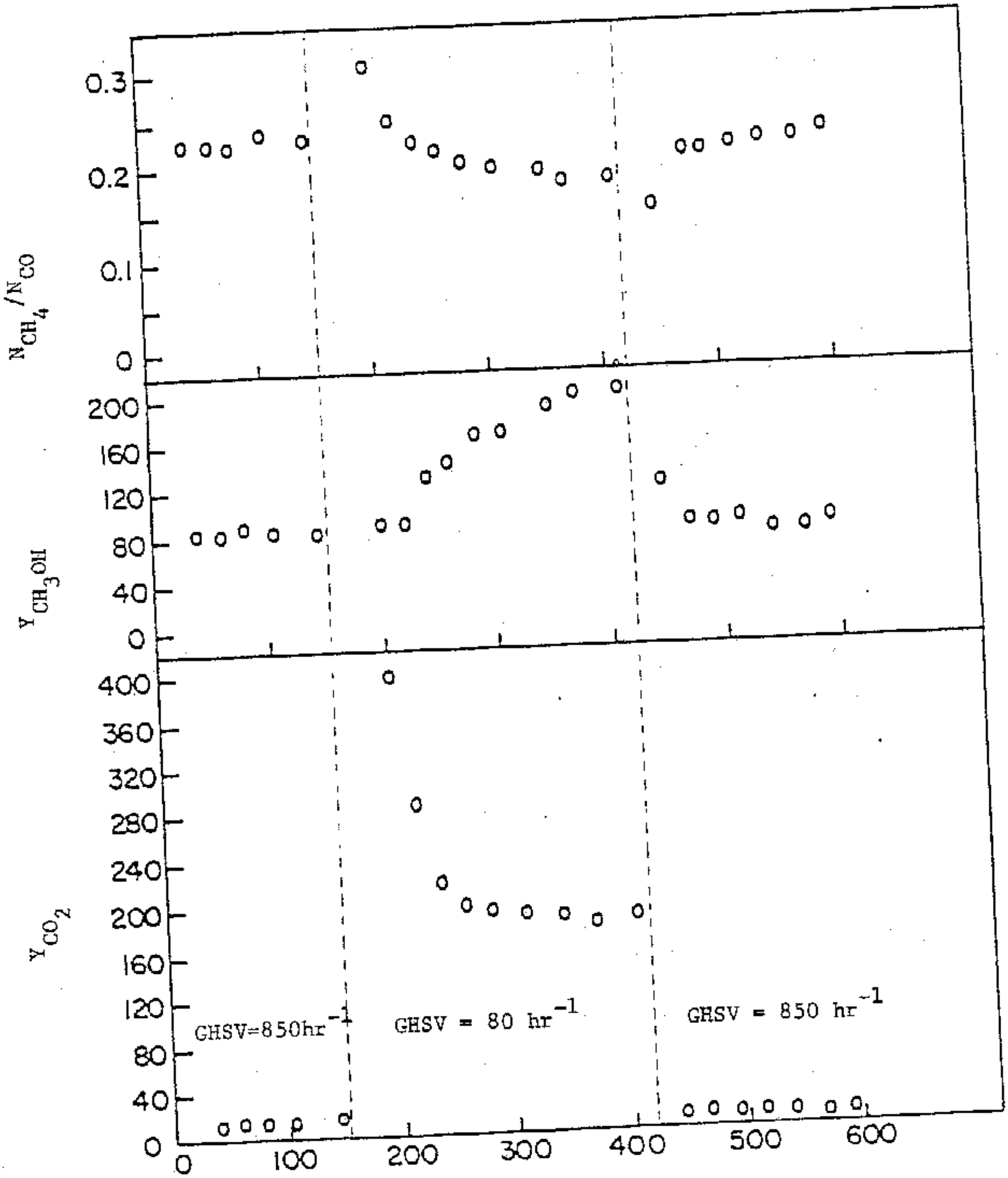

Figure 4.6.9 Carbon dioxide yield (bottom), methanol yield (middle), and N_{CH_4}/N_{CO} ratio as a function of time during the transient response for the Fe catalyst using the 1/3 CO/H_2 feed at 14 atm. and 250°C.

observed for the two feed mixtures suggest that the formation kinetics of the shift reaction surface intermediates is dependent on the bulk gas phase composition. This observation taken by itself is not suprising however it is interesting to note the simultaneous increase in methanol yield while the carbon dioxide yield is decreasing during the transient period (Figure 4.6.9).

