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5.4.5 Secondary Reactions Involving 1-Pentene

The presence of 0.5 mole % 1-pentene in the feed gas does not significantly affect the overall product distribution for all the catalysts at the low CO conversion levels investigated (Section 5.2). However this olefin does undergo extensive hydrogenation and double bond isomerization under FT reaction conditions. Figure 5.4.15 is a plot of the 1-pentene fraction contained in the total C₅ moles as a function of the GHSV at various pressures for the iron catalyst. The space velocity range employed at each pressure corresponds to an approximate CO conversion range of .5 to 4%. The fractional amount of feed 1-pentene which reacts via secondary reactions decreases with increasing pressure. Similar trends are observed for both the FeCo and Co catalyst. These results indicate that olefin readsorption and reaction through secondary pathways plays a diminishing role at higher pressures with respect to shifts in the product distribution.

Figure 5.4.16 presents the 1-pentene and n-pentane mole fractions ($\frac{\text{moles C}_5\text{i}}{\text{total C}_5\text{moles}}$) for the Co catalyst at 1 atmosphere. The open symbols represent fractions obtained with the 1-pentene feed while the solid symbols correspond to a pure 1/3 CO/H₂ feed. The fractions are comparable with both feeds suggesting that the adsorption of the feed 1-pentene is not rate limiting with respect to the secondary reaction kinetics. Similar results were observed for the iron containing catalyst.

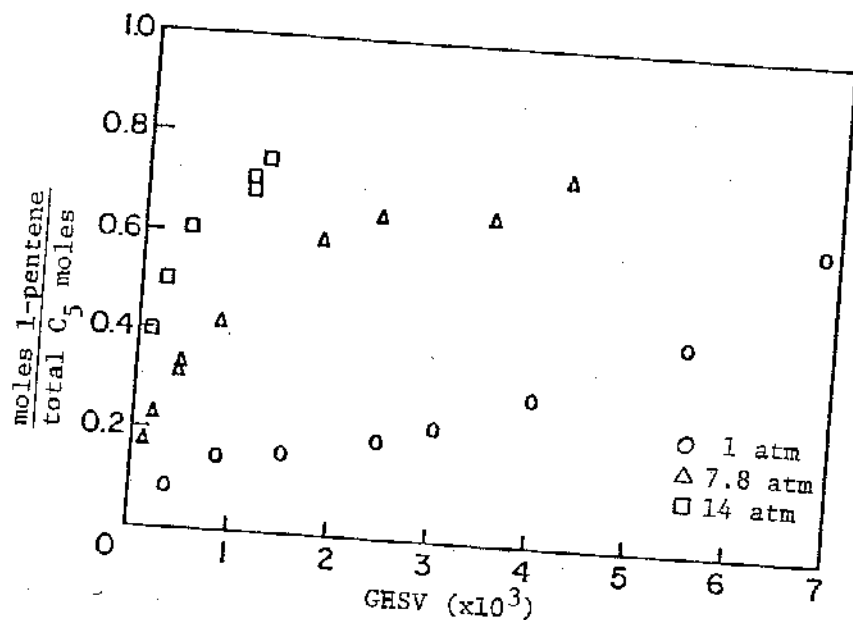


Figure 5.4.15 1-pentene fraction of total C₅ products versus the GHSV for the Fe catalyst using the 0.5% 1-pentene 1/3 CO/H₂ feed at several pressures and 250°C.

