

1/1 CO/H₂ mixture than with the 1/3 mixture. In the case of the Fe catalyst, an increase in the CO/H₂ ratio favors the molar production of hydrocarbon products over that of methanol. Therefore, the methanol product fraction is lower in the 1/1 CO/H₂ feed as compared to the 1/3 mixture. A similar result is obtained with the FeCo and Co catalysts.

4.1.7 Activity Maintenance Versus Irreversible Deactivation

Possible Causes for Losses in Activity.

The CO activities presented in sections 4.1 through 4.3 are obtained at steady state conditions. At the risk of being redundant it is worthwhile to bring up the following point. The loss in activity due to increasing conversion was generally found to be reversible and the activity was independent of "on stream" time after completion of the carburization reaction (approximately 40 minutes). Figure 4.1.11 illustrates the stability in the overall activity of the FeCo catalyst. In this figure the gas hourly space velocity is plotted as a function of CO conversion. The circular data points, were obtained during the first 14 hours of the synthesis experiment while the square points represent data obtained after one full day of continuous on stream operation. The two sets of data overlap along the same curve indicating that there is no appreciable loss in catalytic activity over the total forty hours of continuous on stream operation. With the pure component catalysts, typical experiment constant activity was obtained for a period of approximately twelve hours at all pressures and feed ratios investigated.

