

This indicates that the gas phase ethylene does not hydrogenate as readily on this catalyst as compared to the Fe catalyst where the differences are much smaller. As the GHSV is decreased the ratio associated with both feeds approach similar values as in the case for iron. Similar behavior is observed at 7.8 atmospheres (Figure 5.4.4). The $X_{C_3^=}/X_{C_3}$ ratios for both feed mixtures at one atmosphere pressure are given in Figure 5.4.5. The ratio values obtained using the 1-pentene feed are included in this figure as a matter of convenience. The propylene/propane ratios obtained with the ethylene/CO/H₂ feed lie well above the values obtained with the pure feed. It again appears that the primary gas phase product from the ethylene insertion reaction is propylene. The $X_{C_3^=}/X_{C_3}$ data for the Co catalyst at 7.8 atmospheres are not available since high GHSV values were employed and only trace amounts of propane were produced.

5.4.1.3 FeCo Catalyst

The $X_{C_2^=}/X_{C_2}$ and $X_{C_3^=}/X_{C_3}$ ratios for the alloy catalyst for the alloy catalyst are presented in Figure 5.4.6 for both feeds at a total pressure of one atmosphere. There is a marginal increase in the propylene/propane ratio due to the ethylene in the feed mixture. The ethylene/ethane ratios are identical for both feeds over the entire GHSV region investigated at one atmosphere. These results are a bit surprising in light of the fact that the total partial pressure of the C₂ products is fifty to one hundred times higher in the ethylene/CO/H₂ mixture compared to the pure CO/H₂ mixture over the GHSV range investigated. In section 4.3 ethylene yield data is presented which shows that the alloy catalyst

