

Chapter 4

Reaction Studies Using CO/H₂ Mixtures

The FT synthesis provides an ideal study in which one can generate vast amounts of data with a limited number of experiments. The set of ten or so primary reactions combined with over one dozen secondary reactions produce a reaction network very difficult if not impossible to completely characterize. Consequently only certain products will be analyzed in detail in terms of their yields ($\frac{\text{moles of CO converted to product } i}{\text{mole of feed gas}}$) and specific selectivities ($\frac{\text{moles of } i \text{ formed}}{\text{moles of } j \text{ formed}}$) (4.3). Specific turn over frequencies (4.1) are based on the number of sites determined by hydrogen chemisorption on the reduced catalyst (Chapter 3). Overall product distributions (4.4) are given in terms of component mole fraction of total products. In some cases ratios of various production rates and yields will be given in order to identify trends in catalyst selectivities.

4.1 CO Activity Studies

The CO turnover frequency, N_{CO} , is defined as the molar rate of CO converted to products (excluding CO₂) per catalytic site per second. Figures 4.1.1 through 4.1.5 present the steady state CO activities divided by the total pressure as a function of CO conversion. At all pressures studied the N_{CO} values decreased with increasing CO conversion for both feed mixtures. The only exception is the Co catalyst at 1 atmosphere using the 1/3 CO/H₂ feed, where the CO activity is constant over the conversion range studied (1-7% CO converted). The dependence of the N_{CO} on conversion was previously observed at 1 atmosphere, 1/3 CO/H₂ mixture, by

Amelse et al. (1,5). The decrease in activity with increasing conversion is attributed to some type of product inhibition brought about by the formation of higher molecular hydrocarbons products and/or the increase in water production, since both components can block catalytic sites. Another possibility may be that the production rates of the higher molecular products (which fraction increases a higher CO conversions) have slower intrinsic rates of reaction. Dautzenberg et al. (33) have shown, using a pulse technique analysis, on a Ru/Al₂O₃ catalyst that the low overall activity typical of the FT synthesis is due to the low intrinsic activity of the exposed active sites rather than a small number of very active surface sites suggesting that the decrease in N_{CO} is due to the slower intrinsic rate of multicarbon chain formations. Further discussion on this subject is given in Section 4.6. In the context of the present discussion the decrease in N_{CO} with increasing conversion will be described as inhibition with specific reference to the type.

4.1.1 CO Activities for the Fe Catalyst

The N_{CO}/P_T values for the Fe catalyst using the 1/3 and 1/1 CO/H₂ feed are given in Figures 4.1.1 and 4.1.2. A similar dependence of N_{CO} on conversion is observed for both feeds. The N_{CO} values appear to be proportional to the total pressure in the 1/1 mixture throughout the

Table 4.1.1 Specific CO Turnover Frequencies (N_{CO}) at Various Pressures and Feeds 250°C
 $\times 10^{-3} \frac{\text{molecules}}{\text{site-sec}}$ (nominal 2% Conversion)

Catalyst Feed Co/H ₂ Pressure	Fe		FeCo		Co	
	1/3	1/1	1/3	1/1	1/3	1/1
1	9.0	3.2	1.7	2.2	45	17
7.8	70.2	21.8	13.26	10.0	13.8	9.36
14	46.2	47.6	23.8	10.64	24.8	-