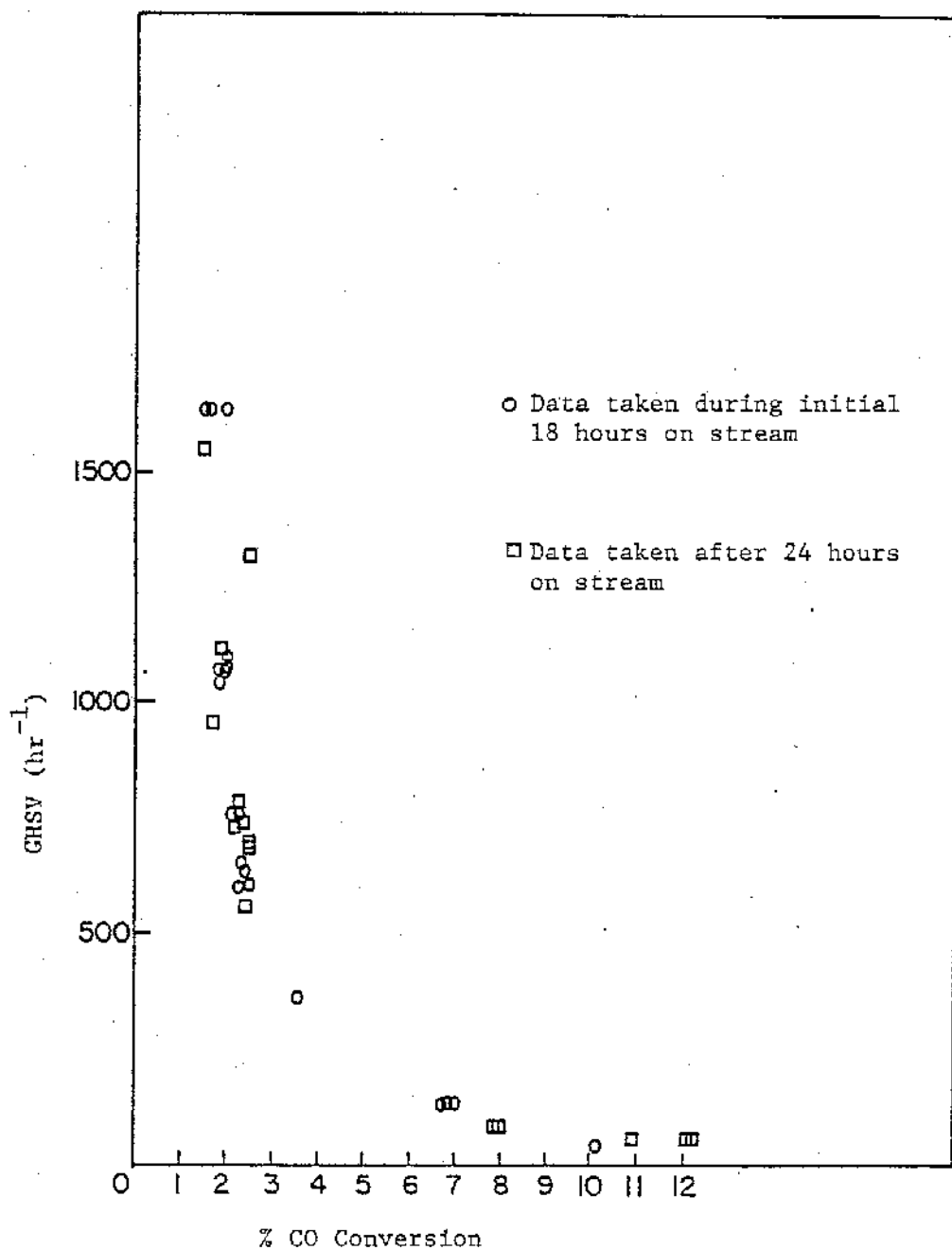


Figure 4.1.11 GHSV - Conversion curve for 40 hours continuous on stream exposure for the FeCo catalyst at 14 atm. using the 1/3 CO/H₂ feed.

Numerous investigators (101,39,84,99,13,96) generally operating at low conversion with a 1/3 CO/H₂ have reported significant losses in CO activity during the second hour on stream with the feed mixture. The activity increases to a maximum during carburization and then continually decreases. On the other hand investigations conducted at integral conversions and higher pressures generally report modest losses in activity during on stream operation measured in days (6,24,129). There has been little attention paid to this discrepancy or to the possible experimental causes which can lead to the observed deactivation.

Surface studies using various electron spectroscopies (40,39,66) have identified the growth of a carbidic carbon overlayer during the synthesis reaction on a clean iron foil. Indeed the formation of an inactive carbonaceous layer over the catalyst surface is cited as the cause for the loss in activity discussed above (101,40,84,39,13,96). It appears from the studies involving iron foils that two types of surface carbon exist on the catalyst surface during the synthesis: carbidic carbon, which may serve as an intermediate in the growth mechanism, and an inactive carbon, which has been identified as being crystalline and graphitic in nature (51,61) at least when observed over nickel.

The formation of carbon containing layers can possibly be due to some type of coking reaction or the Boudouard disproportionation reaction ($2CO \rightarrow C + CO_2$), since the thermodynamics of this reaction are favorable under reaction conditions (Appendix III). If the formation of the inactive carbon layer is due to CO disproportionation one would expect to see more rapid deactivation at higher total pressures of CO/H₂ feeds since the forward rate of this reaction is proportional to the CO partial pressure and the equilibrium shifts to the right at higher pressures. It is unlikely that

this reaction is responsible for the observed activity loss since the CO_2 yields observed at higher pressure are much lower than those observed at one atmosphere (Section 4.2). Some type of coking reaction may be responsible for the deactivation since coke formation is favored at lower pressures. This may explain the stable activities obtained at higher pressures (6,24,129) while lower pressures exhibit a loss in activity.

Surface oxidation during the course of the synthesis can be a possible explanation for activity loss. At high CO conversions the gas phase changes from a reducing agent ($\text{CO} + \text{H}_2$) to an oxidizing one ($\text{CO}_2 + \text{H}_2\text{O}$). However, if this was indeed the case one would expect a larger extent of deactivation at higher conversions rather than the opposite case which is reported in the literature. A more plausible explanation involving surface oxidation might be oxygen contamination of the feed stream. For example, if the reactant gas stream contains 10 ppm O_2 and is passing over (100cc/min) 0.5 gms of the Fe catalyst at one atmosphere about 20% of the surface iron could be converted to Fe_3O_4 in approximately four hours. This calculation indicates that even a very low concentration of oxygen can potentially reoxidize a significant fraction of the catalyst surface. In experiments conducted in this laboratory it was found that an inactive MnO/SiO_2 oxygen trap resulted in a loss of catalytic activity during the course of an experiment. Dwyer and Somerjai (40) report a 75% decline in activity during the first two hours of onstream operation, using an Fe foil, however no detectable oxygen Auger peak was observed on the used catalyst (39).