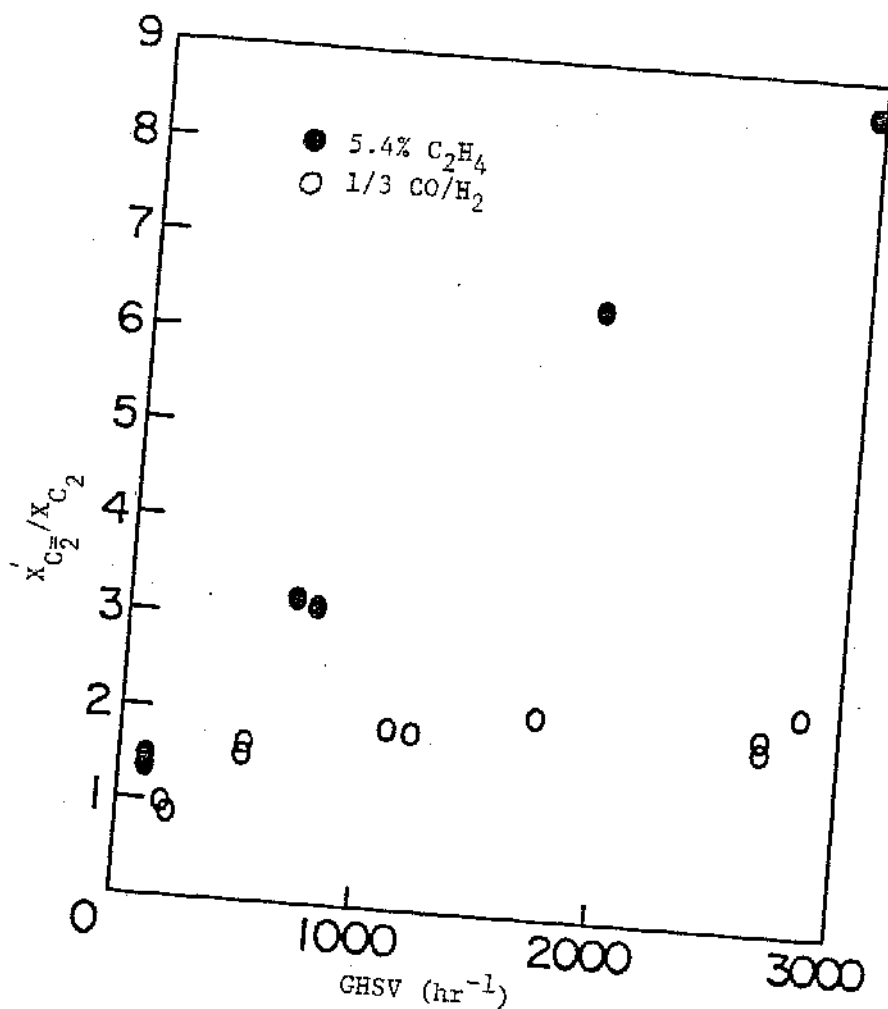


Figure 5.4.4 Ethylene to ethane mole fraction ratio versus the space velocity for the Co catalyst using the ethylene containing and pure 1/3 CO/H_2 feeds at 7.8 atm. and 250°C.

