4.3.3 Low Molecular Weight Olefin Yield for Co Catalyst with 1/3 CO/H_2 Feed

The effect of secondary reactions on the ethylene yield is very pronounced for the Co catalyst (Figure 4.3.5). At CO conversions greater than 3.5% the ethylene yield begins to level off, indicating that the production rate of this component reaches its maximum at a relatively low CO conversion level compared to the Fe catalyst. The propylene yield increases linearly with increasing CO conversion over the conversion range studied and decreases with increasing pressure for a fixed CO conversion(Figure 4.3.6). The olefin/paraffin production rate ratios for the C_2 and C_3 products decreases with both increasing pressure and conversion. The 1-butene yield increases with pressure and the isomerization activity is less than that of iron at all pressures studied.

4.3.4 Comparative Ethylene and Propylene Yields and Selectivities for All Three Catalysts

Figure 4.3.7 presents the ethylene yields for the pure component and alloy catalysts at one atmosphere. Over the conversion range studied the FeCo catalyst produces the most ethylene per mole of CO reacted while the CO catalyst produces the least. The enhanced yield of the FeCo catalyst as compared to the Fe and Co catalyst most probably represents an electronic effect brought about by alloy formation (119,5). The $N_{C_2^=}/N_{C_2}$ values for the alloy catalyst are essentially identical to that of the pure Co catalyst and are higher than that of iron at one atmosphere (4.3.8). From these results one can conclude that the FeCo catalyst not only produces more ethylene per CO consumed but less ethylene is consumed via secondary reactions, as compared to the pure component catalysts.

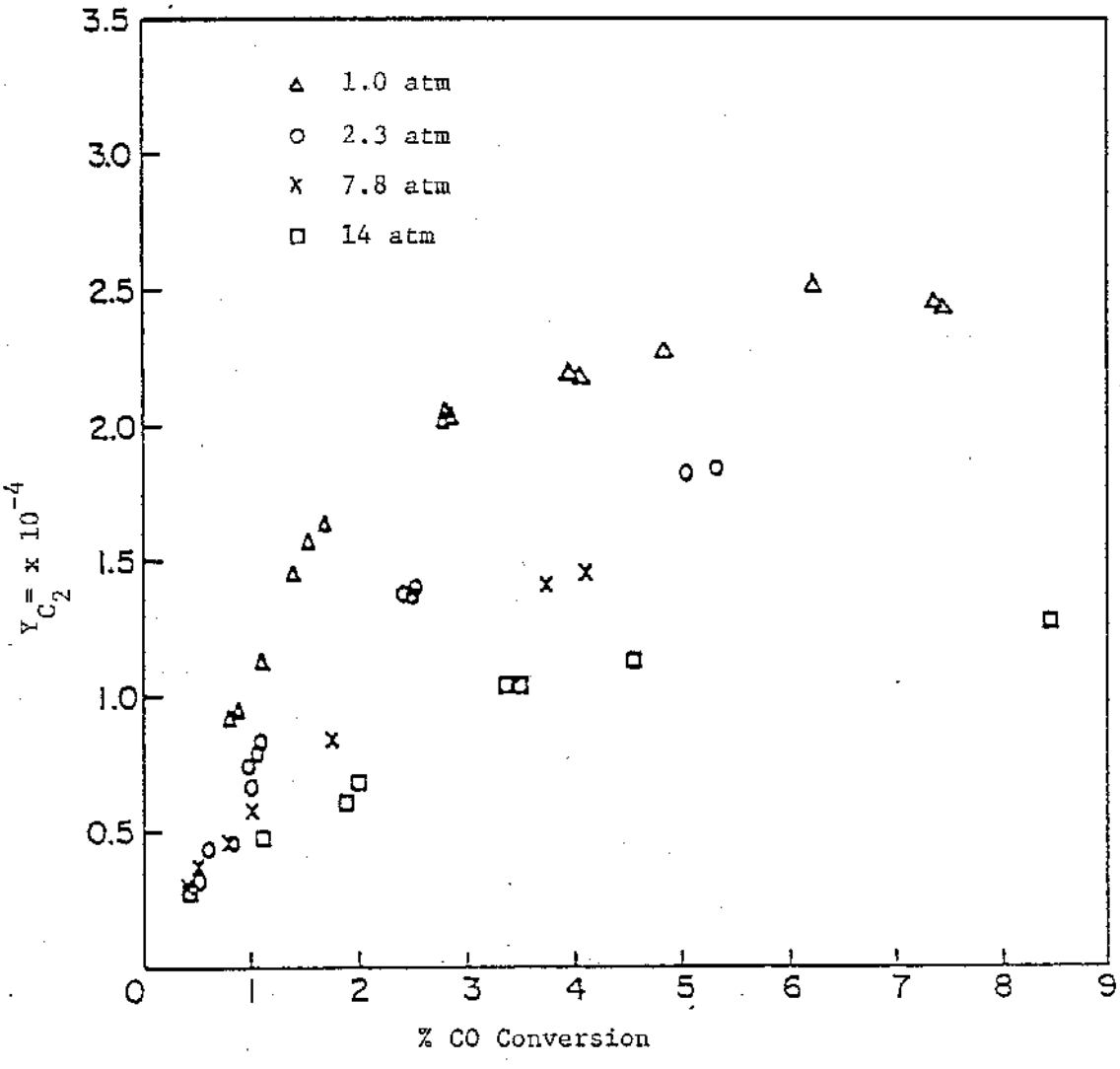

Figure 4.3.5 Ethylene yield versus % CO conversion the Co catalyst at several pressures using the 1/3 CO/H_2 feed.