It appears that there are unanswered questions regarding the stability activity of iron based catalysts. The deactivation observed

under differential conditions is surprising since many previous investigations (6) conducted at integral conversion levels exhibit stable activity for long periods of time (> day). Most likely in many of the older studies less attention was paid to contamination by impurity components (O_2 , SO_2 , etc.) in the feed gas as compared to more recent investigations. In summary it appears that no simple conclusions can be made regarding the nature of deactivation during the FT synthesis. The specific mechanism causing the loss in catalytic activity may depend upon a combination of factors including catalyst morphology, conversion level, and feed composition.

4.2 Water Gas Shift Activity

4.2.1 Effects of Pressure and Feed Composition

The water gas shift reaction, given below in equation 4.2.1, was monitored for all conditions



4.2.1

Since the CO and H_2 concentrations do not appreciably change over the conversion range studied, the ratio of the effluent mole fraction of CO_2 to that of H_2O , X_{CO_2}/X_{H_2O} , provides a convenient parameter in which to measure the extent of the shift activity. This ratio is essentially a ratio of production rates, N_{H_2O}/N_{CO_2} .

Amelse (5) reported that the FeCo catalyst has a higher shift activity than that of pure Fe or Co at one atmosphere using the 1/3 CO/H_2 feed. Similar results were obtained in the present investigation (Figure 4.2.1). The FeCo and Fe catalyst exhibit identical shift activity at