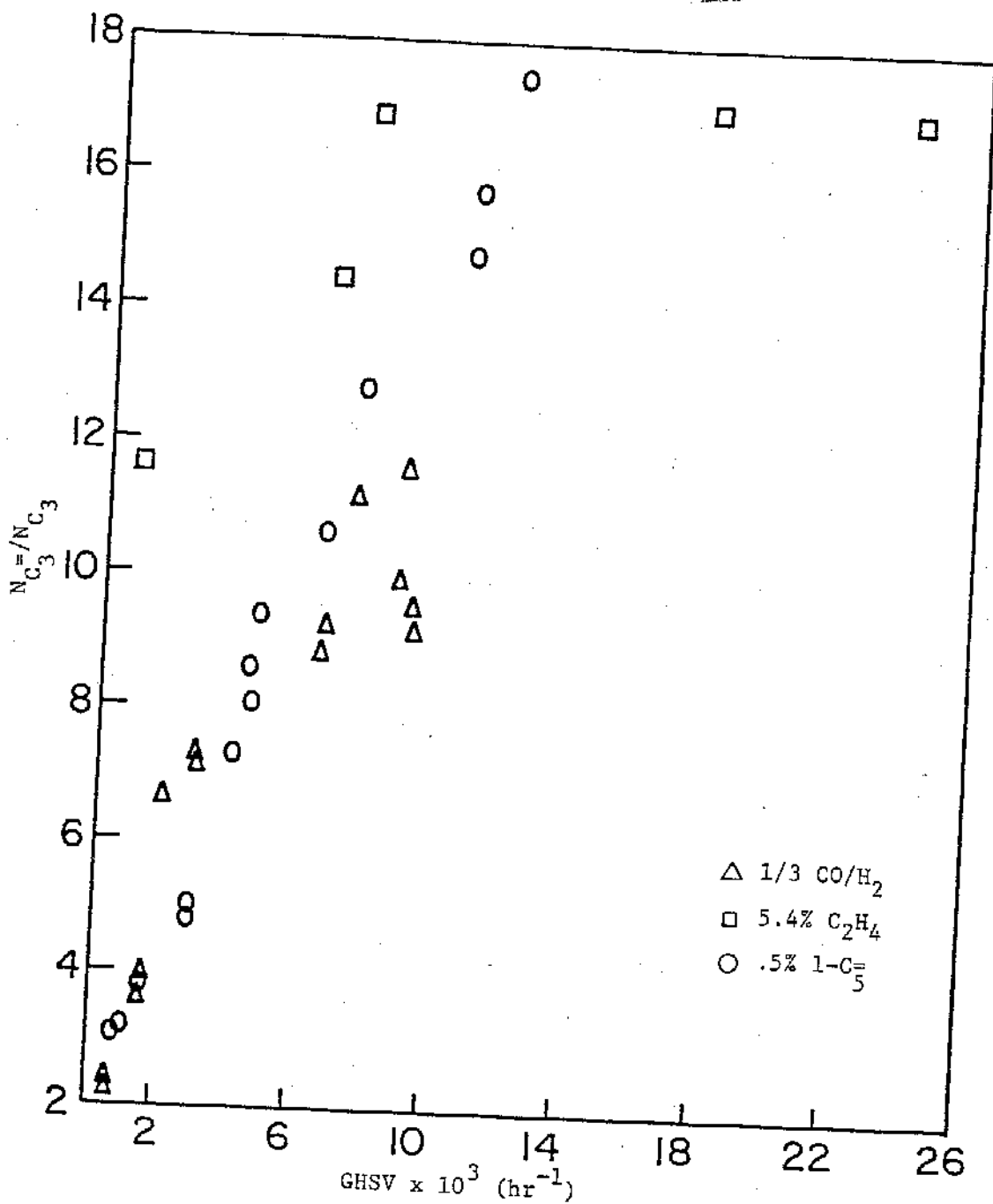


Figure 5.4.5 $N_{C_3^=} / N_{C_3}$ ratio versus the GHSV for the Co catalyst at one atmosphere using the 1-pentene, ethylene and pure 1/3 CO/H₂ feeds.