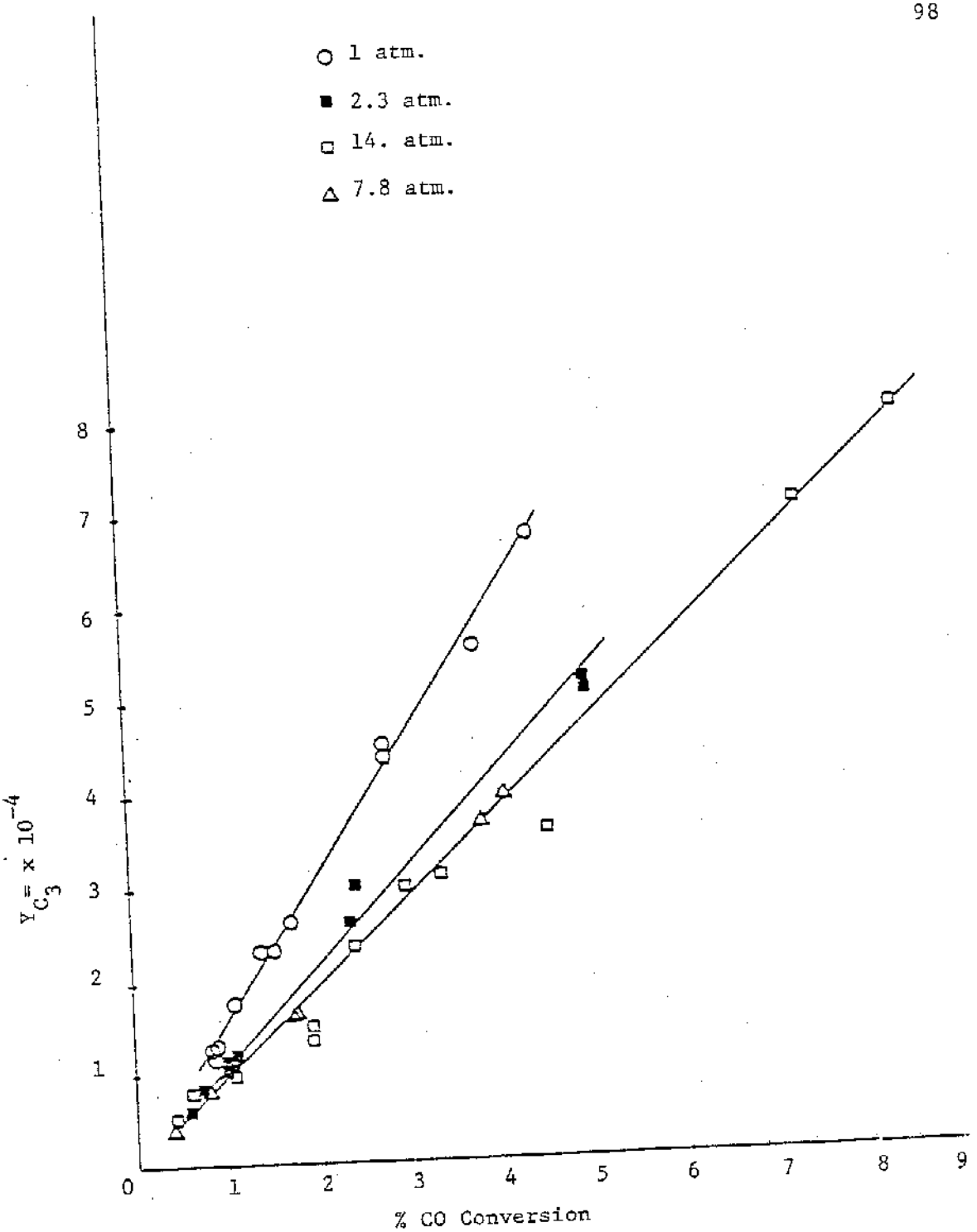

Figure 4.3.6 Propylene yield versus % CO conversion for the Co catalyst at several total pressures using the 1/3 CO/H_2 mixture.

