5.2.1.4.4 Establishment of Catalytic Stability with Tests at H_2:CO Feed Ratio = 2, 225°C at Inlet and 35 atm

Tests with Catalyst 4966-96-1 with ~5 nm ruthenium particles indicated that the selectivity to undesirable light hydrocarbons was low but catalytic stability may not be good. Further investigations with ~5 nm ruthenium particles were conducted in order to establish stability using another catalyst.

Catalyst 4966-119 with 1.5% Ru (by wt.) had approximately 1/3 (by wt.) of the ruthenium in the form of 100 nm or larger particles, therefore, probably catalytically insignificant. The rest of the ruthenium was in the form of intermediate size particles. Of these intermediate size particles, 80% were 4-6 nm and 20% were 8-10 nm in size.

Catalyst 4966-119 was tested in Runs 34-36 in order to establish catalytic stability at H_2:CO feed ratio = 2, 225°C at inlet and 35 atm.

In Run 34 Catalyst 4966-119 was tested with a feed having a H_2:CO ratio = 1.9. Since 1.9 was slightly lower than the H_2:CO usage ratio, the H_2:CO ratio at the catalyst outlet decreased below 1.9 with increase in the conversion level. Other conditions were 225°C at inlet, 35 atm and 170 gas hourly space velocity (Figures 5-186 through 5-190).

The CO conversion decreased from 100% to 60% during the first 60 hours, and remained between 60% to 50% during the following 60 hours (Figure 5-186). The initial light hydrocarbon selectivities, at 90-100% CO conversion, were low: $\leq$3-4% C_1-C_4. The light hydrocarbon selectivities, then, increased with decrease in the conversion level. However, the increase in C_1-C_4 selectivities was more rapid than that expected from a decrease in the conversion level alone, probably indicating that the catalyst selectivity was also unstable (Figures 5-188 and 5-189).

Figure 5-186. Catalyst 4966-119 with Mostly 4-6 nm Ruthenium Particles: Conversions in Run 3[a] (H_2:CO Feed Ratio = 2.0, 225°C at Inlet, 34 atm)