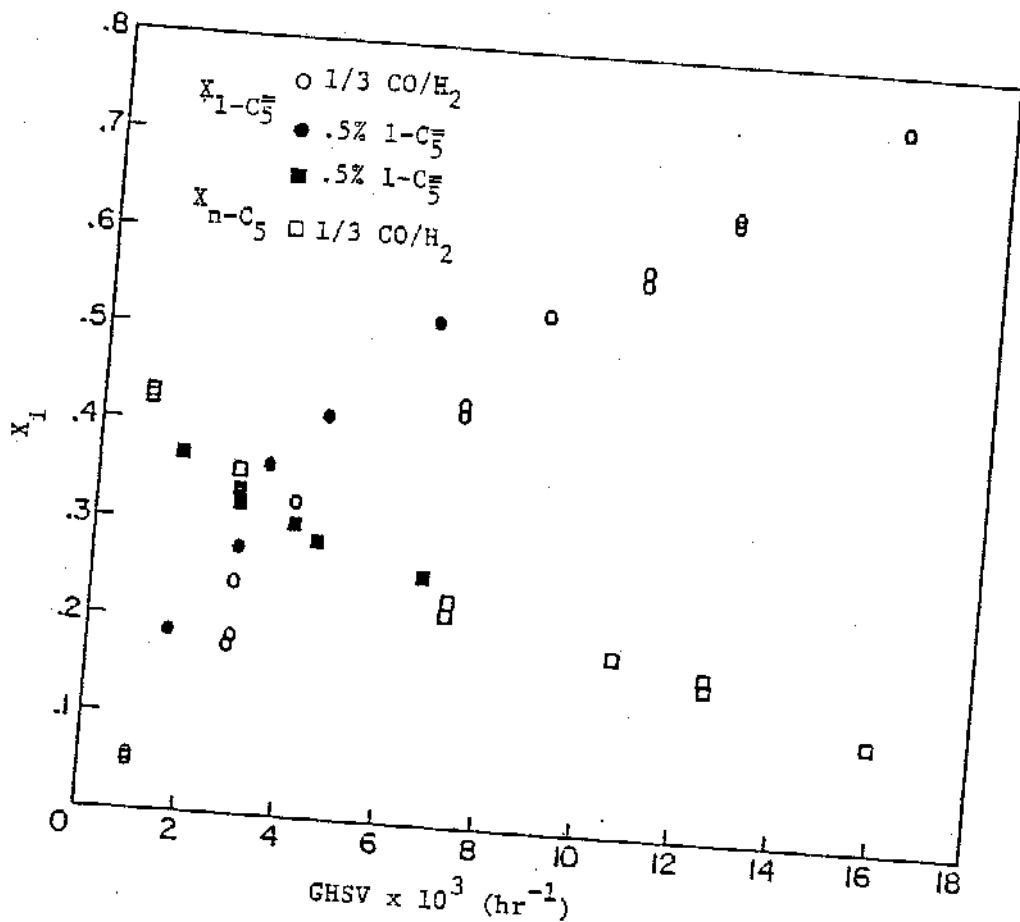
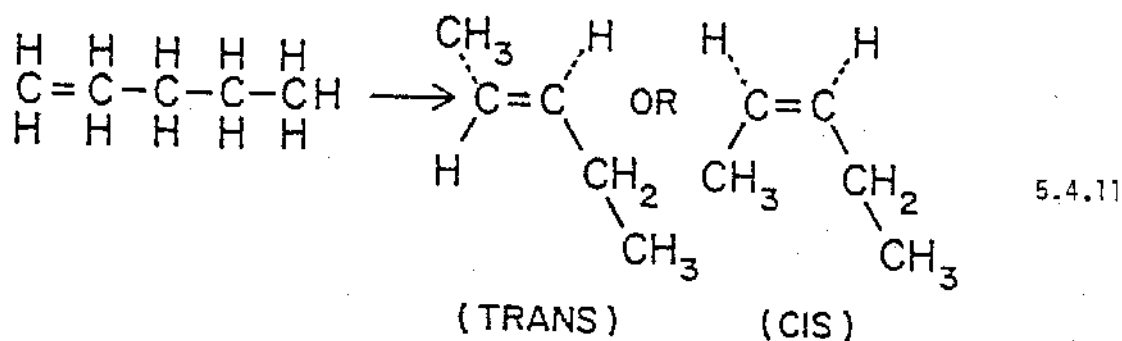


Figure 5.4.16 1-pentene and n-pentane fractions of total C₅ products versus the GHSV for the Co catalyst using the 1-pentene containing and pure 1/3 CO/H₂ feed at 1 atm and 250°C.

The 1-pentene and n-pentane mole fractions are plotted as a function of the GHSV for all three catalysts at 7.8 atmospheres in Figure 5.4.17. The Co catalyst produces the smallest amount of n-pentane over this CO conversion range. This is expected since this catalyst exhibits the highest olefin/paraffin selectivities. The n-pentane yield of the alloy catalyst is essentially identical to the Fe catalyst over the GHSV range investigated. This is not surprising since these two catalyst yield similar $\text{NC}_2^-/\text{NC}_2$ and $\text{NC}_3^-/\text{NC}_3$ selectivities at these conditions.