4.6.5.2 Proposed Shift Reaction Mechanisms

The water gas shift reaction can proceed via a redox mechanism (69,109) given below

$$H_2O + S \rightarrow H_2 + O.S \qquad 4.6.6A$$

$$CO \cdot S + O \cdot S \rightarrow CO_2 \cdot S + S \qquad 4.6.6B$$

where S denotes an active surface site

A·S denotes an adsorbed species A

Successful rate expressions have been based on this model such as those presented in Section 4.2. However, more recent mechanistic investigations (121) indicate that coadsorbed CO and H_2O may react through a formate intermediate as shown below.

$$CO \cdot S + H_2O \cdot S - HCOOH \cdot S - H_2 + CO_2 \qquad 4.6.7$$

Infrared spectroscopic studies have revealed the presence of a formate type surface intermediate (106.115). Subsequent mechanistic investigations (121) have found that the kinetics of the shift reaction over a Cu/ZnO catalyst are consistent with a mechanism involving the decomposition of a stable formate-type surface intermediate as the rate limiting step.

4.6.4.2 Proposed Methanol Production Mechanism

A proposed reaction mechanism for the methanol synthesis reaction is given below (72,34)

$$CO \cdot S + OH \cdot S \rightarrow HOCO \cdot S \qquad 4.6.8A$$

$$HCOO \cdot S + 2H \cdot S \rightarrow OCH_2OH \cdot S \qquad 4.6.8B$$

$$OCH_2OH \cdot S + 2H \cdot S \rightarrow H_2O \cdot S + OCH_3 \cdot S + S \qquad 4.6.8C$$

$$OCH_3 \cdot S + H \cdot S \rightarrow CH_3OH \cdot S + S \qquad 4.6.8D$$

The formate type surface intermediate shown in equation 4.6.8.A is similar to the intermediate involved in the shift reaction (Equation 4.6.7). If these two reations occur via a common intermediate under FT conditions than enhanced methanol yields would be expected at higher pressures since the increased hydrogen partial pressure would favor methanol production (Equations 4.6.8B through 4.6.8D) compared to CO_2 production via the shift reaction (Equation 4.6.7). The surface hydroxyl groups (Equation 4.6.8A) can be provided by the readsorption and decomposition of water on the shift reaction/methanol synthesis site since this compound is produced in the hydrocarbon FT synthesis.

A more recent proposal which may explain the increase in methanol yields a decrease in shift activity at higher pressures involves the hydrogenation of carbon dioxide into methanol (81,60,104) illustrated below

$$CO + H_2O \rightarrow CO_2 + 2H_2 \xrightarrow{+H_2} CH_3OH + H_2O \qquad 4.6.9$$

This proposed reaction scheme is based on radioactive tracer experiments with labeled CO. The level of radioactivity in the methanol corresponded to the level found in the CO_2 and not to the level present in the CO reactant (60). Additionally, no methanol synthesis occurred when CO_2 or H_2O were absent in the reactant stream. An arguement against this proposal (72) involves the thermodynamics of the reaction involving the hydrogenation of carbon dioxide. At reaction temperatures this reaction is thermodynamically unfavorable (72). It is still uncertain whether or not CO_2 plays a significant role as a reactant in the methanol synthesis.

CHAPTER 5

SYNTHESIS STUDIES IN OLEFIN ENHANCED FEEDS

5.0 The presence of gas phase hydrocarbons can affect the overall selectivity of a FT catalyst through secondary reactions (Chapter 2). In this chapter the product yields and methane activities obtained in both pure and two olefin containing CO/H_2 mixtures are compared. The two olefin enhanced mixtures contain either 5.4 mole % ethylene or .5 mole % 1-pentene with a balance of CO/H_2 at a 1/3 molar ratio.