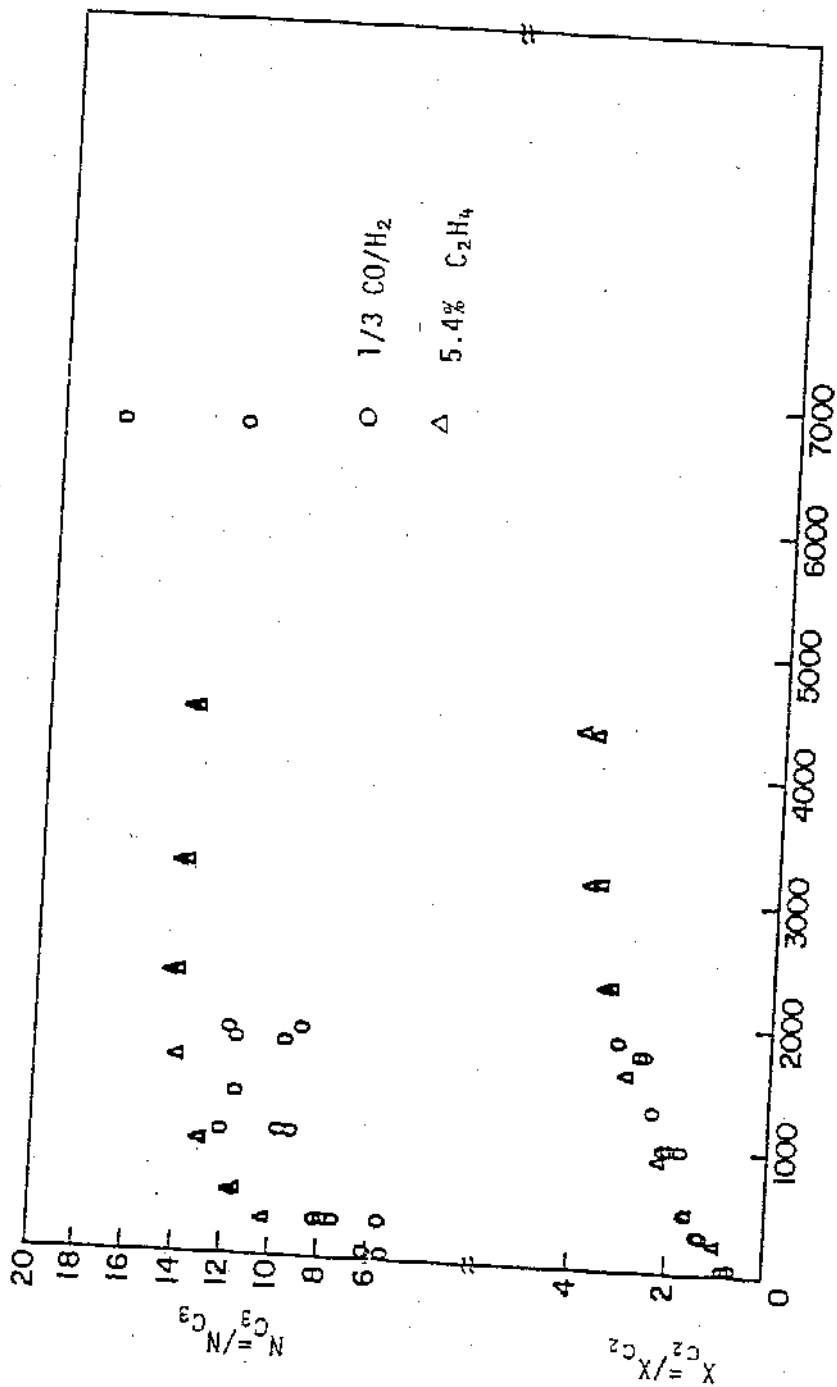


Figure 5.4.6 The ethylene/ethane mole fraction ratio and the propylene/propane selectivity as a function of GHSV for the FeCo catalyst using the ethylene containing and pure 1/3 CO/H₂ feed at 1 atm and 250°C.

has the highest intrinsic ability to produce ethylene on a total CO consumed basis at one atmosphere. The fact that the ethylene/ethane selectivity appears to be independent of the ethylene and ethane gas phase concentration indicates that the adsorption/desorption kinetics of these products play a small role (if any) in determining their rate of production. This subject is discussed in Section 5.4.2.

Figure 5.4.7 presents the $X_{C_2^=}/X_{C_2}$ and $X_{C_3^=}/X_{C_3}$ data for the alloy catalyst at 7.8 atmospheres. At this pressure there is no change in the propylene/propane ratio. This is due to the enhanced hydrogenation activity at the higher pressure. The $X_{C_2^=}/X_{C_2}$ ratios are again identical for both the ethylene and pure CO/H₂ feed. In the next sections the kinetics of ethylene hydrogenation are reported and the secondary reactions of ethylene are discussed in relation to the overall FT reaction mechanism.

5.4.2 Hydrogenation of Feed Gas Ethylene

Comparison of the $X_{C_2^=}/X_{C_2}$ ratios for the iron containing catalysts indicates that a large fraction (typically >30%) of the feed ethylene hydrogenates. These ratios are typically 0.5 to 3.0 for both the ethylene and pure CO/H₂ feed. If no feed ethylene undergoes hydrogenation the $X_{C_2^=}/X_{C_2}$ ratios would typically range from 70 to 100 over the GHSV range investigated, so even in the case of the cobalt catalyst where the ratios vary from 1.0 to 9.0 there is a substantial amount of hydrogenation. In order to obtain some insight into the secondary olefin hydrogenation step and how it possibly relates to the FT synthesis reactions it is worthwhile to compare the hydrogenation activity of the catalyst at the conditions investigated.