The 0.5 mole % 1-pentene in the CO/H₂ feed undergoes extensive double bond isomerization into both cis and trans 2-pentene. The reaction can be written as shown below



5.4.11

At one atmosphere over the Fe catalyst, the combined 2-pentene yields account for over 60% of the total C₅ products while at higher pressures the yields decrease (Figure 5.4.18). Similar behavior is observed for the FeCo and Co catalyst (Figures 5.4.19 and 5.4.20). Increasing pressure increases the n-pentane yields for the Fe and FeCo catalyst as shown in Figures 5.4.21 and 5.4.22. The Co catalyst exhibits unusual behavior in the n-pentane yield-pressure trend. Increasing pressure decreases the n-pentane yield (Figure 5.4.23) in addition to the 2-pentene yields. At 7.8 atmospheres the 1-pentene is possibly hydrocracking over this catalyst and this may be the preferred reaction

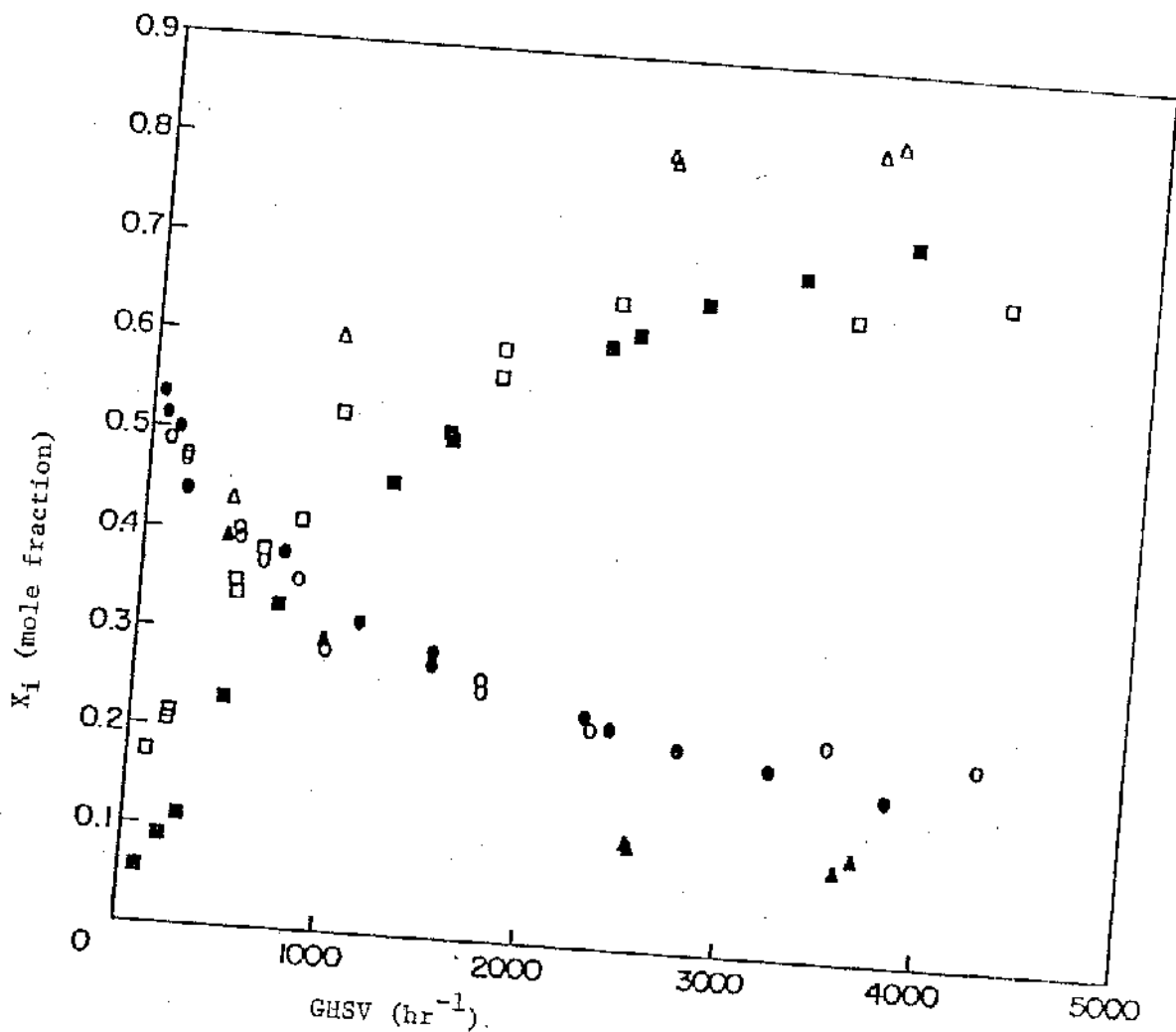


Figure 5.4.17 Mole fractions of 1-pentene and n-pentane versus the GHSV for all three catalysts using the 0.5% 1-pentene 1/3 CO/H₂ feed at 7.8 atm and 250°C.