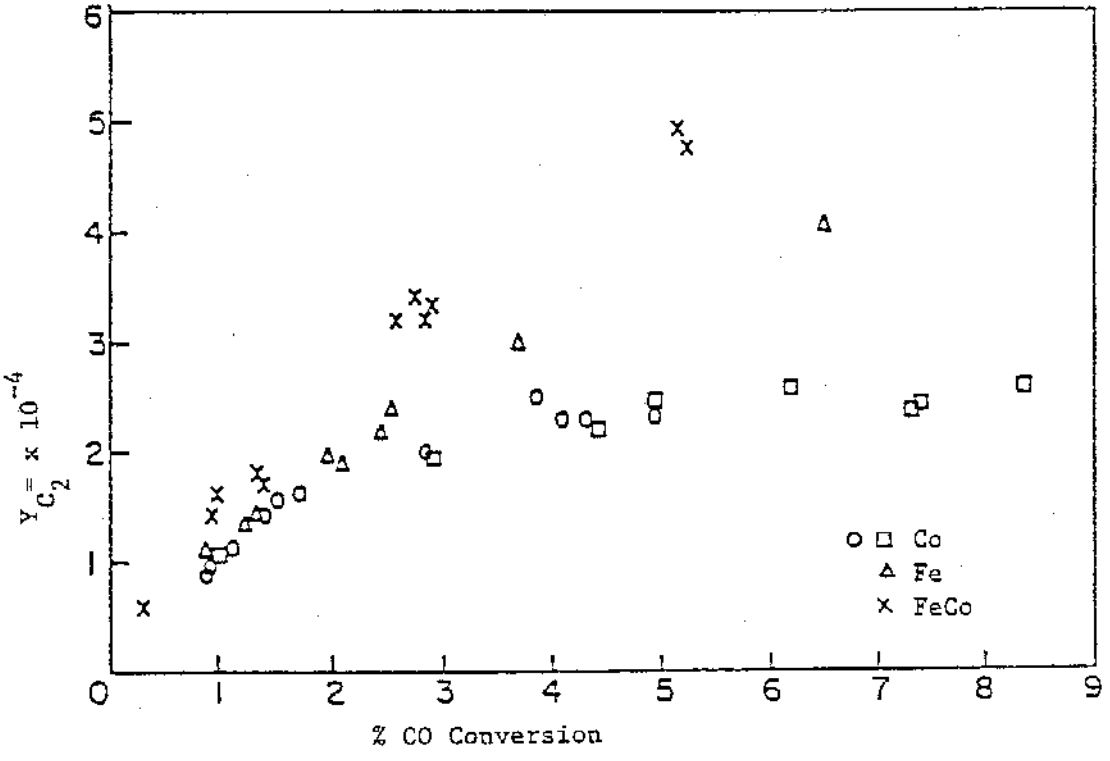

Figure 4.3.7 Ethylene yield versus % CO conversion for the Fe,Co, and FeCo catalysts in the 1/3 CO/H_2 feed at 1 atm. and 250°C.

All three catalysts yield similar amounts of propylene at 1 atmosphere as shown in Figure 4.3.9. The $N_{C_3^=}/N_{C_3}$ values (Figure 4.3.8) are largest for the Co catalyst with the alloy yielding slightly lower values. The iron catalyst has the lowest ratio indicating a higher relative hydrogenation rate as compared to the other catalyst. At 7.8 atmospheres the propylene yield of the alloy catalyst is slightly higher than that of the pure component catalysts which produce similar yields (Figure 4.3.10). The ethylene yields for the iron containing catalysts are similar, being higher than that of Cobalt (Figure 4.3.10). As will be seen in the next section, at higher pressures, the product distribution of the pure component catalysts contain a larger fraction of higher molecular weight products ($C_{n>5}$) as compared to the alloy catalyst.

The propylene yields for all three catalysts are similar at 14 atmospheres, as shown in Figure 4.3.11. At this pressure the ethylene yield is the same for the Fe and FeCo catalysts, being higher than that obtained for the Co catalyst (compare with Figures 4.3.1 and 4.3.5). It is interesting to compare the $N_{C_2^=}/N_{C_2}$ and $N_{C_3^=}/N_{C_3}$ values for these catalysts at this pressure (Figure 4.2.12). Previously it was stated that the $N_{C_2^=}/N_{C_2}$ and $N_{C_3^=}/N_{C_3}$ values decreased with increasing pressure for the Co catalyst. (Compare Figure 4.3.8 with 4.3.12). At 14 atmospheres the Co catalyst still has the highest olefin to paraffin ratios but now the FeCo catalyst gives the lowest ratios. At one atmosphere the $N_{C_2^=}/N_{C_2}$ and $N_{C_3^=}/N_{C_3}$ ratios for the alloy were significantly higher than those of iron (Figure 4.3.8), but at 14 atmospheres these ratios are considerably less than those of the pure component catalysts. The FeCo catalysts generates higher yields of ethane and propane as compared to the Fe and Co catalysts (Figure 4.3.13). Nakamura et al. (82) report

that a maximum in C_2 and C_3 selectivity occurs for a 50Fe/50Co bulk phase compositions. It is interesting to note that Auger surface studies on a bulk phase 50Fe/50Co (82) catalyst revealed a surface atom ratio of 20Fe/80Co. This ratio corresponds to the bulk phase ratio of the alloy catalyst employed in the present study. Auger studies performed on this 80Fe/20Co alloy catalyst at Northwestern University's surface science facility were inconclusive in determining the surface componsition. High electrom beam intensities were employed due to the low signal to noise ratio. Consequently the catalytic surface was severly sputtered eventually leading to the destruction of the metal particles. The Fe and Co Auger electron intensities obtained were at a atomic ratio of 4/1 Fe/Co corresponding to the bulk composition. The enhanced hydrogenation activity of the alloy catalyst is discussed in the next section and Chapter 5 with respect to overall product distribution and secondary reactions. A comparison of the 1-butene product yield (Figure 4.3.14) shows that the Fe and FeCo catalyst at 14 atmospheres produce similar yields while the Co catalyst produces somewhat less for a fixed CO conversion. The C_4 isomerization activity of the iron containing catalysts are similar and both yield comparable amounts of n-butane.