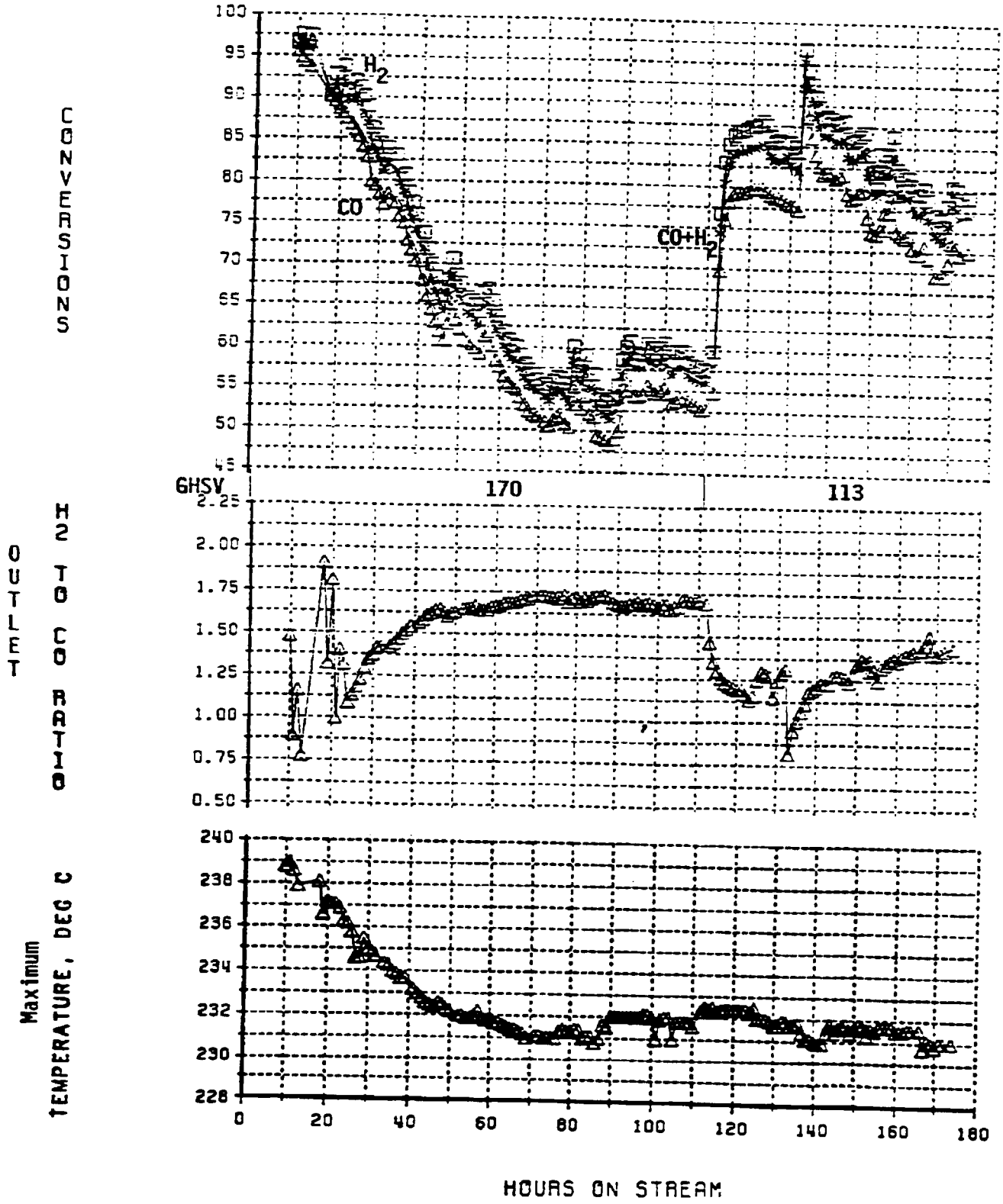


Figure 5-187. Catalyst 4966-119 with Mostly 4-6 nm Ruthenium Particles:Water Gas Shift Activity in Run 34 (H_2:CO Feed Ratio = 2.0, 225°C at Inlet, 34 atm)