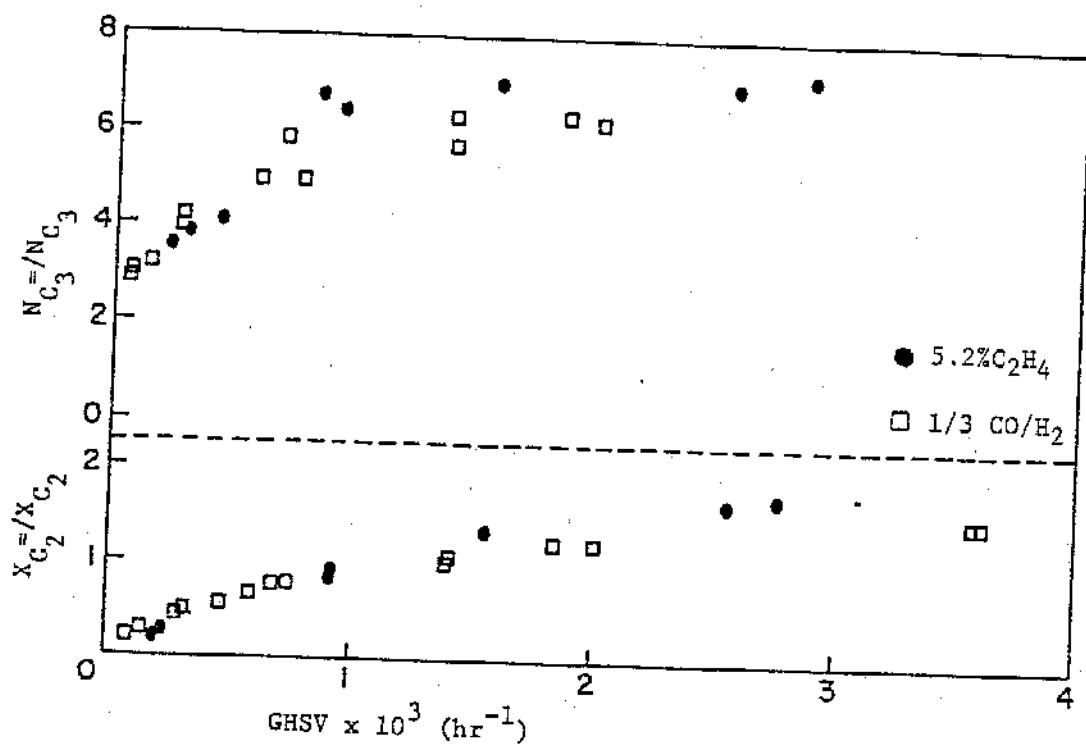


Figure 5.4.7 Ethylene to ethane and propylene to propane selectivities versus the GHSV for the FeCo catalyst with the ethylene containing and pure 1/3 CO/H $_2$ feeds at 7.8 atm and 250°C.

N_{HC_2} catalyst are listed in Table 5.4.1 at some typical reaction conditions employed in this investigation. The N_{HC_2} values are calculated in a manner similar to that used to determine the CO activities (Section 4.1). The total number of available catalytic sites is determined by hydrogen chemisorption over the reduced metallic catalyst. Since the olefin hydrogenation mechanism (Section 2.3.3 (H4,H5)) involves two active sites, the number of active sites available for ethylene hydrogenation is half the total number determined by hydrogen chemisorption. Calculation of N_{HC_2} by this method may not be quantitatively correct since the hydrogenation mechanism for metallic surfaces may be completely different than the mechanism over FT surfaces. In any case the values listed in Table 5.4.1 provide a basis for comparison among the catalyst.

Table 5.4.1 Ethylene Hydrogenation Activity

Catalyst	GHSV (hr ⁻¹)	Pressure (Atm)	$N_{HC} \times 10^{-1}$		Growth (4) Probability (a)
			Molecules ethane formed site-sec	N_{CO}/N_{HC_2} (2)	
Fe	5100	1.0	11.5	.13	
	825(3)	1.0	3.0	.2	> .43
	4443	7.8	85.0	.07	
	526	7.8	14.0	.5	> .53
FeCo	4387	1.0	6.5	.06	
	494(3)	1.0	1.4	.1	> .47
	2796	7.8	18.5	.1	
	467	7.8	17.0	.08	> .44
Co	24100	1.0	30.0	.16	
	15700(3)	1.0	28.0	.16	> .46
	1868	7.8	14.0	.1	
	142	7.8	5.0	.3	> .77

- 1) Based on number of sites determined by H_2 chemisorption on reduced metallic catalyst. Assuming two sites are involved in the hydrogenation reaction.
- 2) CO turnover frequency (N_{CO}) corresponds to value obtained in CO/ H_2 feed at comparable GHSV. (Section 4.1)
- 3) GHSV values in brackets correspond to comparable ethylene molar flow rates.
- 4) From Table 4.6.1.

The hydrogenation activity is generally strongly dependent upon the GHSV in a manner similar to the CO activity (N_{CO}) discussed in Section 4.1. In most cases decreasing the GHSV (increasing CO conversion) results in lower ethylene hydrogenation activity. The exceptions (FeCo at 7.8 atm and Co at 1 atm) to this general behavior can provide some clues into the nature of this inhibition and how it is related to the synthesis process. Before discussing the two exceptions, the predominant trend is compared to the observed decrease in CO activity with increasing GHSV presented in section 4.1.

Product inhibition or possible reversible deactivation of active sites are two possible reasons for the observed decrease in the CO activity with increasing conversion (decreasing GHSV). Indeed both are plausible since a greater amount of heavier possibly slower desorbing products are formed at lower GHSV values as well as larger quantities of water which can reversibly deactivate FT sites. The percentage increase in either water or heavier FT products in going to a smaller GHSV need not be that great in order to have a measurable effect on the overall rate since these products are produced on the active sites and can readily inhibit their activity if the desorption kinetics are slow. If one assumes that a similar type of inhibition effect is occurring on the ethylene hydrogenation sites and these sites exist as separate entities independent of the FT sites the observed decrease in the N_{HC_2} values at lower space velocities cannot be readily justified.