The experimental procedure employed in the reaction studies involving these feeds is identical to that reported in Chapter 3 unless otherwise stated. The only major difference in the experimental apparatus when using the 1-pentene feed as compared to the other feeds is the cold trap temperature. In this case the silica cold trap operated at approximately -10°C rather than -78°C. This is due to the relatively low vapor pressure of the 1-pentene in the feed. Consequently, condensable components in the reactant gas (i.e., H_2O) are not as effectively removed from this feed resulting in some possible changes in the catalytic activity and selectivity under these conditions. However during the course of an experiment using the 1-pentene CO/H_2 feed there generally was no appreciable loss in catalytic activity, as determined by measuring total product areas as a function of time during the course of an experiment.

Because of the relatively large amounts of olefin in the feed gas accurate mass balances involving the olefin component could not be obtained due to the inherent inaccuracies in GC peak area measurements (≈ ±5%). Consequently the CO turnover frequencies could not be measured when using the olefin containing feeds. All product yield, activity and selectivity comparisons amoung the various feeds are made at comparable space velocities. The methane activity obtained with the olefin feeds can be used as an indicator to evaluate the effect of the relatively high 1-pentene and ethylene concentrations on the overall CO activity.

5.1 Methane Activities in Olefin Enhanced Feeds

5.1.1 Fe Catalyst

The methane activities for all three catalyst are presented as a function of the gas hourly space velocity (GHSV) in figures 5.1.1 through 5.1.6. For the Fe catalyst (Figure 5.1.1 and 5.1.2) the presence of the feed olefin results in a decrease in the methane activity (N_{CH_4}) relative to the value obtained with the pure feed at the same GHSV. It is interesting to compare the magnitudes of the decrease in N_{CH_4} due to the presence of 1-pentene in the feed with the decrease due to increasing the CO conversion (decreasing the GHSV). For instance at 7.8 atmospheres with the pure CO/H_2 feed (Figure 5.1.2) the N_{CH_4}/P_T values decreases from approximately $2.5 \times 10^{-3} \frac{\text{molecules } CH_4}{\text{site-sec-atm}}$ to a value of $.85 \times 10^{-3}$ for a change in GHSV from 3000 hr^{-1} (2% CO conversion) to 200 hr^{-1} (9% CO conversion). If this decrease is solely due to gas phase hydrocarbon products inhibiting active sites through readsorption one would expect a much larger depression in the methane activity associated with the olefin containing feeds since the amount ethylene in the feed corresponds to well over 30% CO conversion and the amount of 1-pentene corresponds to about 7% CO conversion. It appears that the methane activity is only partially dependent on the gas phase hydrocarbon concentration.