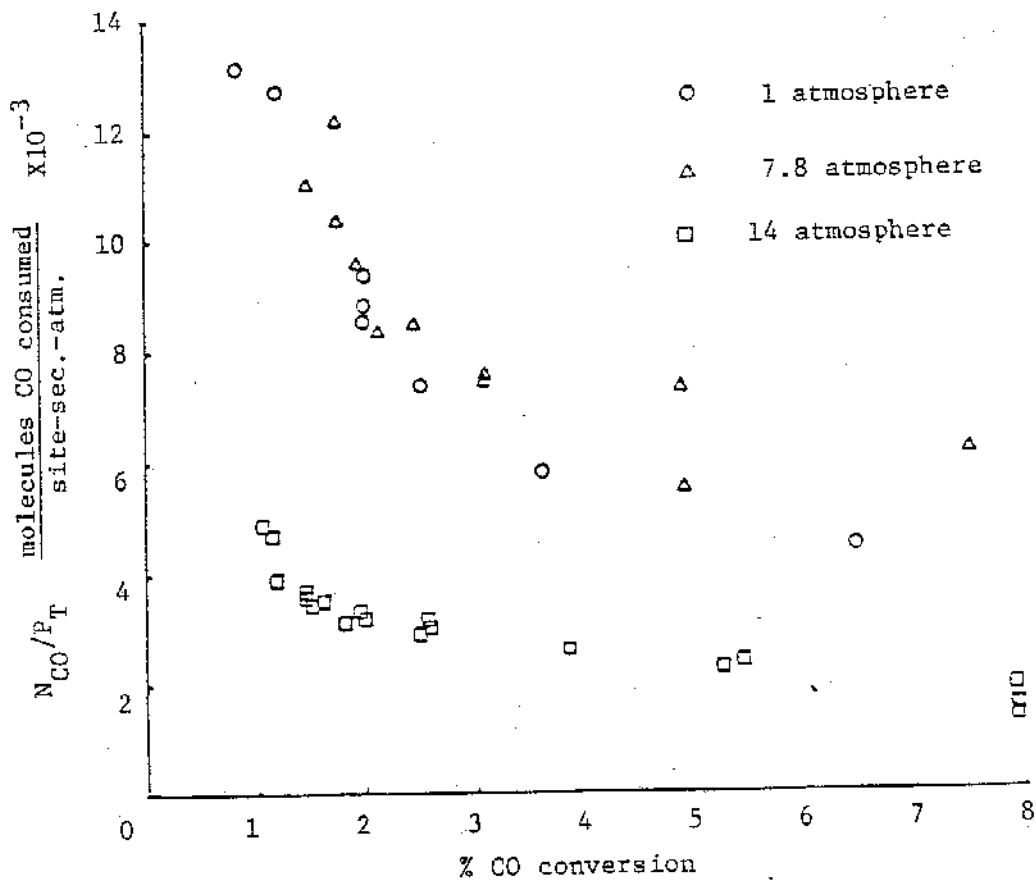


Figure 4.1.1 N_{CO}/P_T versus % CO conversion for the Fe catalyst at 1, 7.8, and 14 atmospheres with the 1/3 CO/H₂ feed.