The N_{CO}/N_{HC_2} ratios (Table 5.4.1) indicate that generally the hydrogenation activity decreases faster than the CO activity with decreasing GHSV. This implies that if a common inhibition effect is

affecting both activities it is more pronounced for ethylene hydrogenation. If independent hydrogenation sites exist on the catalyst surface they could only be inhibited by the FT products since it is unlikely that ethane (or for that matter any paraffin product) will inhibit ethylene hydrogenation. In order to adsorb onto a hydrogenation site the product molecule would first have to desorb off the FT site. If the slow desorption kinetics are responsible for the decrease in N_{CO} , how can the larger relative decrease in N_{CH_2} occur? One possible explanation is that there is a much smaller number of hydrogenation sites relative to the increase in products which can inhibit hydrogenation sites are indeed being blocked by nondesorbing FT products one would not expect the olefin/paraffin ratios, for a given carbon chain to decrease at lower GHSV values when this inhibition would be more pronounced. In section 5.4.3 data obtained with the .5 mole % 1-pentene feed strongly indicates that the overall hydrogenation activity of the C_2 and C_3 olefins is unaffected by the presence of the high concentration of the C_5 olefin in the feed gas.

An additional experimental result which indicates that hydrogenation sites do not exist independently of the synthesis sites are the comparable $X_{C_2^=}/X_{C_2}$ ratios obtained with both the ethylene and pure CO/H_2 feed (section 5.3). Figure 5.4.8 presents the $X_{C_2^=}/X_{C_2}$ values for the alloy catalyst at 1 and 7.8 atmosphere. If a certain fraction of the total catalytic sites is only active for ethylene hydrogenation one would expect the $X_{C_2^=}/X_{C_2}$ ratio to be proportional to the gas phase olefin concentration at a given GHSV, since dehydrogenation reactions are unlikely due to the high hydrogen partial pressure. The introduction of 5.4 mole % ethylene

■ 1/3 CO/H₂ @ 1 atm.
 ● 5.4% C₂H₄ @ 1 atm.

□ 1/3 CO/H₂ @ 7.8 atm.
 ○ 5.4% C₂H₄ @ 7.8 atm.