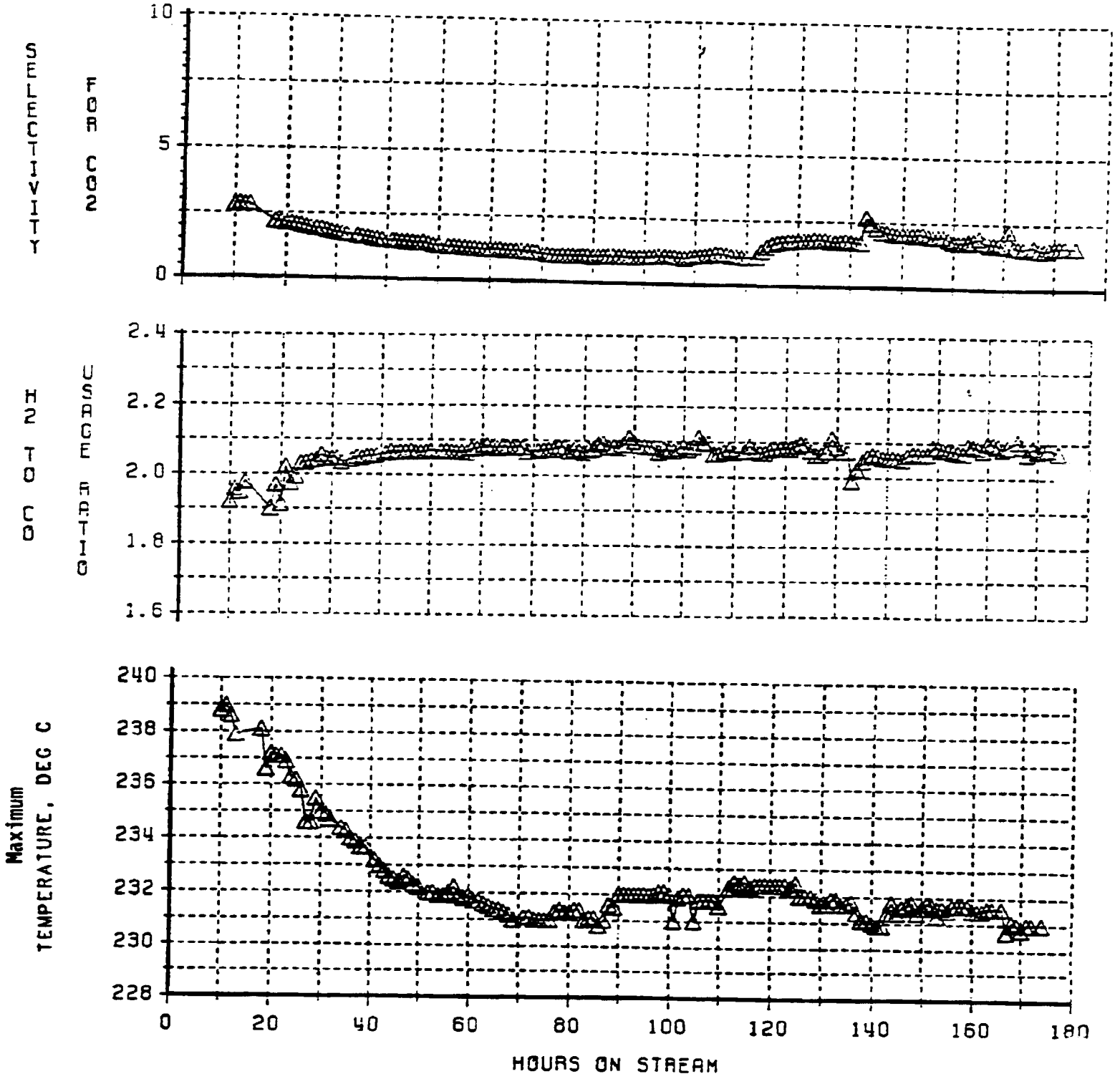


Figure 5-188. Catalyst 4966-119 with Mostly 4-6 nm Ruthenium Particles: C_1 and C_2 Selectivities in Run 34 (H_2:CO Feed Ratio = 2.0, 225°C at Inlet, 34 atm)