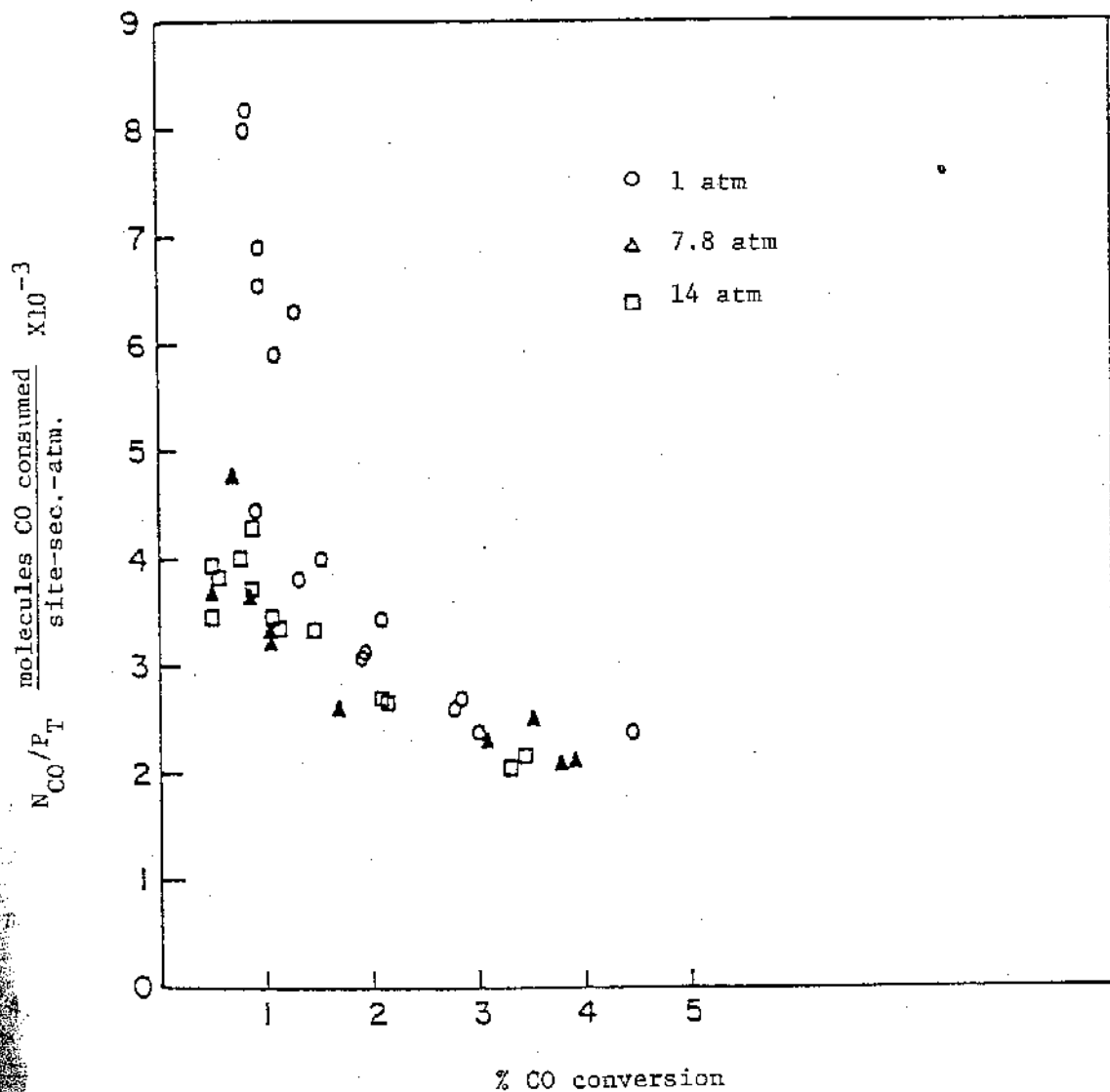


Figure 4.1.2 N_{CO}/P_T versus % CO conversion for the Fe catalyst at 1, 7.8 and 14 atmospheres with the 1/1 CO/H₂ feed.

pressure and CO conversion range studied. The data points with N_{CO}/P_T values greater than 5.0 are initial activities measured within the first three hours. During the course of an experiment the initial flow rates are very high in order to insure low conversion. Once the catalyst is fully carburized and steady state activity is obtained the flow rate is incrementally decreased in order to obtain data at higher CO conversions. Upon the return to lower conversions the increase in N_{CO} to its original higher value indicates that no deactivation occurred during the course of the experiment since the observed inhibition effect is reversible. This was the case for the N_{CO} activities obtained for the Fe catalyst in all cases except at 1 atmosphere using the 1/1 feed. In the case the activity measured at a relatively constant space velocity dropped from $15 \times 10^{-3} \frac{\text{moles CO consumed}}{\text{site-sec}}$ to a value of approximately 6×10^{-3} during the first three hours on stream. Upon the return to low conversions at the end of the experiment the activity was found to be well below the initial value. This point is brought up only to illustrate the loss of catalyst activity due to a high CO/H₂ ratio. It should be pointed out that the Boudouard reaction is thermodynamically favored at all the reaction conditions studied and can possibly play a role in the aforementioned deactivation (Appendix III). Additionally at 250°C carbon deposition can occur more readily the 1/1 mixture compared to the 1/3 CO/H₂ mixture (78).

4.1.2 CO activity for the Co catalyst

The CO activity of the Co catalyst using the 1/1 feed is presented in Figure 4.1.3. There again is an inhibition effect similar to that observed with Fe. The Co catalyst maintained constant activity at all CO conversions (1-6%) with the 1/3 feed. This was the only case studied in

which the N_{CO} values were independent of conversion. The N_{CO} values obtained at the pressures investigated are presented in table 4.1.1.