The depression in N_{CH_4} with increasing conversion may be due to some

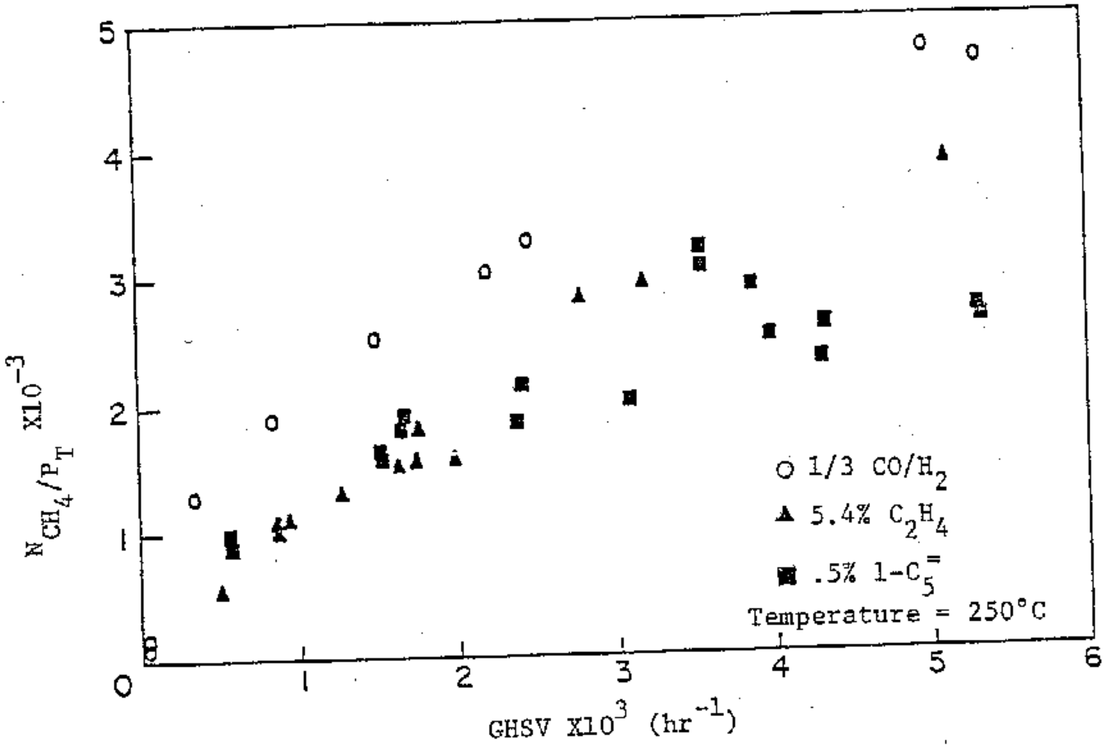

Figure 5.1.1 N_{CH_4}/P_T versus GHSV for the Fe catalyst using the olefin 1/3 CO/H$_2$ feeds at 1 atm.

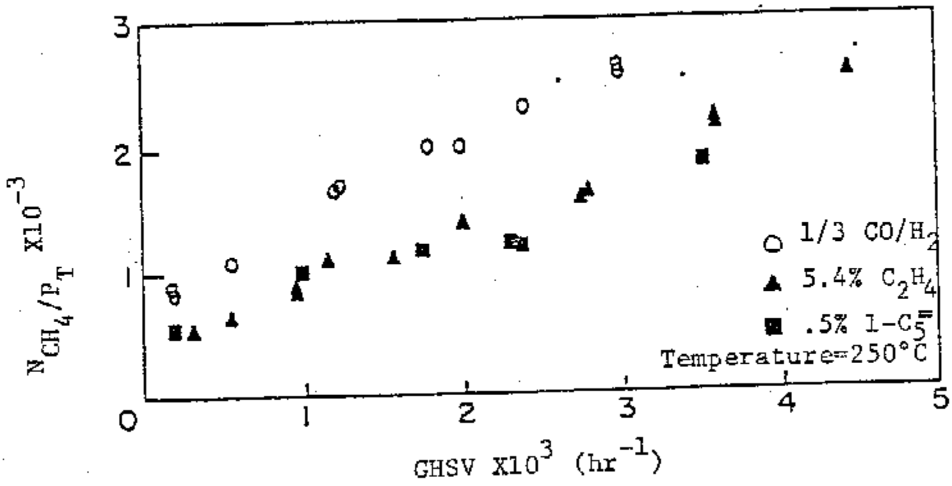

Figure 5.1.2 N_{CH_4}/P_T versus GHSV for the Fe catalyst using the olefin enhanced 1/3 CO/H$_2$ feeds at 7.8 atm. and 250°C.

type of self inhibition by methane since the functional form of the N_{CH_4} vs GHSV curve appears to be similar for both types of feed at the two pressures investigated. Discussions involving various kinetic possibilities for this behavior are given in section 6.3. The absence of any olefin hydrocracking is apparent and indeed in section 5.2 data is presented to further substantiate this point.

5.1.2 FeCo Catalyst

The methane activities for the alloy catalyst obtained with all three 1/3 CO/H_2 feeds are presented in Figures 5.1.3 and 5.1.4 for one and 7.8 atmospheres respectively. The N_{CH_4} values for this catalyst appear to be independent of feed olefin content over the various compositions studied. These results suggest that the methane activity is insensitive to the gas phase hydrocarbon composition. The depression in N_{CH_4} with increasing CO conversions is most likely due to the intrinsic kinetics of the methanation mechanism and its relationship to the overall FT synthesis mechanism. This subject will be further discussed in Chapter 6.

