4.1.4 Comparison of Rate Data with Proposed Kinetic Expressions

The specific turnover frequencies for each of the catalysts at various feed and pressure conditions are given in Table 4.1.1. Since only two feeds were employed in the rate studies the kinetic orders of the reactants could not be determined. For both the Fe and FeCo catalyst the CO activity increased with increasing pressure up to 7.8 atmosphere for both feed mixtures. For both catalysts the relative increase in rate from 1 to 7.8 atmosphere is greater for the 1/3 mixture than the 1/1 mixture. This suggest that the overall rate is more dependent on the hydrogen partial pressure as opposed to the carbon monoxide partial pressure. This is in agreement with many of the kinetic models proposed in the literature (6, 123) which are of the form

$$(-r)_{CO} = k\, P_{H_2}^{x}\, P_{CO}^{y} \qquad 4.1.1$$

where

P_i is the partial pressure of component i

$(-r)_{CO}$ rate of consumption of CO

x typically ranges from .5 to 1.3

y typically ranges from -.6 to 0.0

k rate constant for the reaction

Several authors (6,36,11) have suggest the following kinetic expressure for bulk iron catalyst operating at integral conversion at total pressures exceeding one atmosphere

$$(-r)_{CO} = \frac{k\,(H_2)}{1 + b\,\frac{(H_2O)}{(CO)}} \qquad 4.1.2$$

where (A) is the bulk gas phase concentration component A

b is a temperature dependent coefficient

This expression accounts for the activity loss due to site inhibition by water. Atwood and Bennett (11) have successfully applied this relation. The general rate expression for CO consumption at higher pressure (>1 atm) is most probably more complicated than that given in equation 4.1.1. Integral reaction rates obtained over a commercial Co/SiO_2 catalyst have been reported by Borghard and Bennett (24). They found that the CO consumption rate (at >79% CO conversion) decreased over two fold in a 1/3 CO/H_2 mixture as compared to a 1/2 CO/H_2 mixture at 20 atmospheres. At 14 atmospheres with a 1/1 feed the rate (at 10% CO conversion) decreased about 19 times as compared to that obtained at 20 atmospheres with a 1/1 feed. Similar decreases were observed over a Fe^2O_3/Al_2O_3 catalyst. Anderson et al (7) found that the combined rate of H_2 and CO usage of a Co/Kieselguhr catalyst was constant over a pressure range of 1 to 7.8 atmosphere.

4.1.5 Methane Differential Selectivity

The ratio of the methane activity to the CO activity, methane differential selectivity ($\frac{N_{CH4}}{N_{CO}}$), are plotted as a function of CO conversion for the Fe and FeCo catalyst in Figure 4.1.6. At one atmosphere with the 1/3 feed these two catalysts produce similar amounts of methane for a given amount of CO consumed.

The decrease in the methane differential selectivity at higher CO conversions indicates that the methane turnover frequency is decreasing