- Fe □ 1-pentene
 ○ n-pentane
- FeCo ■ 1-pentene
 ● n-pentane
- Co △ 1-pentene
 ▲ n-pentane

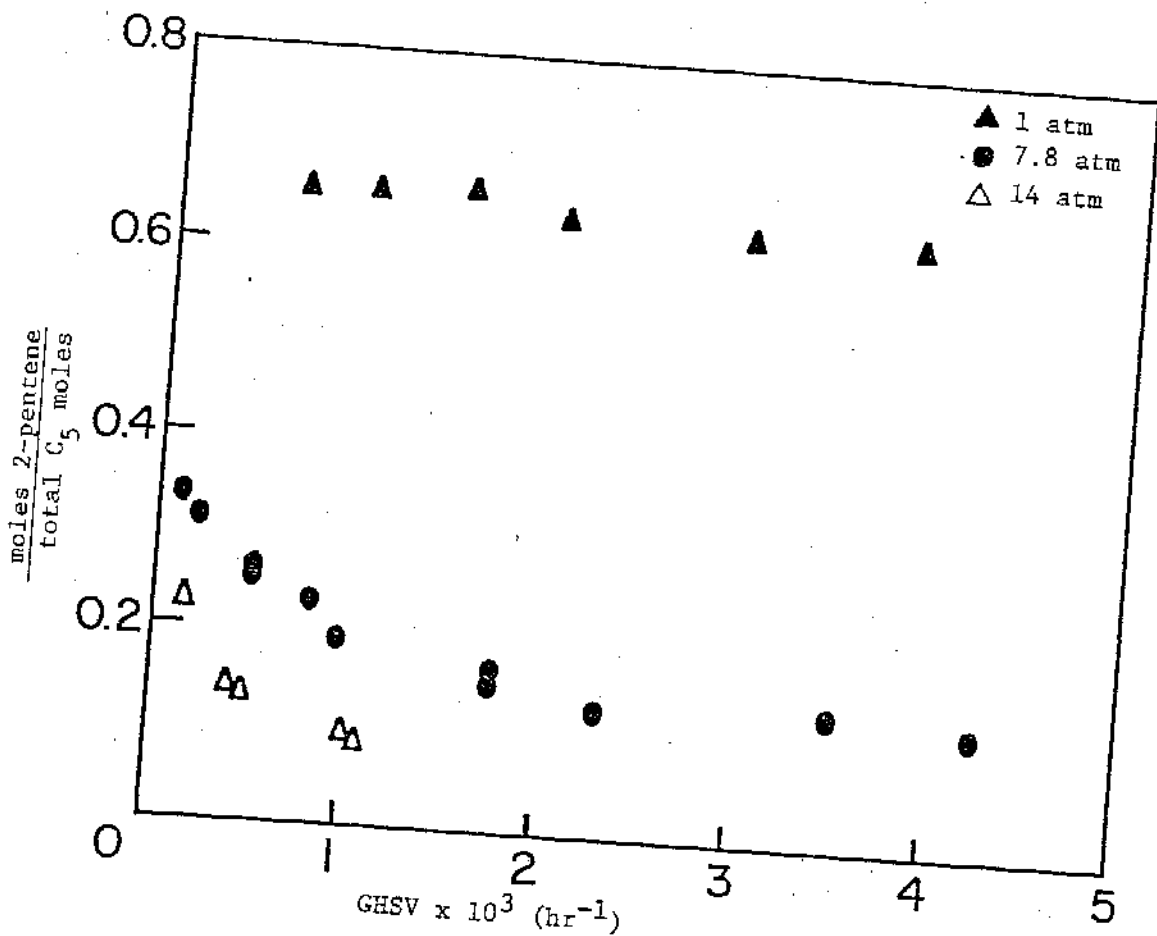


Figure 5.4.18 2-pentene fraction of total C₅ moles versus the GHSV for the Fe catalyst using the 0.5% 1-pentene 1/3 CO/H₂ feed at various pressures and 250°C.