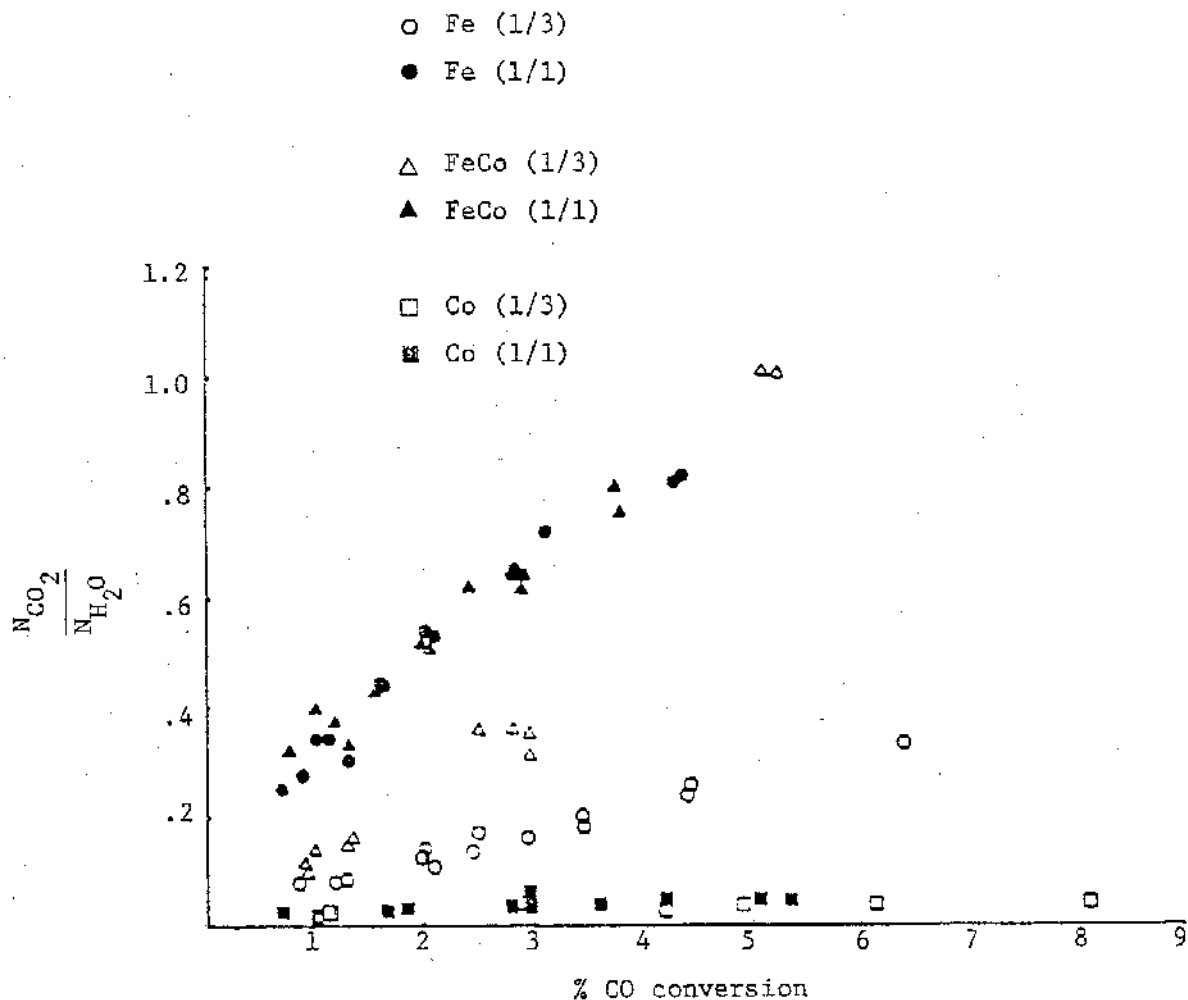


Figure 4.2.1 Shift activity versus % CO conversion for all three catalysts at 1 atmosphere and 250°C using the 1/3 and 1/1 CO/H₂ feeds.

one atmosphere with the 1/1 feed. The increased CO/H₂ ratio enhanced the shift activity of the iron containing catalyst while the NCO₂/NH₂O ratios obtained for the Co catalyst appear to be independent of feed composition.

Increasing pressure decreases the shift activity as shown in Figure 4.2.2. These data are for the Fe catalyst using the 1/3 feed, however similar results, but to lesser extent, were observed for the 1/1 feed. At 14 atmospheres with the 1/3 CO/H₂ feed both iron containing catalysts exhibit similar shift activity, while the Fe catalyst has a slightly enhanced shift activity compared to the FeCo catalyst using the 1/1 feed mixture (Figure 4.2.3). The Co catalyst shift activity decreases slightly with increased pressure for the 1/3 feed while the activity appears to increase at higher pressures using the 1/1 feed. These results are presented in Figure 4.2.4. It should be noted that the changes in the NCO₂/NH₂O values are of a much smaller magnitude for the Co catalyst as compared to the corresponding changes in the iron containing catalyst.

4.2.2 Water Gas Shift Equilibrium and Rate Models

The equilibrium constant for the shift activity, K_{SA}, is given below

(69)

$$K_{SA} = \frac{[CO_2][H_2]}{[H_2O][CO]} = e^{-[(4577.8/T) - 4.33]} \quad 4.2.2$$

where [A] is the molar concentration of species A $\left(\frac{\text{moles}}{\text{volume}}\right)$

T Absolute temperature (°K)