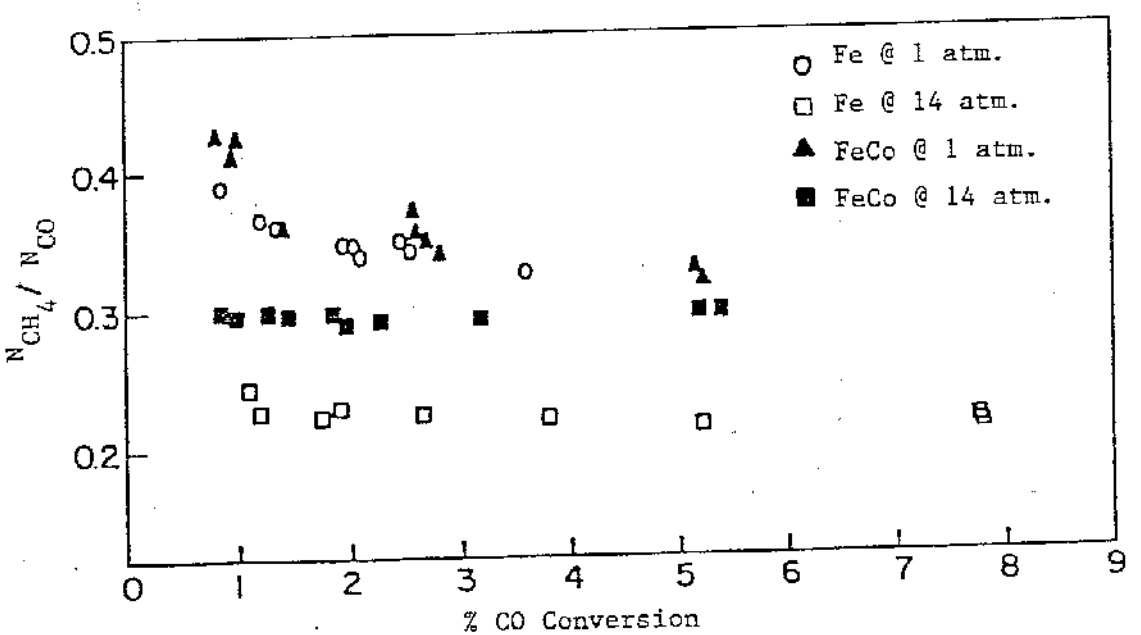

Figure 4.1.6 N_{CH_4} / N_{CO} versus % CO conversion for the Fe and FeCo catalysts using the 1/3 CO/H_2 feed at 1 and 14 atm. T= 250 C.

faster than the CO turnover frequency with increasing CO conversion. There is a plausible explanation for this behavior. At higher CO conversions (lower gas hourly space velocities) there is a higher probability for product readsorption and subsequent secondary reactions such as hydrogenation and chain initiation. These secondary reactions may preferentially block specific sites active to methane. In Chapter 5 data are presented that show methane activity is preferentially reduced compared to other products by the introduction of ethylene or 1-pentene into the 1/3 CO/H_2 feed for the Fe catalyst.

The methane differential selectivity of the Co catalyst using the 1/3 CO/H_2 feed is given in Figure 4.1.7. The N_{CH_4}/N_{CO} values are found to be essentially constant at one atmosphere throughout the conversion range studied. The inhibition effect observed in the iron containing catalyst is absent for this catalyst at these conditions. At low conversions the N_{CH_4}/N_{CO} values of the Fe and FeCo catalysts are similar to that of cobalt but throughout the conversion range, 1 to 5% CO converted, the Co catalyst has the highest selectivity. At 14 atmospheres the methane differential selectivity of all three catalyst catalysts is lower relative to the values obtained at one atmosphere. At 2% CO conversion the Co catalyst's N_{CH_4}/N_{CO} value decreases from a value of approximately .45 to a value of .28 (Figure 4.1.7) while the corresponding value for Fe are .35 and .23. The reduction in methane selectivity at 14 atmosphere amounts to roughly 65% of the one atmosphere values compared to only a 15% reduction in the methane selectivity of the alloy catalyst under the same conditions (.35 to 2.9). Clearly this represents a fundamental change in the catalytic behavior of the FeCo catalyst compared to the pure component catalyst. The enhanced selectivity of the FeCo catalyst