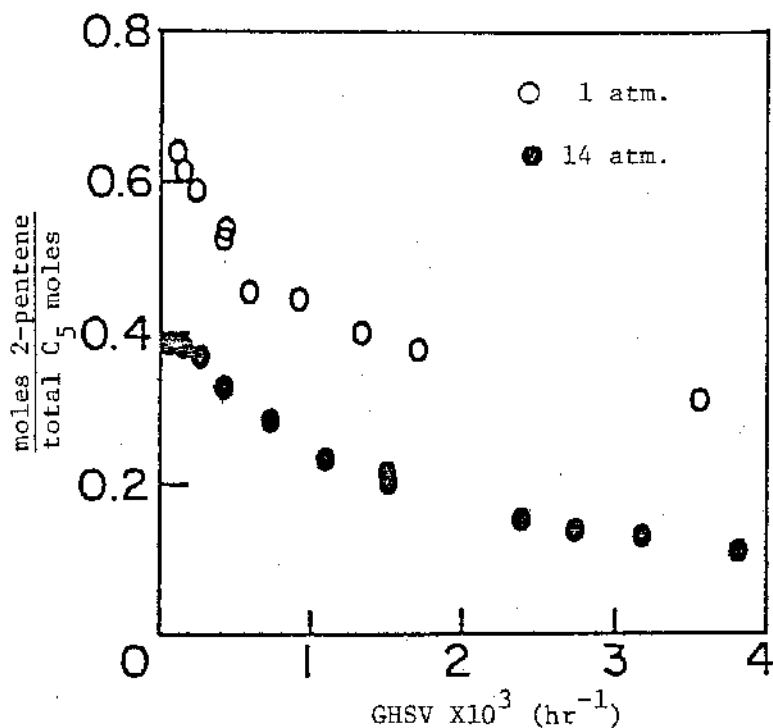


Figure 5.4.19 Fraction of 2 pentene in total C₅ products for the FeCo catalyst using the 1-pentene/1/3 CO/H₂ feed at 1 and 14 atm. Temp. = 250°C.

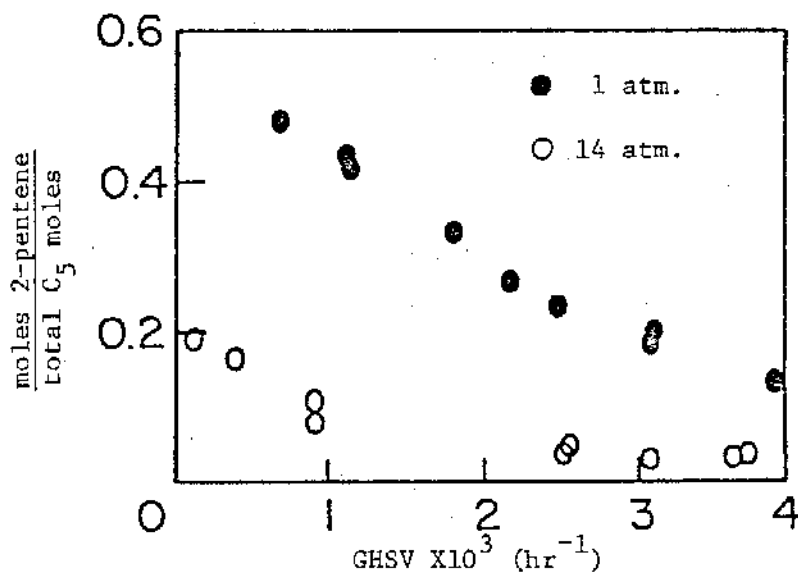


Figure 5.4.20 Fraction of 2-pentene in total C₅ products for the FeCo catalyst using the 1-pentene/1/3 CO/H₂ feed at 1 and 14 atm. Temp. = 250°C.

pathway at these conditions. In any case these results further support the argument that secondary olefin incorporation into growing hydrocarbon chains is not the predominant reaction pathway responsible for long chain products at elevated pressures. The 1-pentene undergoes isomerization and hydrogenation over pure Davidson 62 silica gel however the rates of these reactions are found to be approximately 50 times less than observed with the catalyst.

The incorporation of α olefin products is indeed partially responsible for chain growth, however internal (β) olefins are not believed to be reactive in secondary chain growth reactions. The large extent of α to β olefin isomerization is consistent with the observed lower molecular weight product distributions obtained at one atmosphere compared to those obtained at higher pressures. The production of internal olefins effectively removes that carbon chain from any subsequent secondary chain growth reactions.

The cis and trans 2-pentene yields (based on total C_5 product) produced with the 1-pentene CO/H_2 mixture appear to be comparable to the yields produced with the pure CO/H_2 feed. This comparison cannot be readily made for all catalysts and conditions studied since the pure feed yields are very small in most cases making quantitative analysis of the isomers difficult. Results obtained with the Co catalyst at one atmosphere are given in figure 5.4.24. Similar results are obtained with the n-pentane yields.