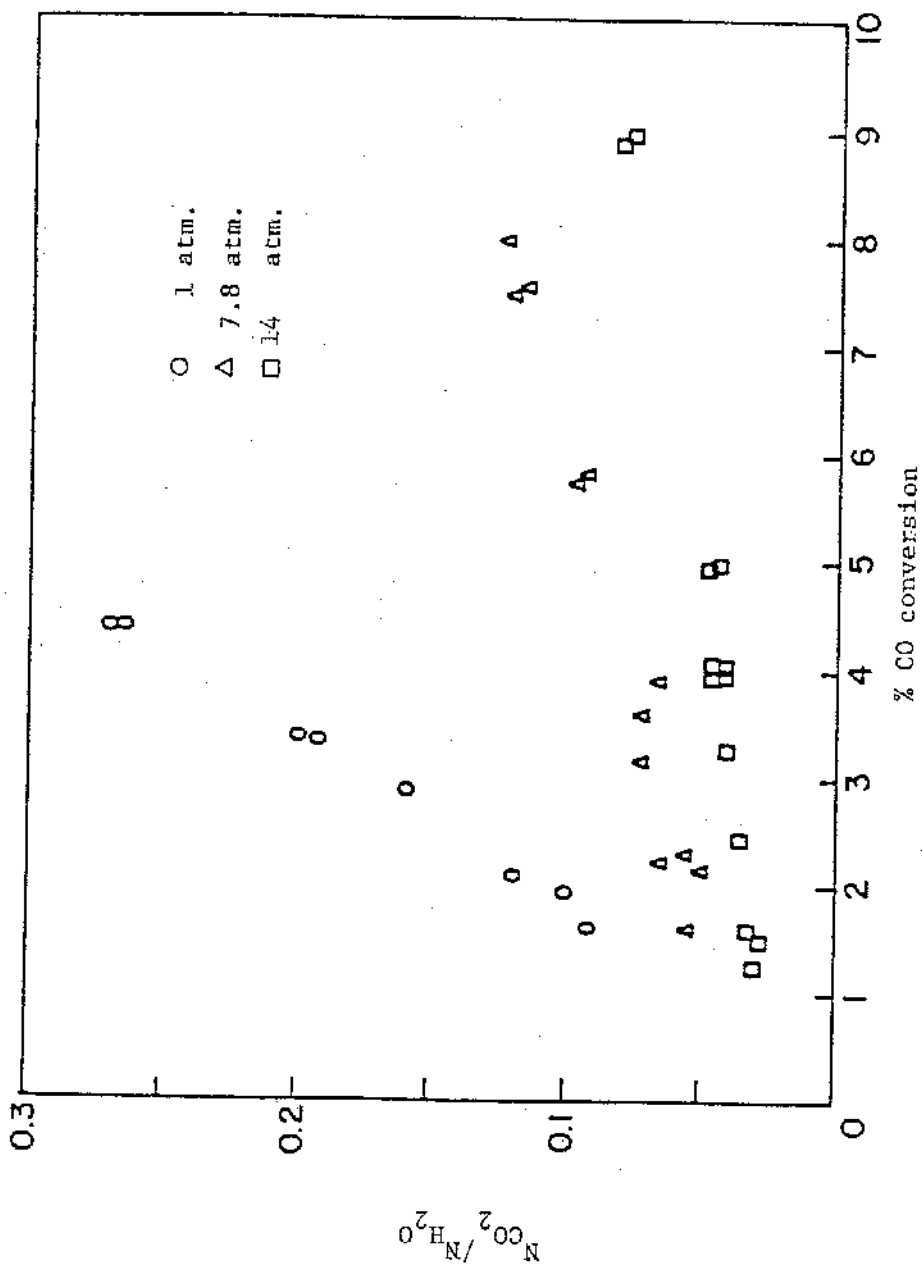


Figure 4.2.2 Shift activity versus % CO conversion for the Fe catalyst at various pressures using the 1/3 CO/H₂ feed at 250°C.