4.1.3 CO activity for the FeCo Catalyst

Figure 4.1.4 is a plot of N_{CO}/P_T versus CO conversion for the FeCo catalyst over the range of pressures employed with the 1/3 CO/H₂ feed. Most of the data appear to fall along a general curve suggesting that the CO activity is proportional to the total pressure for this feed ratio. The data points represented by the open circles and open triangles tend to lie above the general curve. These activities were obtained at 2.3 atmospheres after the catalyst was carburized at 14 atmospheres. The solid circles and triangles represent data obtained at 2.3 atmospheres in which the catalyst was either carburized at 7.8 atmospheres (Δ) or carburized at 2.3 atmospheres (\bullet). These points tend to lie above the general curve. The enhanced activities at 2.3 atmospheres obtained by exposing the catalyst to higher pressures suggest that the CO activity at a given pressure may be dependent upon the previous pressure history of the catalyst. Further work is needed to clarify this possibility. The higher N_{CO} values obtained in this case are not due to any transient product desorption due to decreasing the pressure since the product distributions associated with these data are typical of those obtained at low pressures.

The N_{CO}/P_T values for the Fe-Co catalyst with the 1/1 CO/H₂ feed are presented in Figure 4.1.5. There is over a 70% reduction in activity at one atmosphere in going from .5 to 4% CO conversion. At higher pressure the decrease in activity is about 50% over the same conversion range.