5.4.5 Proposed Reaction Sequence Leading to C_5 Products

The reaction sequence proposed in section 5.4.2.2 receives additional support from the selectivity studies presented in the previous section. The presence of independent hydrogenation sites is unlikely in

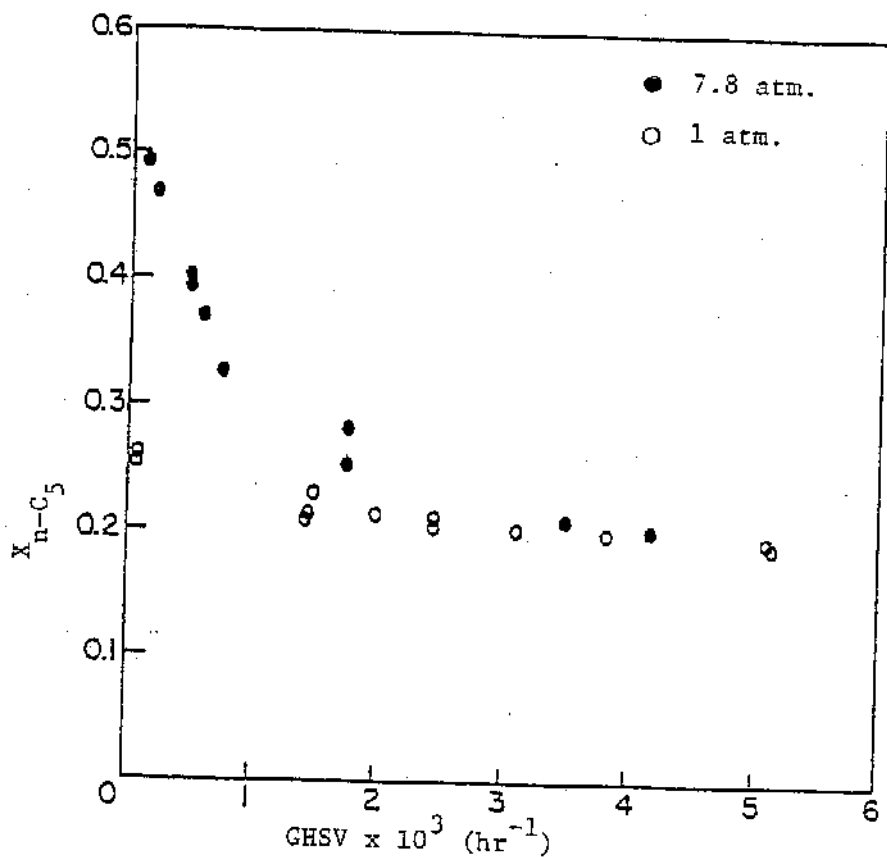


Figure 5.4.21 The n-pentane fraction of total C_5 products versus the GHSV for the Fe catalyst using the 1-pentene CO/H_2 feed at 1 and 7.8 atm. Temperature = 250°C.

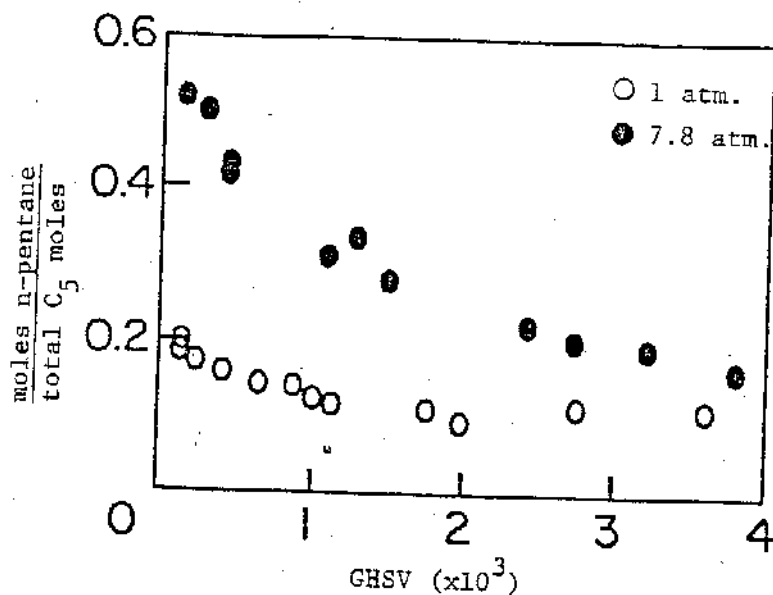


Figure 5.4.22 The n-pentane fraction of total C₅ products versus the GHSV for the FeCo catalyst using the 1-pentene feed at 1 and 7.8 atm. Temp. = 250°C.