4.3.5 Methane Yields for All Three Catalysts

The methane yields for all three catalysts are presented in Figure 4.3.15. At low conversions (< 2%) the yields of this product are comparable, however, at higher conversions Co produces a larger amount. In section 4.1 the N_{CH_4}/N_{CO} ratio is found to be independent of CO conversion for the Co catalyst at one atmosphere using the 1/3 feed (Figure 4.1.7). For the iron containing catalyst N_{CH_4}/N_{CO} decreases with

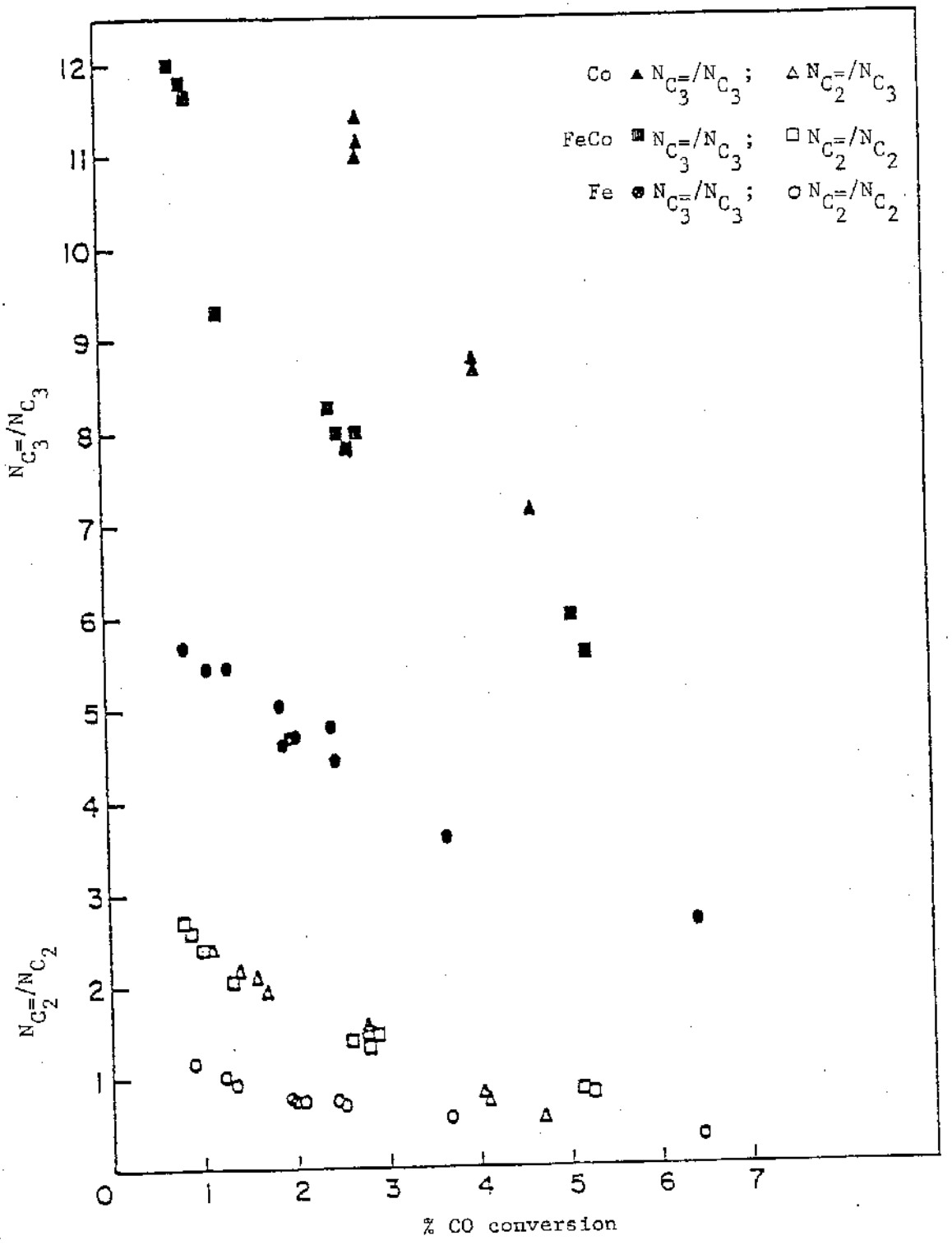

Figure 4.3.8 Propylene/propane and ethylene/ethane ratios versus % CO conversion for all three catalysts at 1 atm. in the 1/3 CO/H_2 feed.