5.1.3 Co Catalyst

At one atmosphere the methane activity of the Co catalyst appears to be constant and equal for all three feed mixtures (Figure 5.1.5). This result is not suprising since the CO activity for this catalyst is found to be conversion independent for the 1/3 CO/H_2 feed (Section 4.1). At 7.8 atmospheres the methane activity is found to be similar for both the pure CO/H_2 and ethylene enhanced feed (Figure 5.1.6). However at this

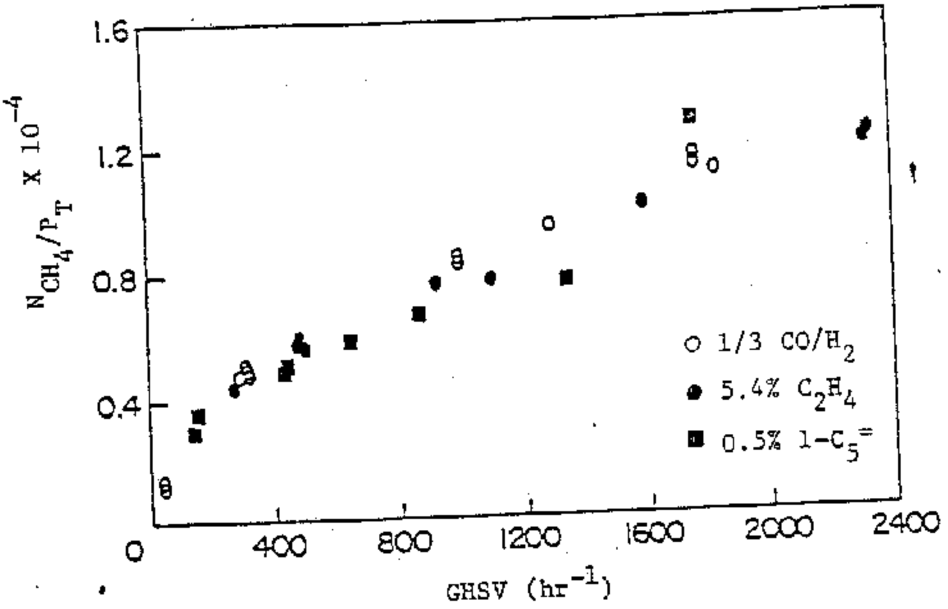

Figure 5.1.3 Methane activity versus GHSV for the FeCo catalyst using the olefin containing and pure 1/3 CO/H_2 feeds at 1 atm. and 250°C.

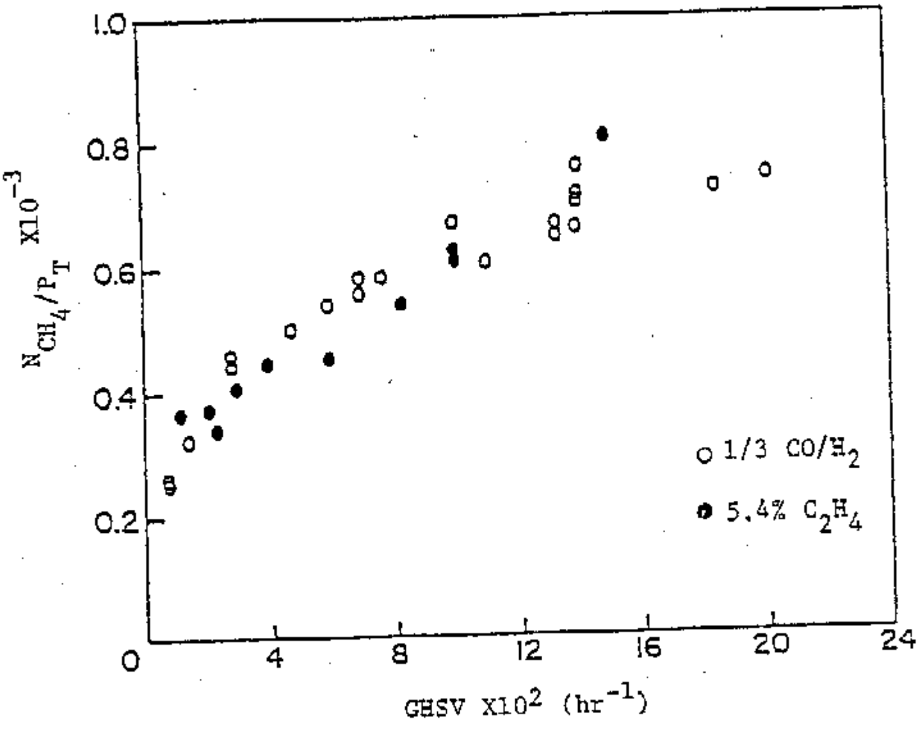

Figure 5.1.4 Methane activity versus GHSV for the FeCo catalyst using the ethylene containing and pure 1/3 CO/H_2 feeds at 7.8 atm. and 250°C.