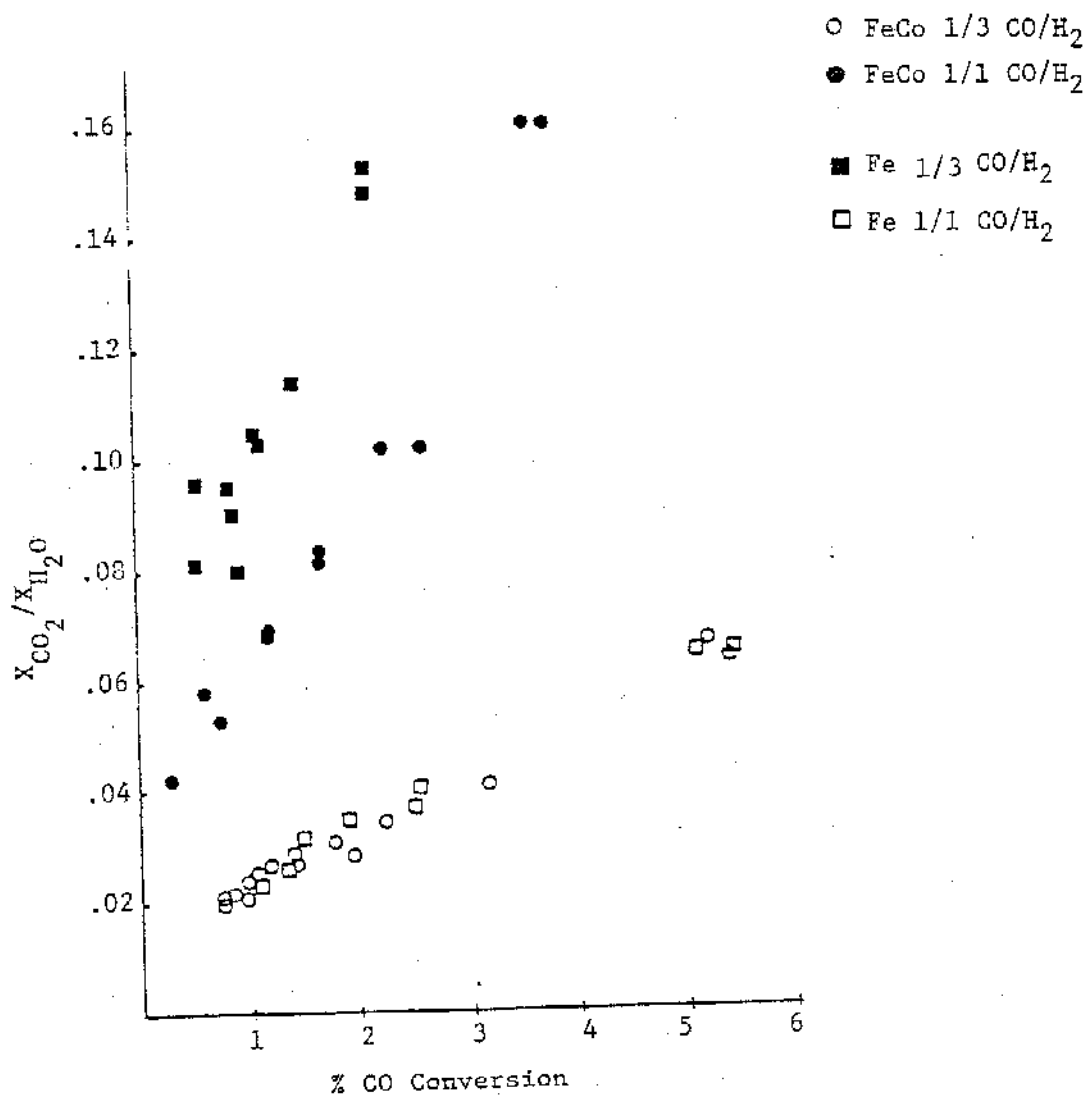


Figure 4.2.3 Shift activity versus % CO conversion for the Fe and FeCo catalyst at 14 atmospheres with the 1/1 and 1/3 CO/H₂ feeds.