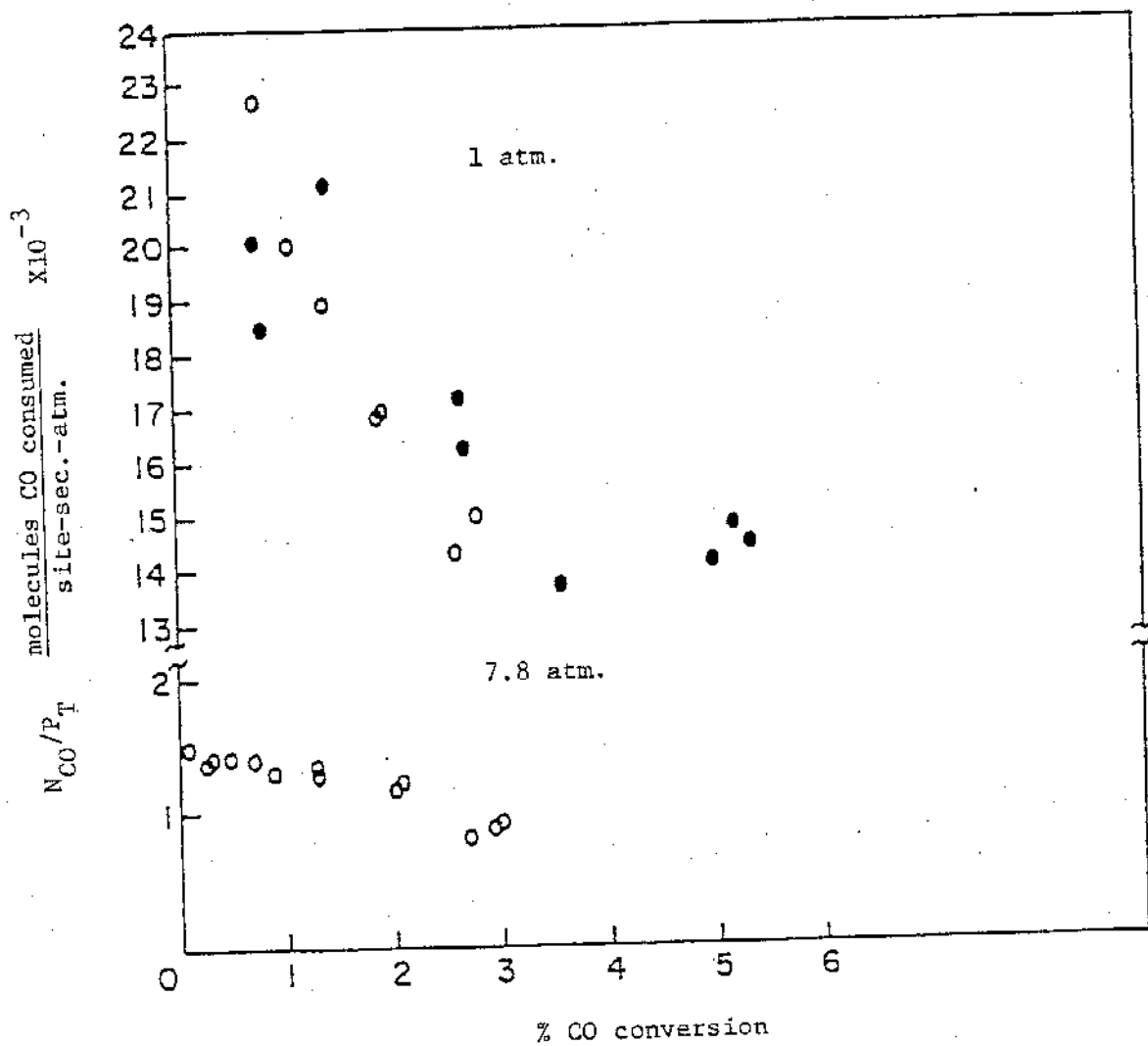


Figure 4.1.3 N_{CO}/P_T versus % CO conversion for the Co catalyst at 1 and 7.8 atmospheres with the 1/1 CO/H₂ feed.