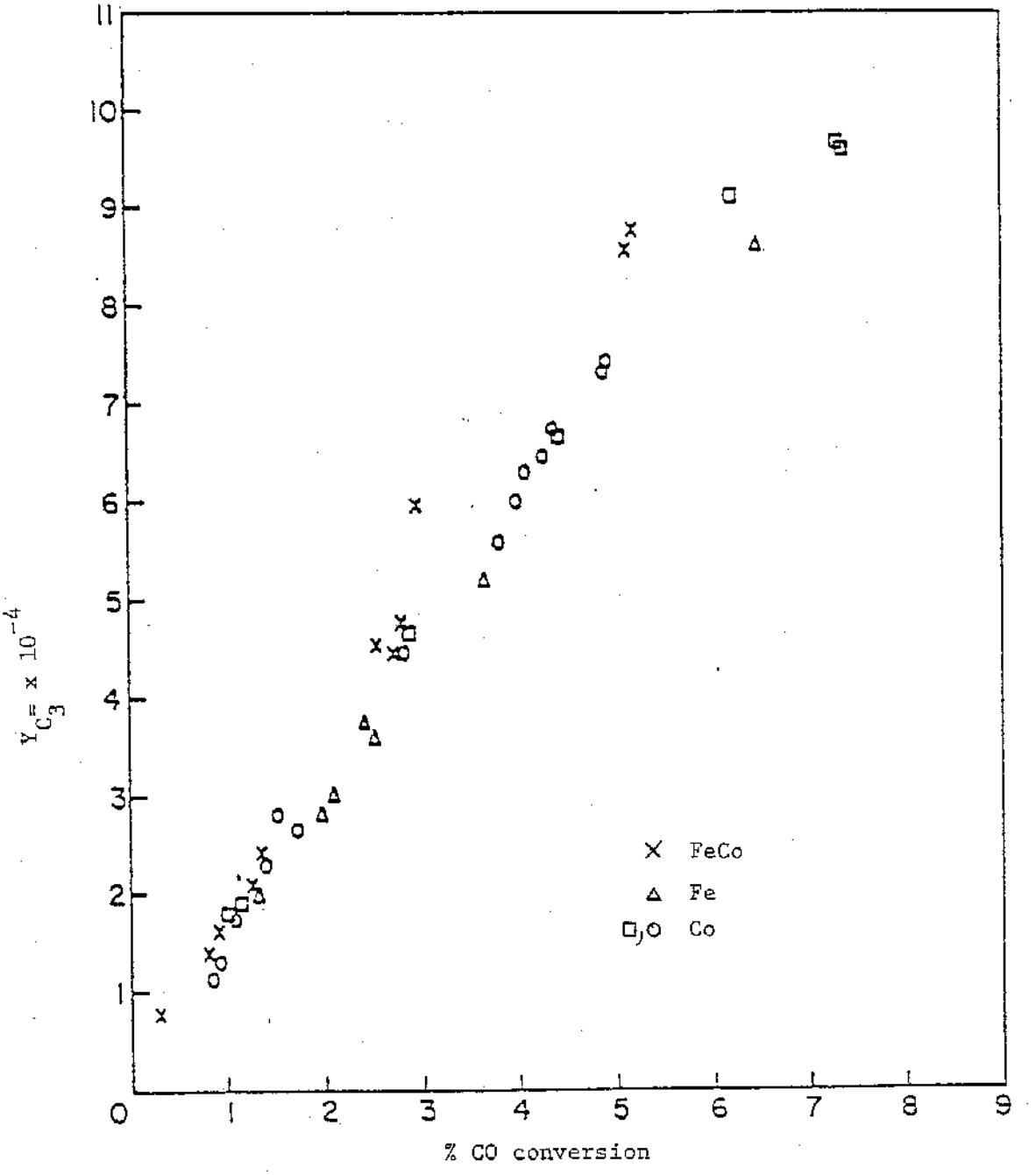

Figure 4.3.9 Propylene yield versis % CO conversion for all three catalysts at 1 atm. Using the 1/3 CO/H_2 feed.