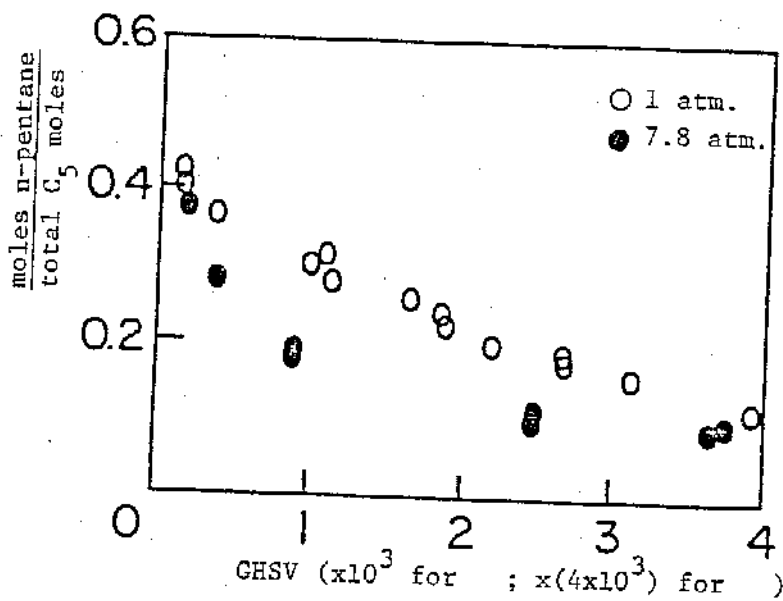


Figure 5.4.23 The n-pentane fraction of total C₅ products versus the GHSV for the Co catalyst using the 1-pentene feed at 1 and 7.8 atm. Temp. = 250°C.

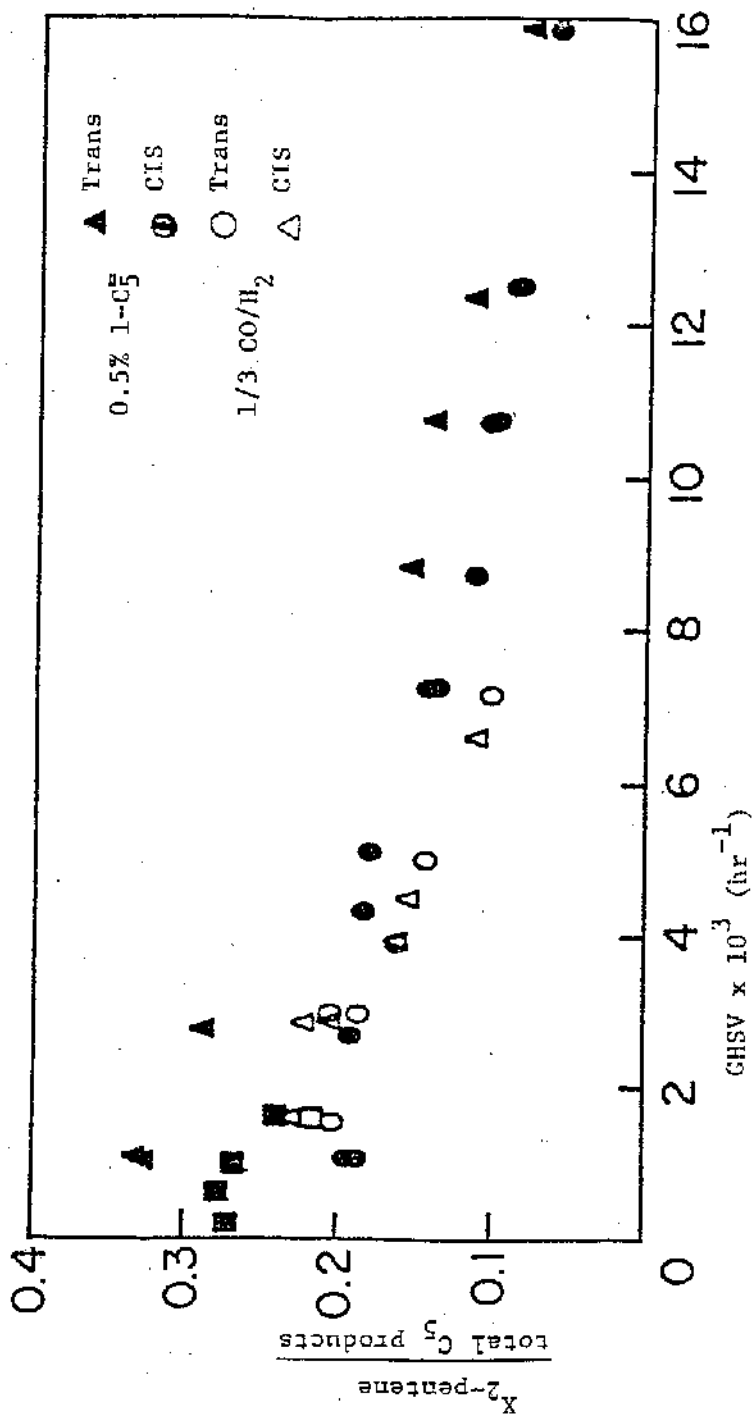
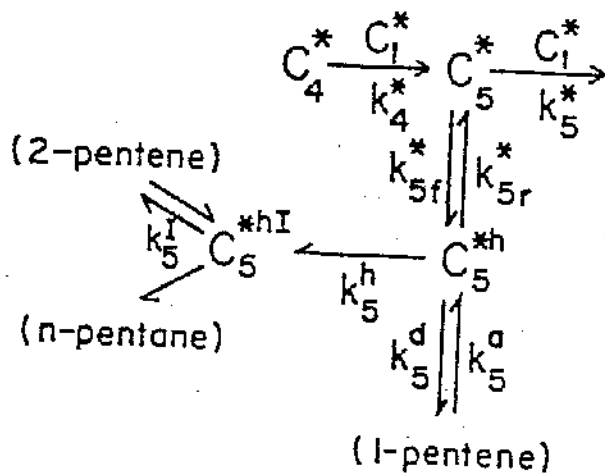