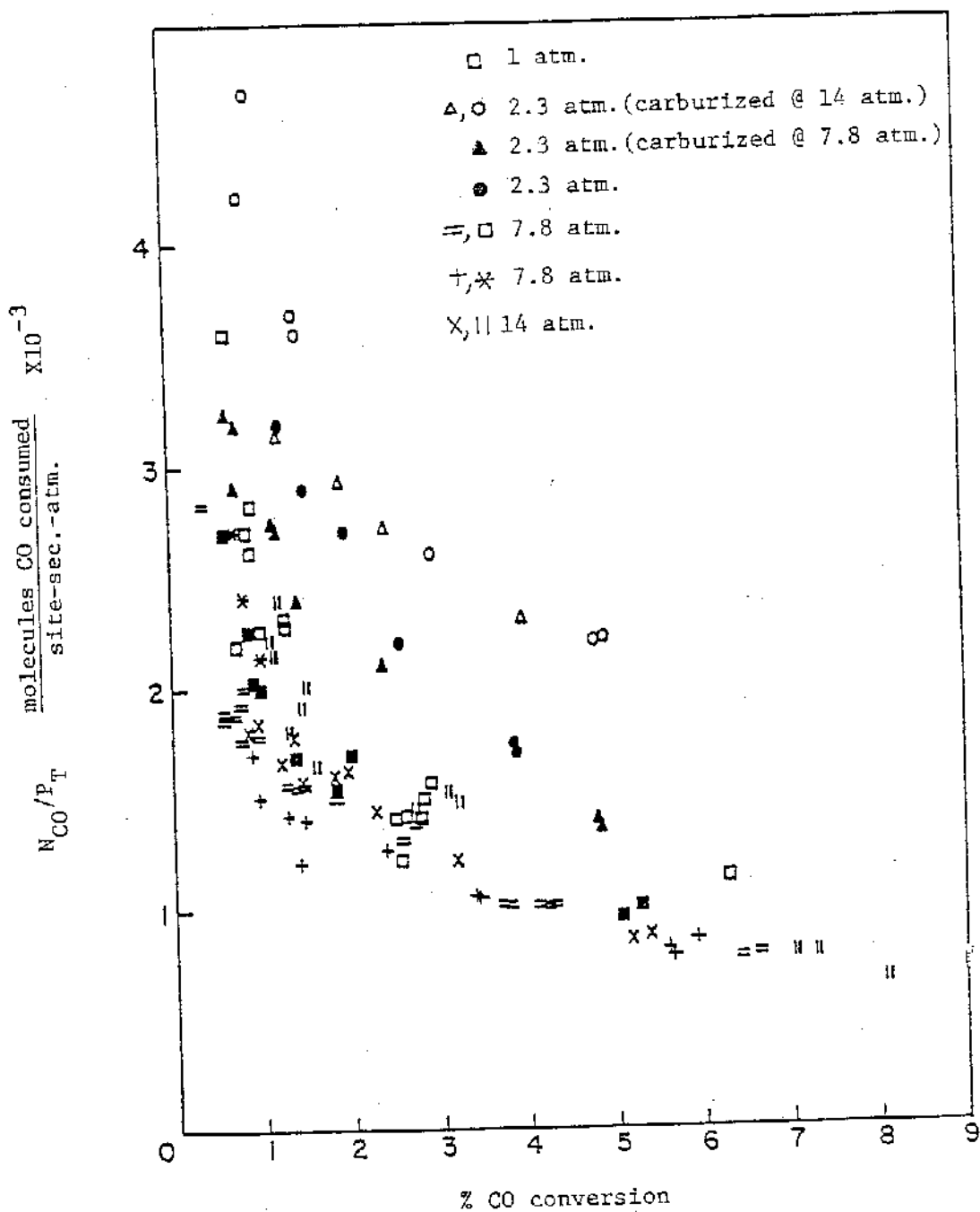


Figure 4.1.4 N_{CO}/P_T versus % CO conversion for the FeCo catalyst at 1, 7.8, and 14 atmospheres with the 1/3 CO/H₂ feed.

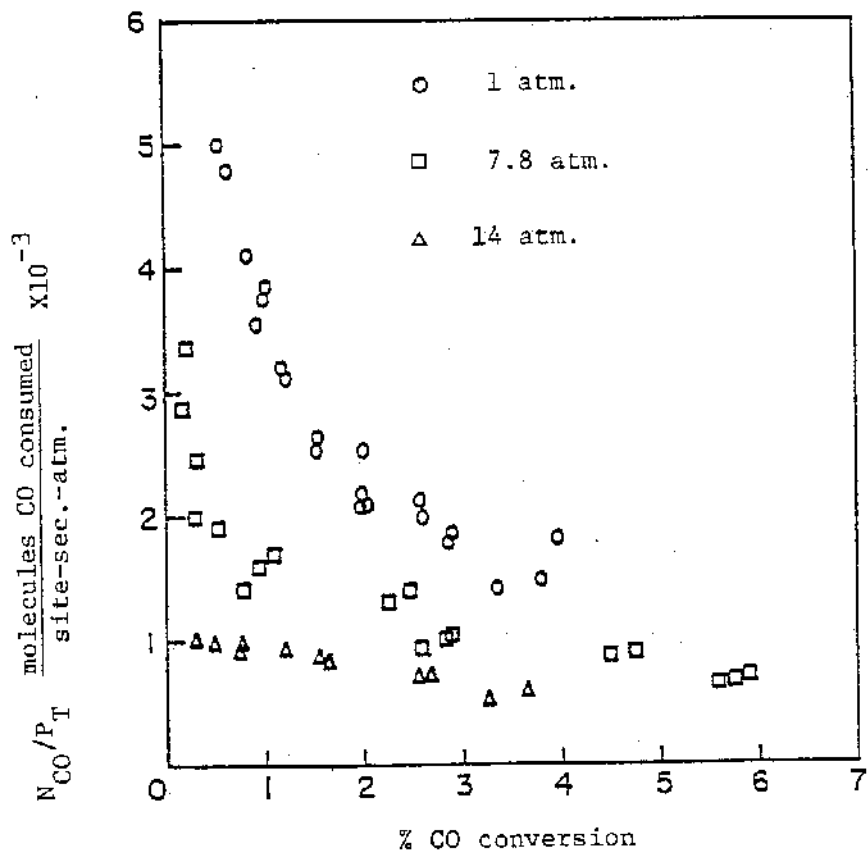


Figure 4.1.5 N_{CO}/P_T versus % CO conversion for the FeCo catalyst at 1, 7.8 and 14 atmospheres with the 1/3 CO/H₂ feed.