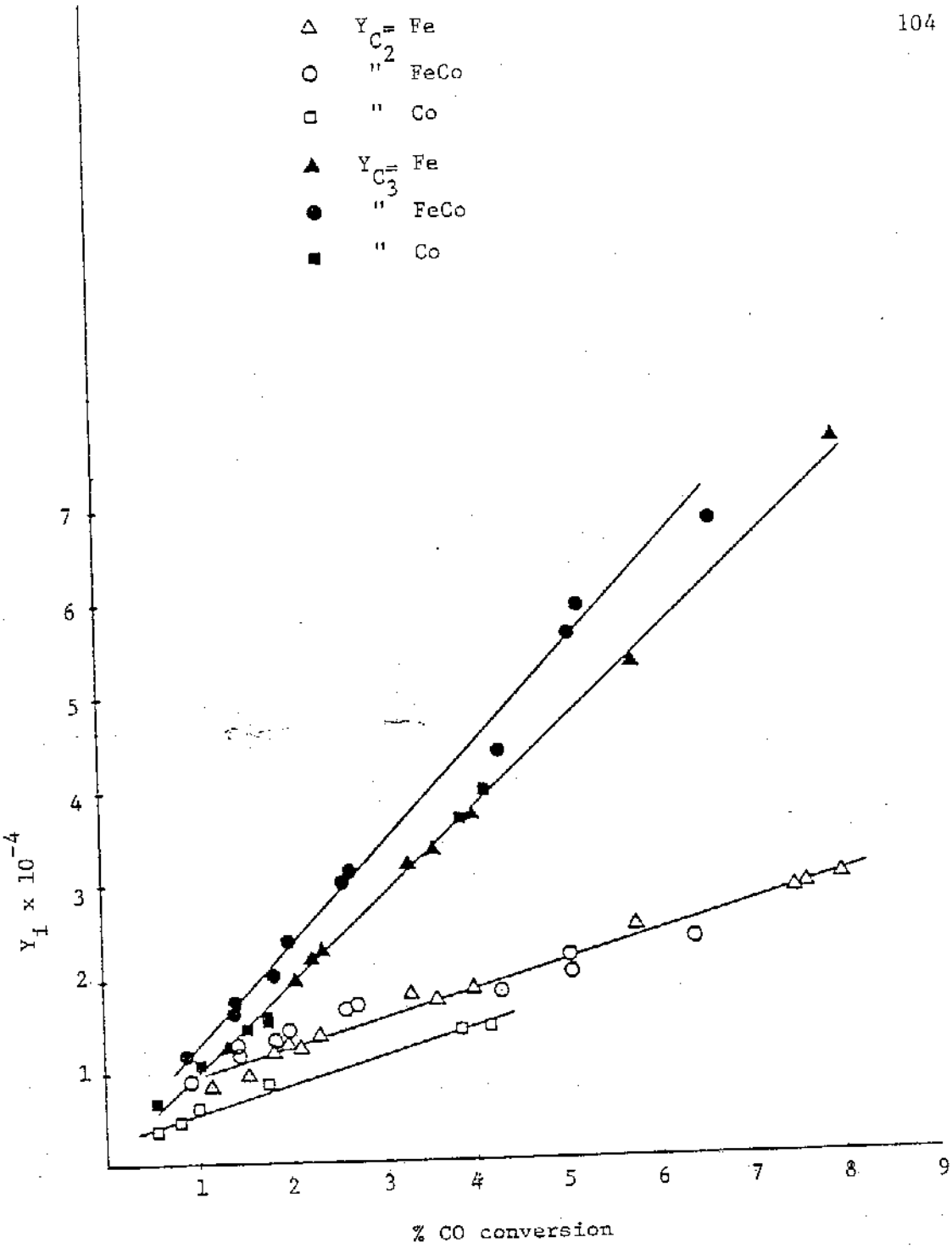

Figure 4.3.10 Ethylene ($Y_{C_2^=}$) and propylene ($Y_{C_3^=}$) yields versus % CO conversion for all three catalysts at 7.8 atmospheres.