Figure 5.4.24 The Cis and Trans 2-pentene fractions of total C_5 versus the GHSV for the Co catalyst using the 1-pentene containing and pure 1/3 CO/H₂ feed at 1 atm and 250°C.

view of the fact that the C_2 and C_3 olefin/paraffin ratios remain essentially unchanged due to the presence of 0.5 mole % 1-pentene in the feed. If these sites existed the high olefin concentration in this feed would most likely partially inhibit their activity and larger C_2 , C_3 and indeed C_5 olefin/paraffin selectivities would be observed compared to selectivities observed with the pure CO/H_2 feed at comparable GHSV values.

As discussed in section 5.4.2, the amount of 1-pentene consumed in FT chain growth reactions is small (typically <1%) and appears to decrease with increasing pressure. These results further support the reaction sequence involving separate surface intermediates for both hydrogenation and FT chain growth. The decrease in 2-pentene yields with increasing pressure suggest the existence of an additional reaction intermediate involved with olefin isomerization. The reaction sequence envisioned for the production of C_5 products is shown below



5.4.12

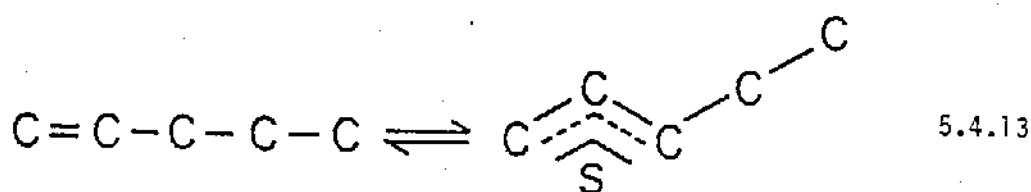
where C_5^* is FT chain growth intermediate
 C_5^{*h} is the intermediate involved with 1-pentene adsorption
 C_5^{*hI} olefin hydrogenation/isomerization intermediate

k_5^h hydrogenation rate constant

k_5^I olefin isomerization rate

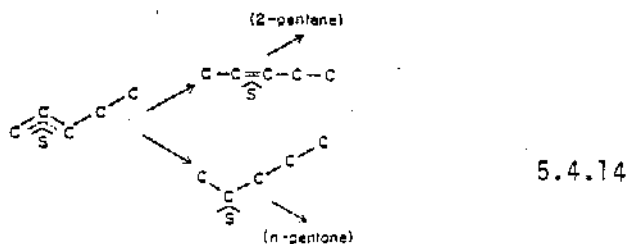
Increasing the total pressure would favor the production of n-pentane from C_5^{*h} as opposed to the isomerization reaction since hydrogenation is positive order in hydrogen partial pressure. The isomerization of 1-pentene to 2-pentene involves a hydrogenation/dehydrogenation sequence on the α and γ carbons respectively (28,98). The dehydrogenation sequence clearly would not be favored with increasing hydrogen partial pressure.

The presence of a common intermediate for both hydrogenation and olefin isomerization is not unreasonable. The intermediate may be π allyl type structure typically encountered in organotransition metal chemistry (28) shown below



π -allyl intermediate

Such intermediates are believed to be involved in olefin isomerization chemistry (28). Adsorbed hydrogen can insert into the π allyl bond resulting in hydrogenation. The parallel reaction sequence is shown below



The hydrogen can either be adsorbed on the same site as the olefin or can add from a neighboring site.