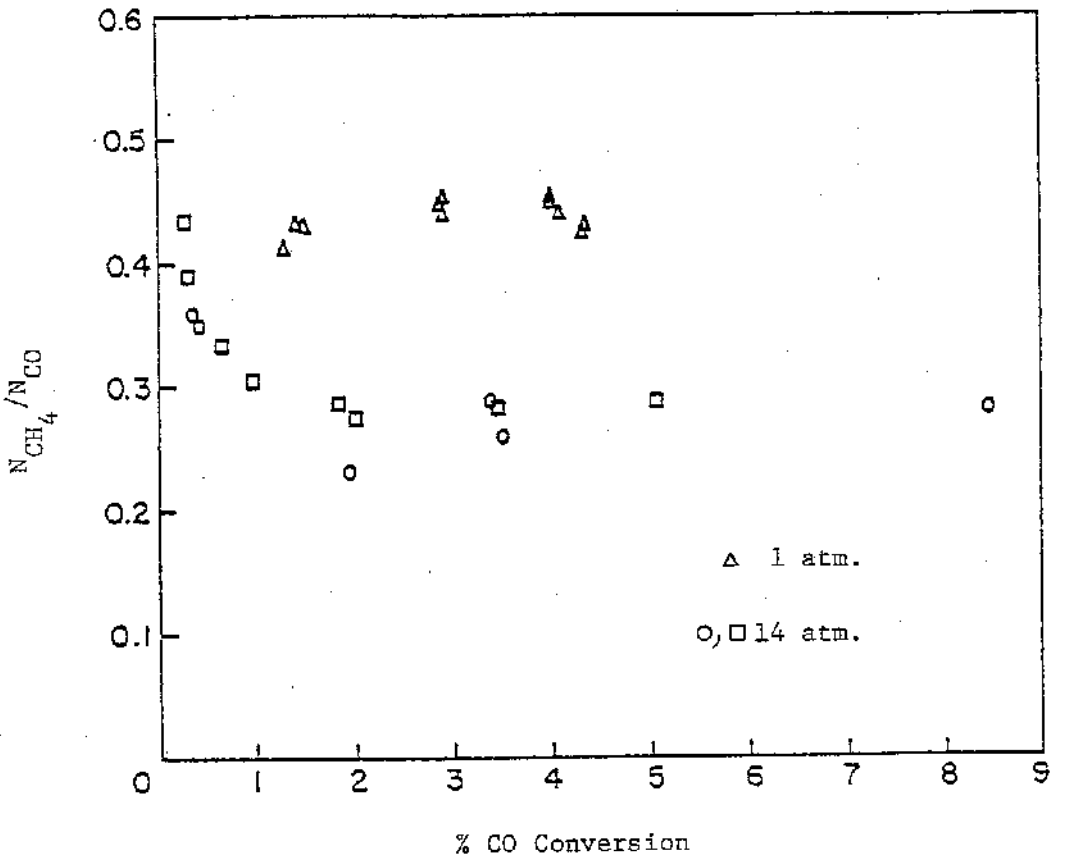

Figure 4.1.7 N_{CH_4}/N_{CO} versus % CO conversion for the Co catalyst at 1 and 14 atmospheres using the 1/3 CO/H_2 feed.

towards low molecular weight products is discussed in subsequent sections.

Figure 4.1.8 presents the N_{CH_4}/N_{CO} values for all three catalysts with the 1/1 CO/H_2 feed. The behavior in the methane selectivity of the FeCo catalyst with respect to pure iron is similar in this case to that observed with the 1/3 feed. The Fe catalyst, having comparable selectivities at one atmosphere, again shows a greater decrease relative to that of FeCo with a pressure increase from 1 to 14 atmospheres. The N_{CH4}/N_{CO} values presented for the Co catalyst in Figure 4.1.8 are at total pressures of 1 and 7.8 atmospheres as opposed to the data at one and 14 atmospheres for the other catalyst. The N_{CH_4}/N_{CO} value obtained for the FeCo catalyst at 7.8 atmospheres and 2% CO conversion is approximately .24, comparable to the value obtained for the Co catalyst. The Fe catalyst yields a methane differential selectivity of .16 at similar conditions (7.8 atm 2% CO conversion), clearly lower than those obtained with the cobalt containing catalyst. In conclusion it seems that both the FeCo and Co catalysts, have similar methane selectivities with the 1/1 feed, while the Fe catalyst possesses the lowest selectivity towards methane.

It is interesting to note the behavior of the methane differential selectivity at CO conversion less than 1%. For all three catalysts at steady state conditions it was found that the N_{CH_4}/N_{CO} values were conversion dependent at very low CO conversion even at high pressures. Although data at these conditions were not routinely obtained Figures 4.1.7 and 4.1.8 present some evidence of a strong conversion dependence at 14 atmospheres of the methane selectivity. These results suggest that methane is most likely the primary product at very low conversion levels and that the formation of longer carbon chains is conversion dependent.