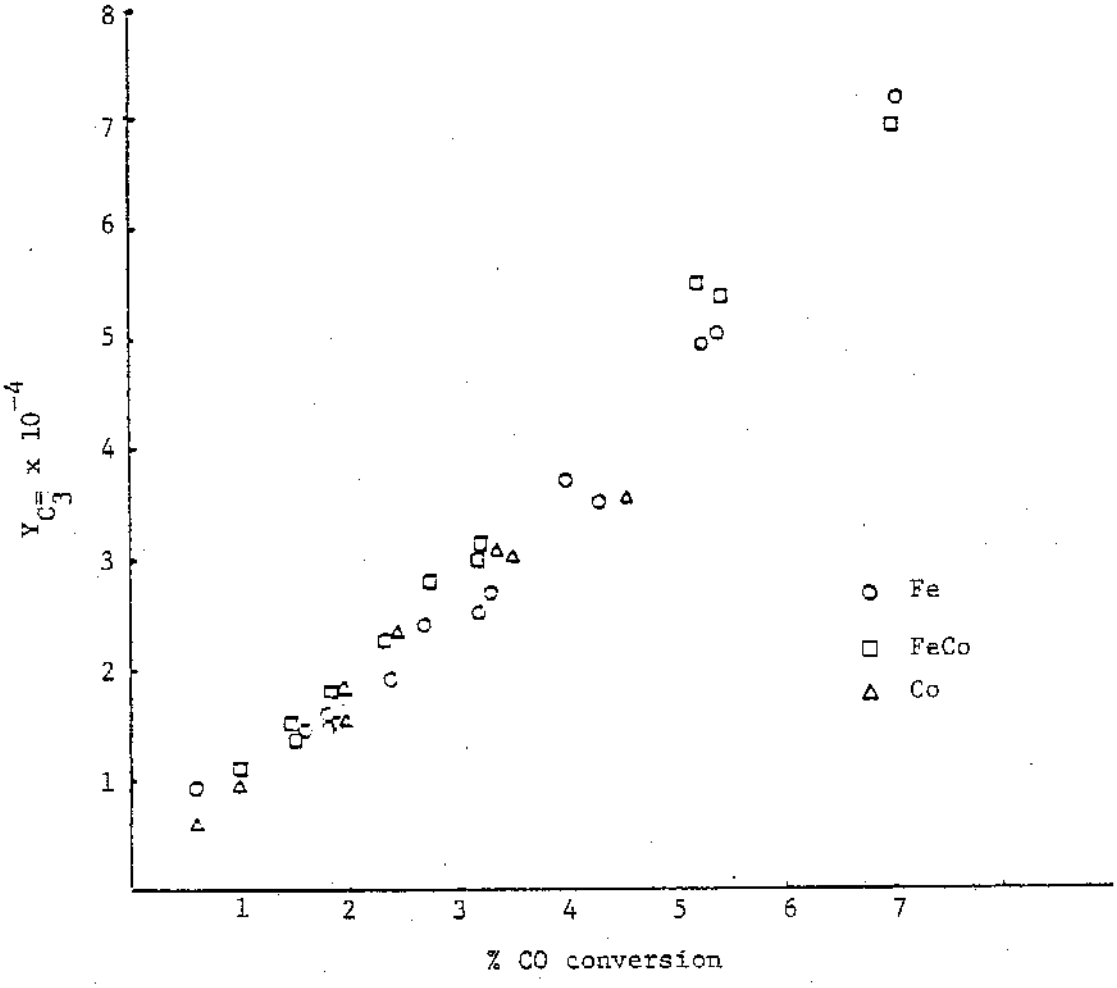

Figure 4.3.11 Propylene yield versus % CO conversion for all three catalysts at 14 atmospheres in the 1/3 CO/H_2 feed.