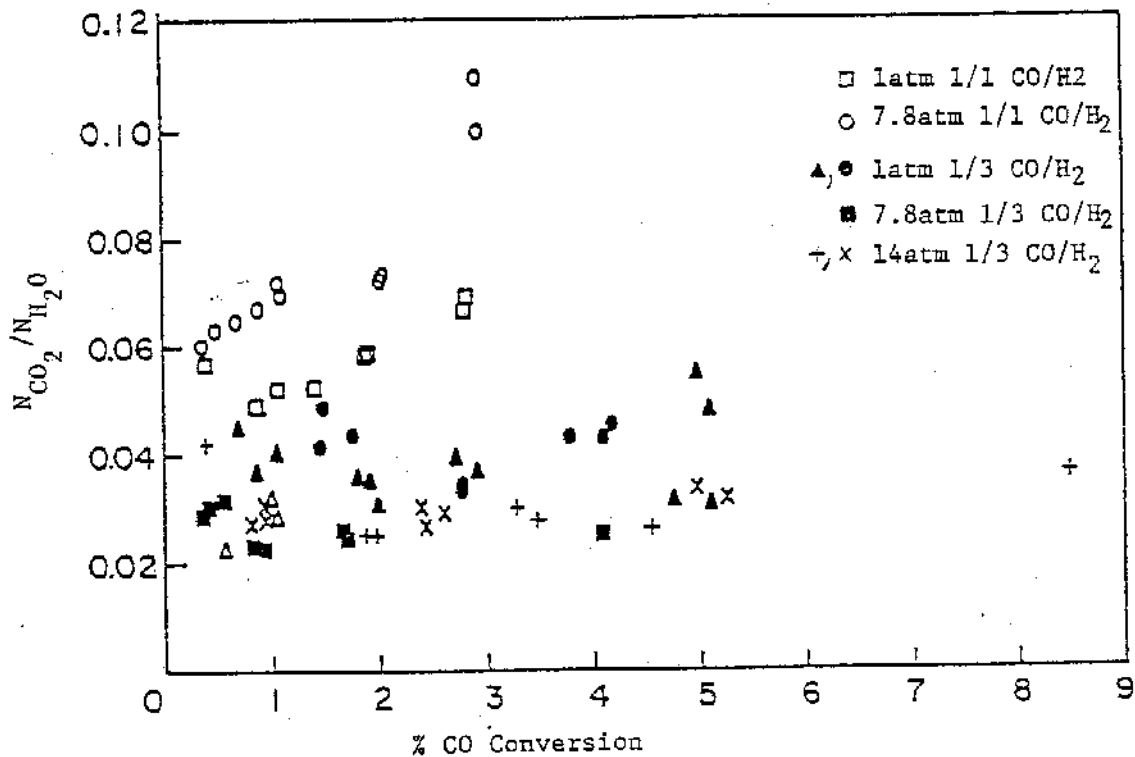


Figure 4.2.4 Shift activity versus % CO conversion for the Co catalyst at several pressures for the 1/1 and 1/3 CO/H₂ feed.

At 250°C the equilibrium values of the $[\text{CO}_2]/[\text{H}_2\text{O}]$ ratio for the 1/3 and 1/1 CO/H_2 feed mixtures would be 27.7 and 41.65 respectively. In the present reaction studies these ratios are typically less than 0.3, clearly indicating that the reaction is far from equilibrium for all the conditions studied. Dry et al. (37) report similar findings over a triply promoted iron catalyst operating at 10 to 20 atmospheres and 255°C with a 1/1 CO/H_2 feed. These results suggest that the shift activity observed is most likely the intrinsic forward rate of reaction 4.2.1, since the amount of CO_2 available for the reverse reaction is negligible.

Most kinetic expressions of the forward shift rate are first or near first order in CO partial pressure (P_{CO}) and some positive fractional order in water partial pressure ($P_{\text{H}_2\text{O}}$) (83). Over an iron-based shift catalyst Kul'kova and Temkin (69) developed the following relation for the forward rate of the shift reaction

$$r = k P_{\text{CO}} (P_{\text{H}_2\text{O}}/P_{\text{H}_2})^{1/2} \quad 4.2.3$$

For the same feed composition the forward shift rate should increase linearly with increasing pressure at a fixed CO conversion. However for both iron-containing catalysts the forward rate decreased with increasing pressure. This might be due to enhanced CO adsorption and/or site blockage by synthesis products. The increase in the $\text{NCO}_2/\text{NH}_2\text{O}$ ratio with increasing CO conversion at higher CO/H_2 ratios indicates that the forward rate is positive order in $P_{\text{H}_2\text{O}}$ and P_{CO} .

The low shift activity of the Co catalyst is expected since it is a generally accepted fact that this metal is a poor shift catalyst. The $\frac{x_{\text{CO}_2}}{x_{\text{H}_2\text{O}}}$ values appear to increase with increasing pressure with the 1/1 feed. This is surprising in light of the fact that the CO turnover

frequency decreases with increasing pressure. The general trends in the Co catalyst shift activity suggest that the kinetics of this reaction are quite different from those of the iron containing catalyst.

High pressure integral reactor studies (6) and low conversion one atmosphere studies (3,5,84) indicate that water is the primary synthesis product in CO hydrogenation to hydrocarbons. Amelse et al. (3,5) demonstrated that the N_{CO_2}/N_{H_2O} values intercept at near zero at zero conversion at one atmosphere. Similar conclusions can be drawn at higher pressures (Figures 4.2.2 and 4.2.3). If CO_2 were an initial product due to the Boudouard disproportionation reaction (eqn. 4.2.4) one would expect much higher N_{CO_2}/N_{H_2O} ratios than observed at low CO conversions.



For the feeds employed in this study at 250°C the equilibrium constant for this reaction (Appendix III) is approximately 10^8 at one atmosphere. Clearly this reaction has a negligible rate at these FT conditions since the values of $\frac{[CO_2]}{[CO]^2}$ are typically less than 10^{-2} and decrease with increasing pressure.

The loss of shift activity for the iron containing catalyst at higher pressures may be related to the increase in methanol formation at higher pressures. The ratio N_{CO_2}/N_{H_2O} defines the fraction of CO molecules converted to CO_2 relative to the amount converted to products since it is assumed that one molecule of H_2O is produced for every molecule of CO reacted. At one atmosphere only a trace amount of methanol is present in the total product yield, however at higher pressures it becomes a dominant product, second only to methane. Product distributions showing