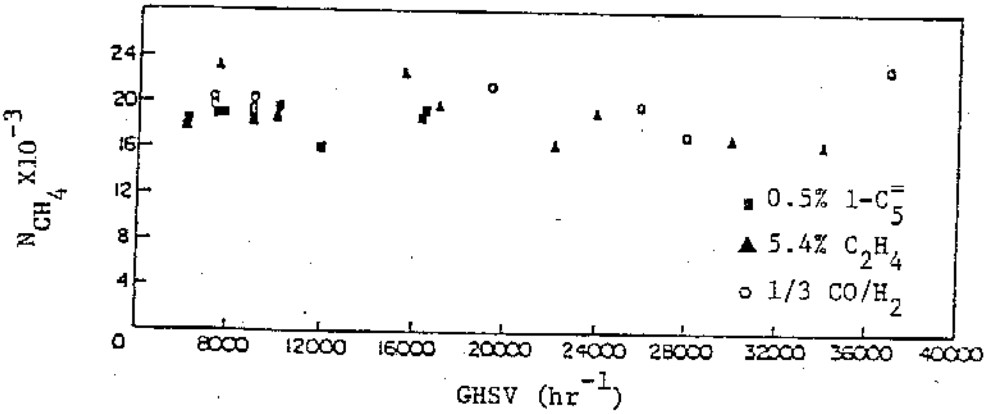

Figure 5.1.5 Methane activity versus the GHSV for the Co catalyst using the olefin containing and pure 1/3 CO/H_2 feed at 1 atm. and 250°C.

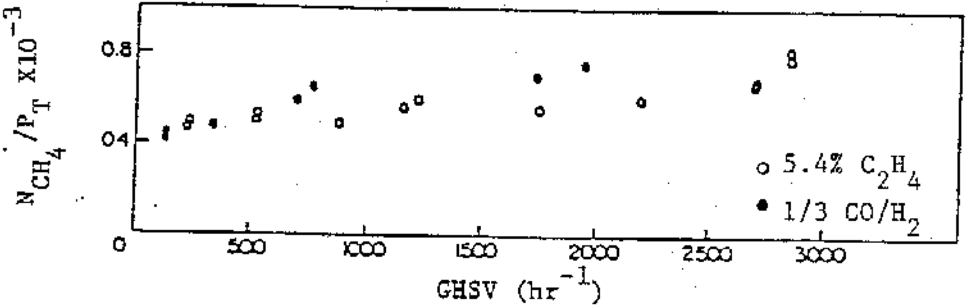

Figure 5.1.6 Methane activity/total pressure versus the GHSV for the Co using the ethylene containing and pure 1/3 CO/H_2 feed at 7.8 atm. and 250°C.

pressure the initial activity obtained with the 1-pentene enhanced feed is found to be a factor of three times higher than that obtained with the other feeds. Unfortunately this particular experiment was not repeated and since there was a significant loss in activity during the course of the run, the data are not included in Figure 5.1.6, but rather in Appendix VI.

5.1.4 Discussion on Methane Hydrocracking

It appears that for the iron based catalyst neither ethylene nor 1-pentene undergoes measurable hydrocracking under the reaction conditions employed in this study. These results agree with the previous findings of Hall, Kokes and Emmett (54). Methane formation via hydrocracking has been studied by Koelbel, Ludwig, and Hammer (65). They report that less than 5% of the methane produced over a commercial bulk Co catalyst is from the hydrocracking of multicarbon products, while the corresponding value for a bulk Fe catalyst is less than 3%. If these percentages of the ethylene are indeed cracking to methane, the increase in N_{CH_4} is not readily measurable since the error associated with the methane peak area is approximately 5% to 10%.

The increased methane activity observed for the Co catalyst at 7.8 atmospheres corresponds to approximately 3.4% of the feed 1-pentene undergoing complete hydrocracking to methane (Appendix VI). The corresponding decrease in total C_5 product area would not be detectable. Consequently this increase could be due to 1-pentene hydrocracking. This subject is further explored in the next section.