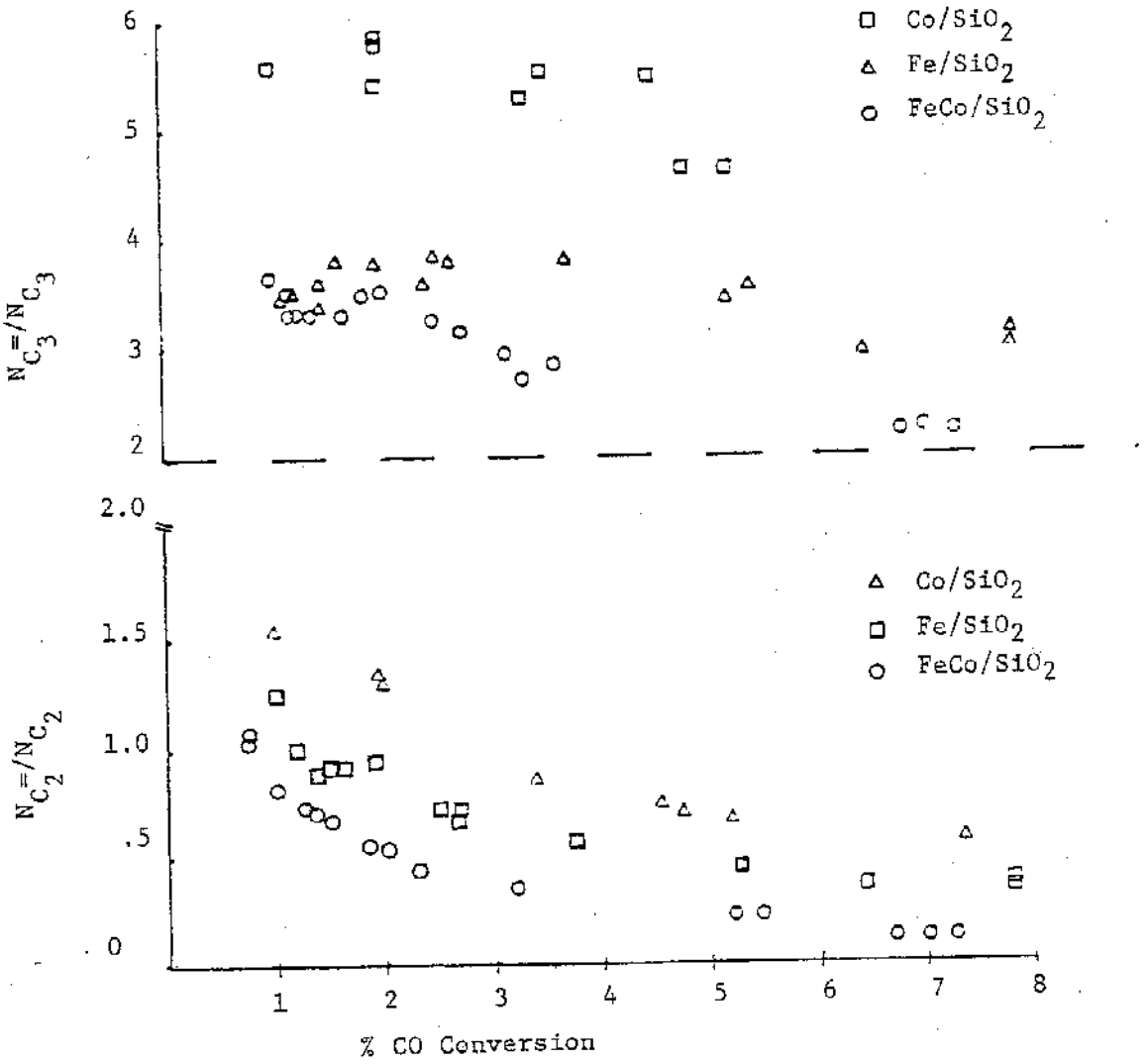

Figure 4.3.12 $N_{C_2^=}/N_{C_2}$ and $N_{C_3^=}/N_{C_3}$ selectivities versus CO conversion for the Fe, Co, and FeCo catalyst at 14 atmospheres in the 1/3 CO/H_2 mixture.

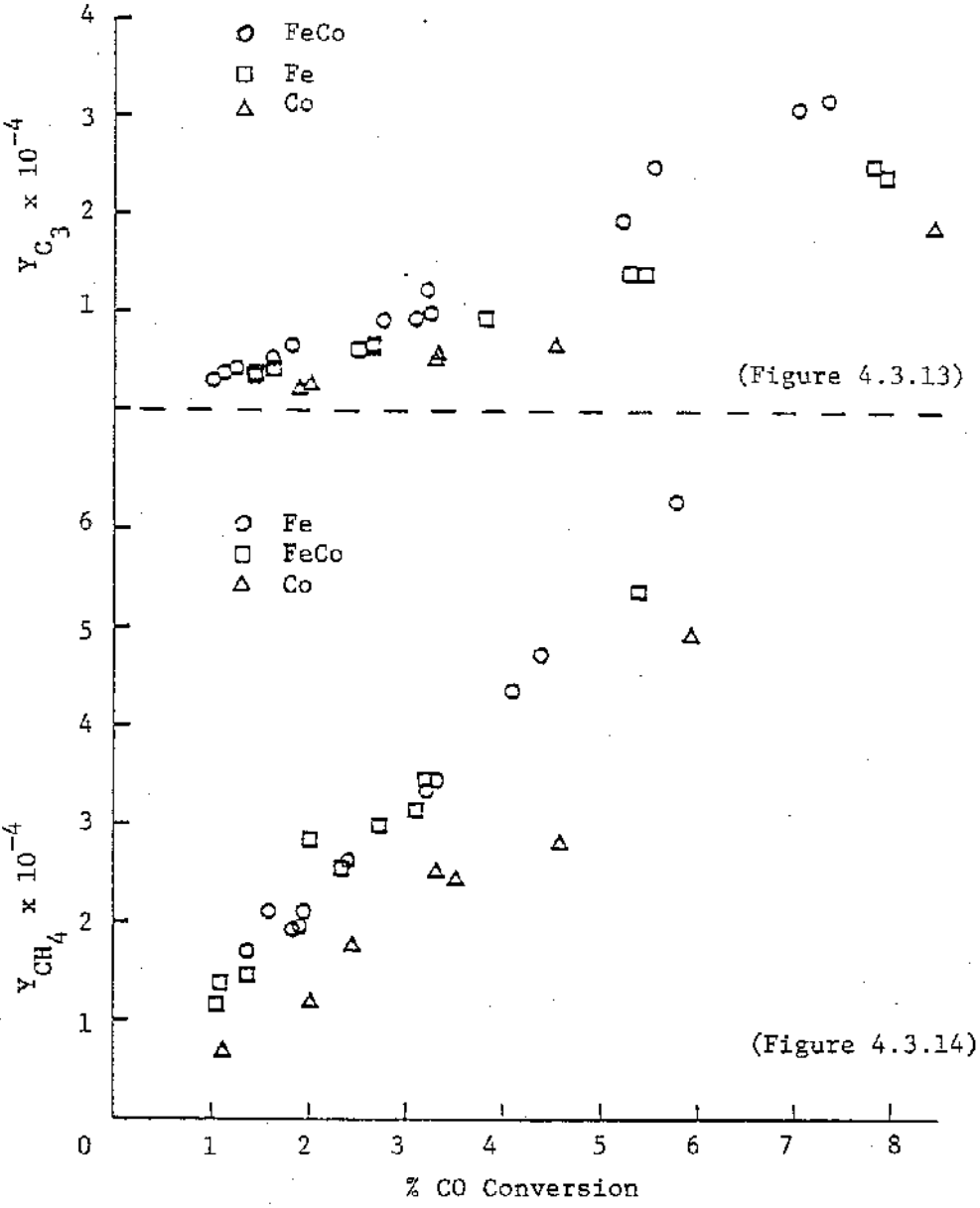

Figure 4.3.13 (top) Propane yield versus percent CO conversion for all three catalysts at 14 atm. and 250°C using the 1/3 CO/H_2 feed.

Figure 4.3.14 (bottom) 1-Butene yield versus percent CO conversion for all three catalysts at 14 atm. and 250°C using the 1/3 CO/H_2 feed.