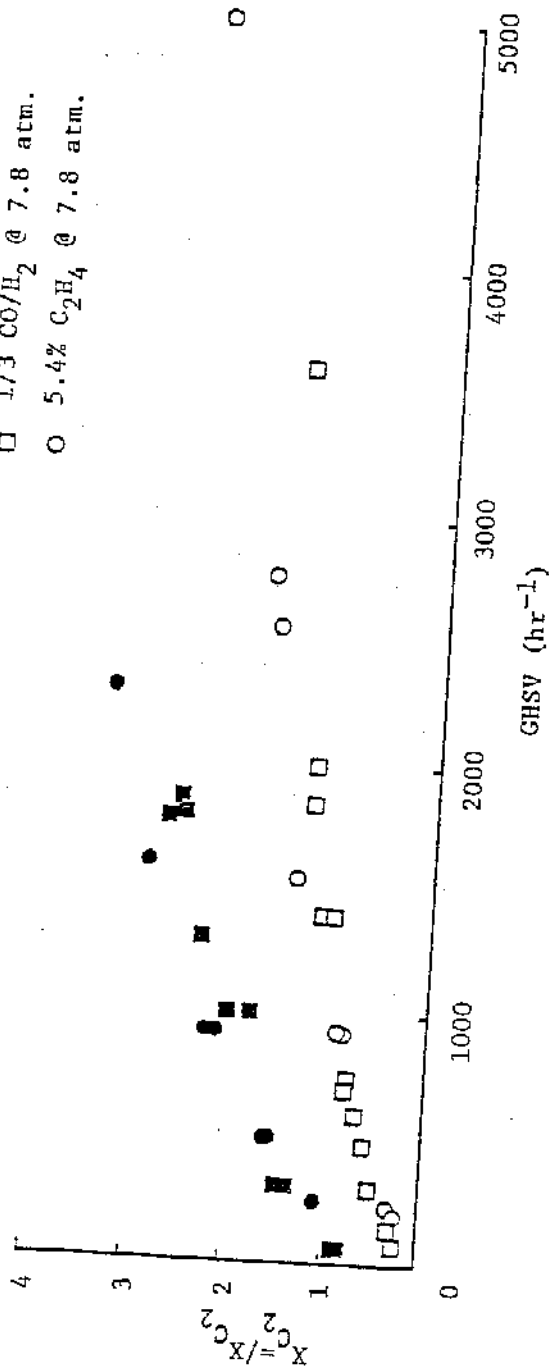


Figure 5.4.8 Ethylene to ethane mole fraction ratio versus the GHSV for the FeCo catalyst using the ethylene containing and pure 1/3 CO/H₂ feed at 1 and 7.8 atm. Temperature = 250°C.

in the feed gas corresponds to a concentration at least fifty times greater than typical ethylene product concentrations obtained with conversion levels typically employed in the pure CO/H₂ feed. If all the gas phase components are competing for a finite fraction of specific hydrogenation sites one would expect the $X_{C_2^=}/X_{C_2}$ ratios to be much higher with the ethylene feed as compared to the pure feed for a given GHSV. The incidental ($X_{C_2^=}/X_{C_2}$) vs GHSV curves obtained with these two feeds at the pressures studied indicate that no such competition is observable. Based on these arguments it appears that separate hydrogenation sites do not exist on the catalyst surface. In section 2.4 results from surface spectroscopy investigations are reviewed and indicate that for iron catalyst, no metallic atoms are detected after exposure to CO/H₂ mixtures. Indeed CO is so strongly adsorbed on such Fe and Co metal surfaces that it is unlikely that even a small fraction of these sites exist (26). The hydrogenation and FT synthesis reactions most likely occur on a common site with different reaction intermediates. This subject as well as the different possible chemical nature of the two intermediates is discussed in sections 5.2 and 6.3.

Referring back to table 5.4.1, two cases are observed where the ethylene hydrogenation activity is found to be independent of the gas hours space velocity (GHSV), the Co catalyst at 1 atm and the alloy catalyst at 7.8 atm. The Co catalyst does not exhibit any decrease in CO activity at lower GHSV values at this pressure. The inhibition effect observed at other conditions is not seen at 1 atmosphere with the 1/3 CO/H₂ feed. The lack of any conversion dependency in the ethylene hydrogenation activity at these same conditions supports the belief that both the

hydrogenation and FT activity are inhibited by some common mechanism.

The alloy catalyst exhibits constant ethylene hydrogenation activity over the GHSV range investigated at 7.8 atmospheres. This behavior is quite different than that observed for the pure component catalyst. In section 4.3 and 4.5 yield and selectivity data are presented which indicates that the FeCo catalyst possesses the highest intrinsic hydrogenation activity on a product basis. The product yields for this catalyst contain the greatest amount of paraffins. Interestingly enough the FeCo SF growth parameter, α , (section 4.5) remains constant 7.8 atmospheres as compared to 1 atmosphere and the product distribution did not shift towards higher molecular weight products (Section 5.6). These results are consistent with a reaction pathway that favors hydrogenation over carbon chain growth. Consequently the constant ethylene hydrogenation activity observed for the FeCo catalyst at 7.8 atmosphere is not unreasonable.

The hydrogenation activity for the Fe and FeCo catalysts increase at 7.8 atmospheres compared to 1 atmosphere (Table 5.4.1). This is expected since olefin hydrogenation rates are positive order in hydrogen partial pressure (48). However for the Co catalyst the activity decreases significantly at the higher pressure. This may reflect a change in the principle reaction pathways available for reaction intermediates. The growth probability α undergoes a sizable increase suggesting that the chain propagation reaction are preferentially enhanced over termination reaction such as hydrogenation at the higher pressure (Table 5.4.1).