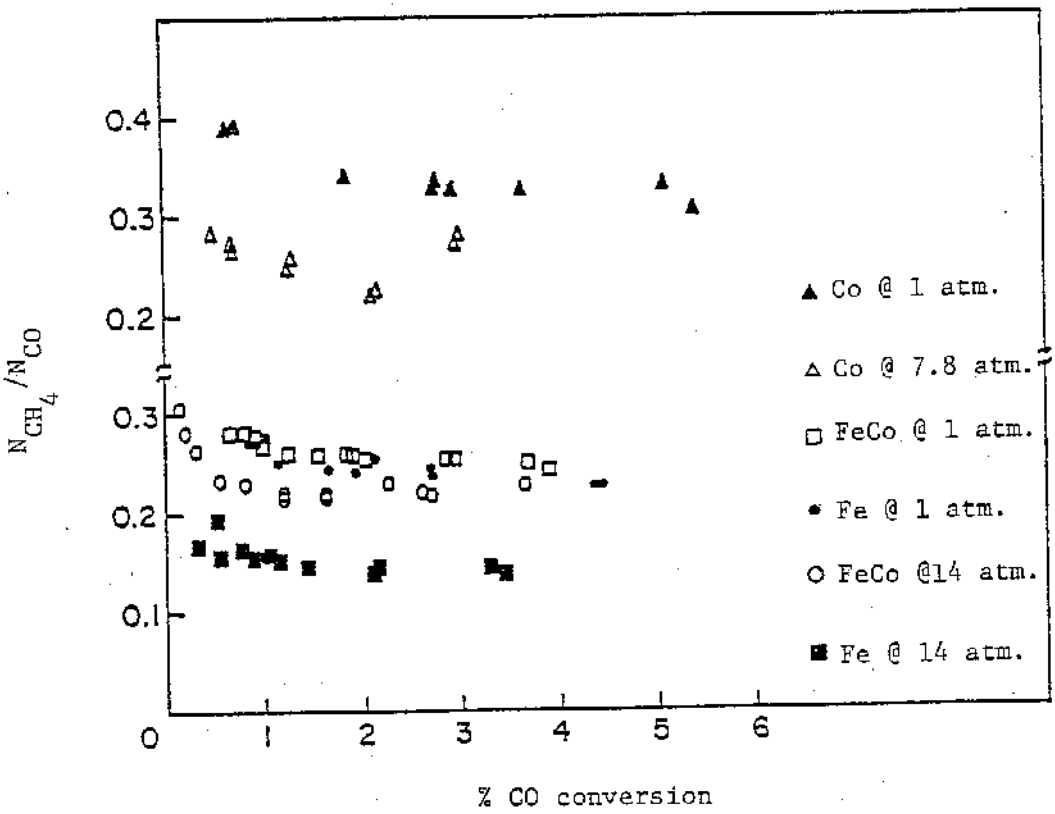

Figure 4.1.8 N_{CH_4}/N_{CO} versus % CO conversion for all three catalysts at several pressures. Using the 1/1 CO/H_2 feed.

This is a commonly observed phenomenon in FT chemistry.

4.1.6 Relative Activities for Methanol

At higher pressures methanol becomes a dominant synthesis product second only to methane for the Fe and FeCo catalyst. In Figure 4.1.9 the mole fraction of methanol in the total synthesis products is plotted against the percent CO converted for the 1/3 feed. The product fraction of methanol decreases with increasing conversion indicating that its production rate is inhibited at higher CO conversions or this product is being consumed via secondary reactions. This effect is similar to that observed with the CO and methane turnover frequencies. The Fe catalyst produced the greatest amount of methanol in the total product yield at 14 atmospheres. The alloy catalyst produces less methanol than the Fe catalyst when compared at this pressure while the fractions produced by the iron containing catalysts are comparable at lower pressures. At 1 atmosphere the molar fraction of methanol in the products for these two catalysts are typically less than 5%, while at 14 atm. the fraction can be as high as 20%.

Figure 4.1.10 presents the results obtained with 1/1 CO/H feed at 14 atmospheres. The fraction of methanol in the total products is now higher for the FeCo catalyst then for pure iron. No methanol was detected in the product stream of the Co catalyst with the 1/1 feed at 1 and 7.8 atmospheres. Comparison of figures 4.1.8 and 4.1.9 reveal that the methanol product fraction decreases at higher CO/H ratios for the Fe catalyst. However the fraction produced by the alloy catalyst remains relatively constant for both feed mixtures.

For a given CO conversion more moles of products are formed with the

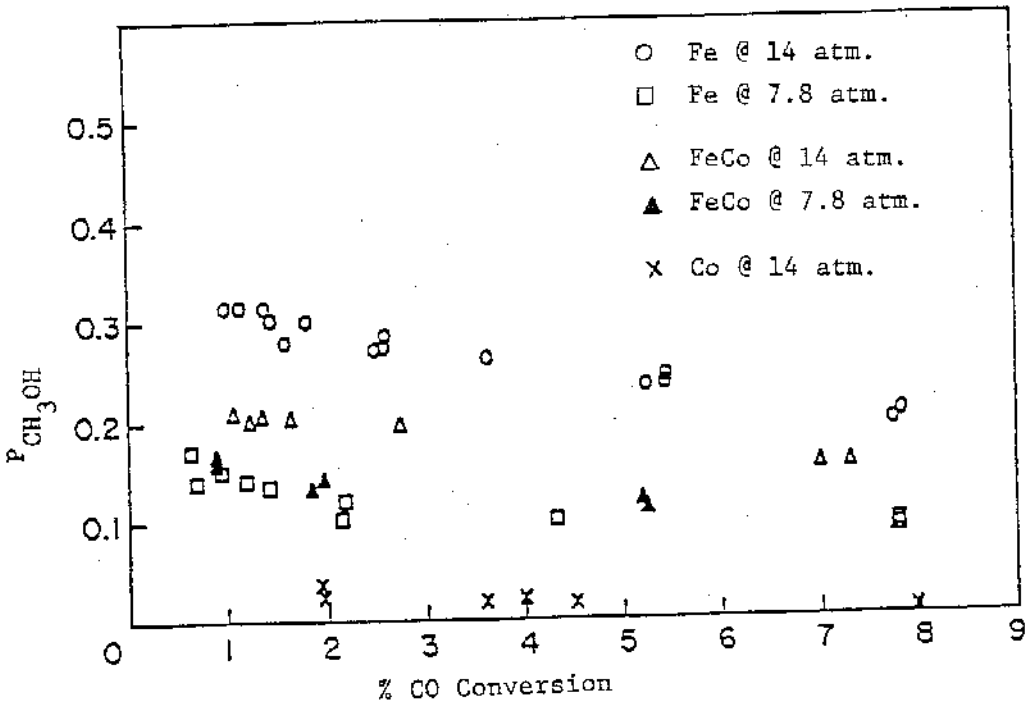

Figure 4.1.9 Methanol product mole fraction versus percent CO conversion for all three catalysts using the 1/3 CO/H_2 feed at 250°C.

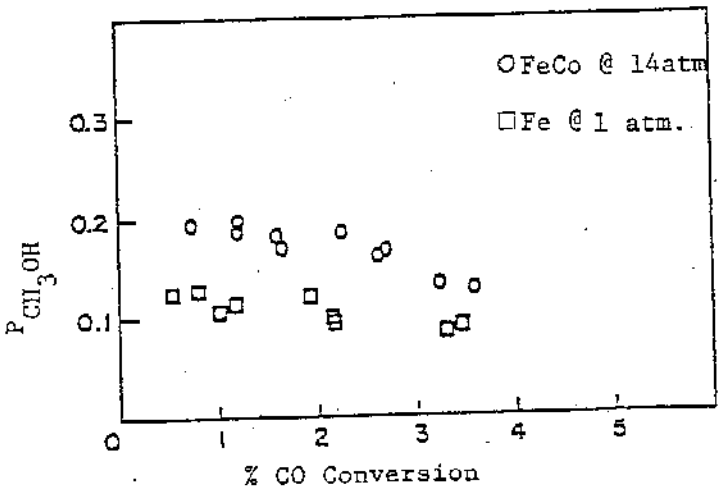

Figure 4.1.10 Methanol product mole fraction versus percent CO conversion for the Fe and FeCo catalysts using the 1/1 CO/H_2 feed at 250°C.