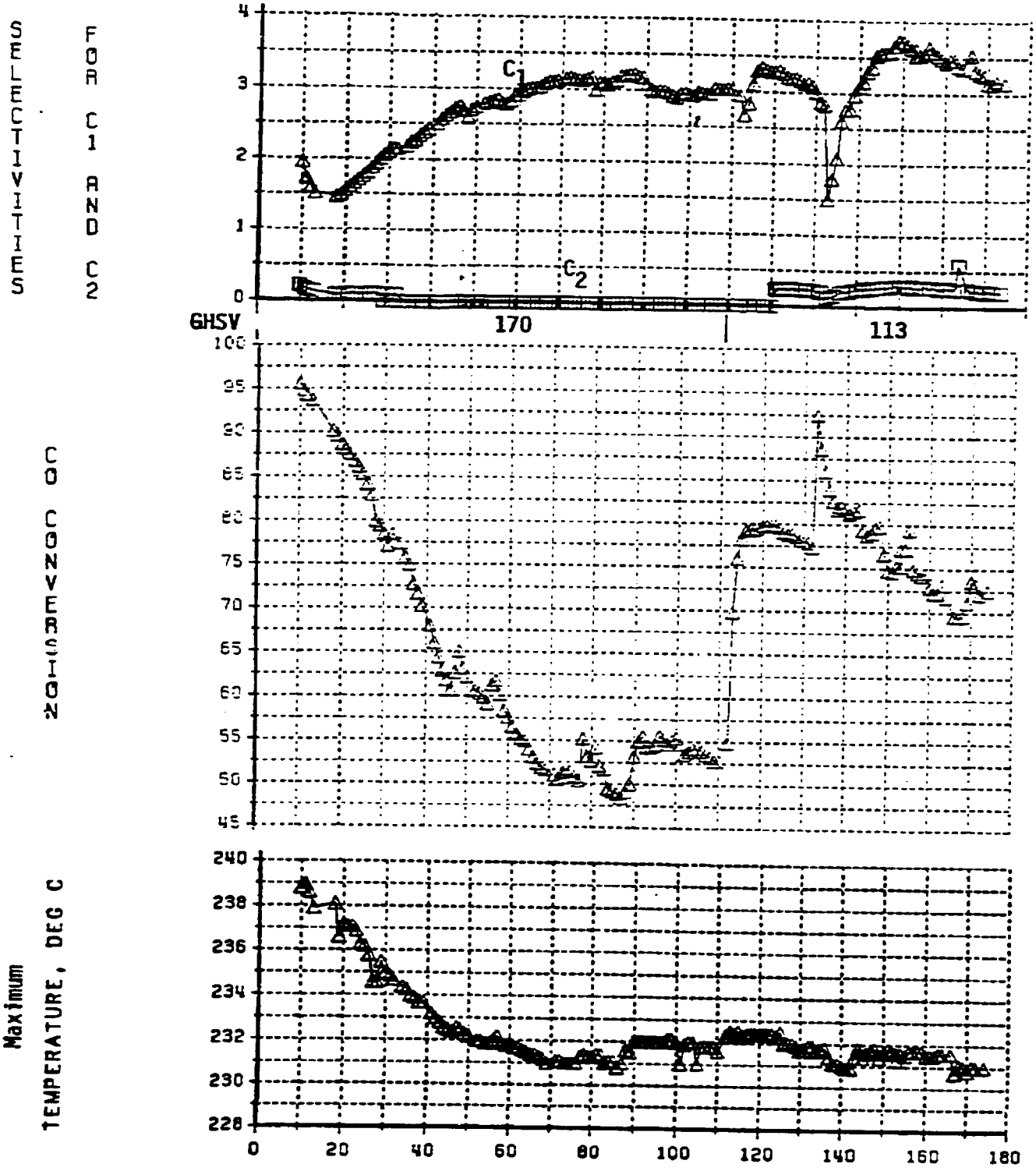


Figure 5-189. Catalyst 4966-119 with Mostly 4-6 nm Ruthenium Particles: C_3 and C_4 Selectivities in Run 34 (H_2:CO Feed Ratio = 2.0, 225°C at Inlet, 34 atm)

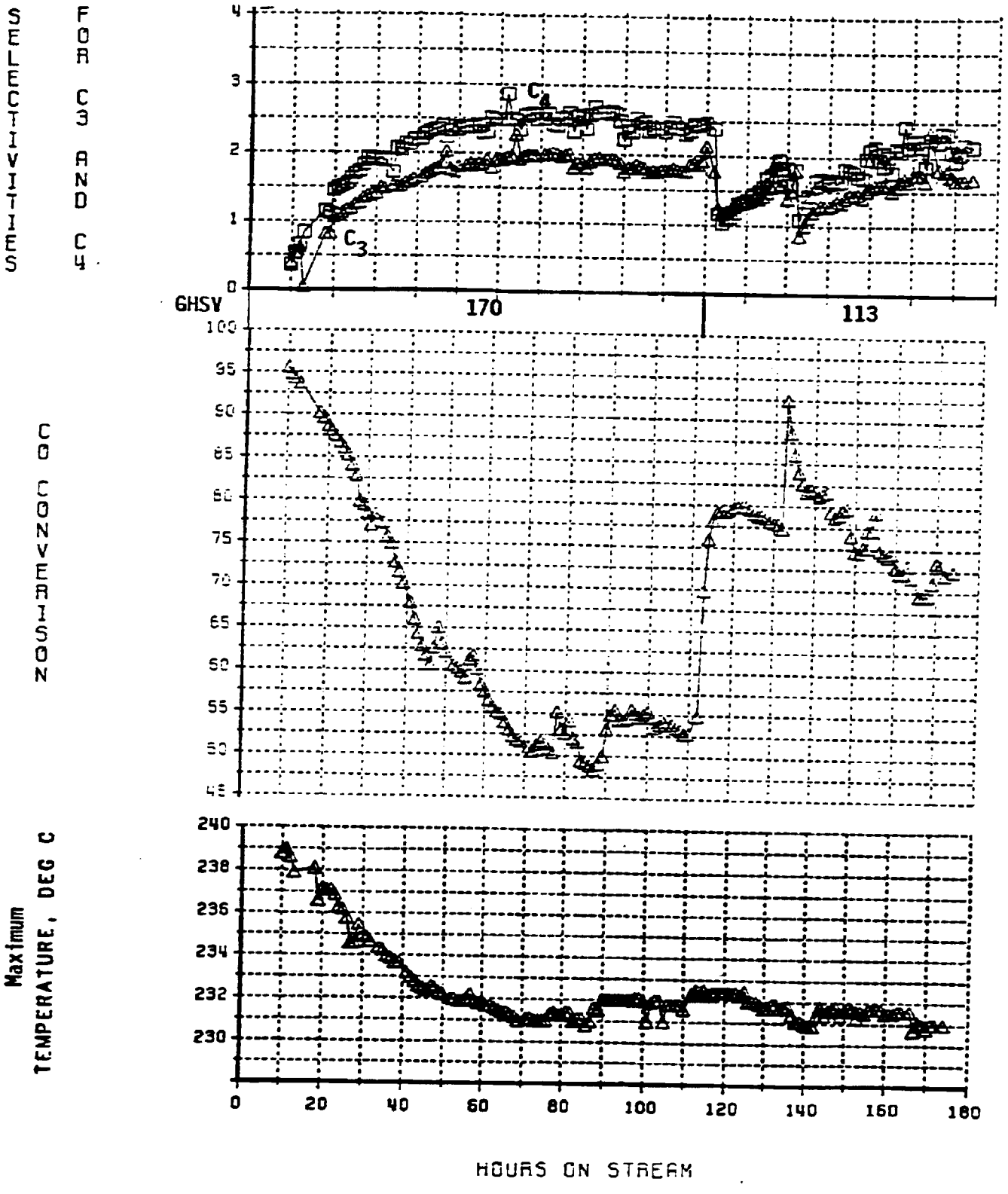
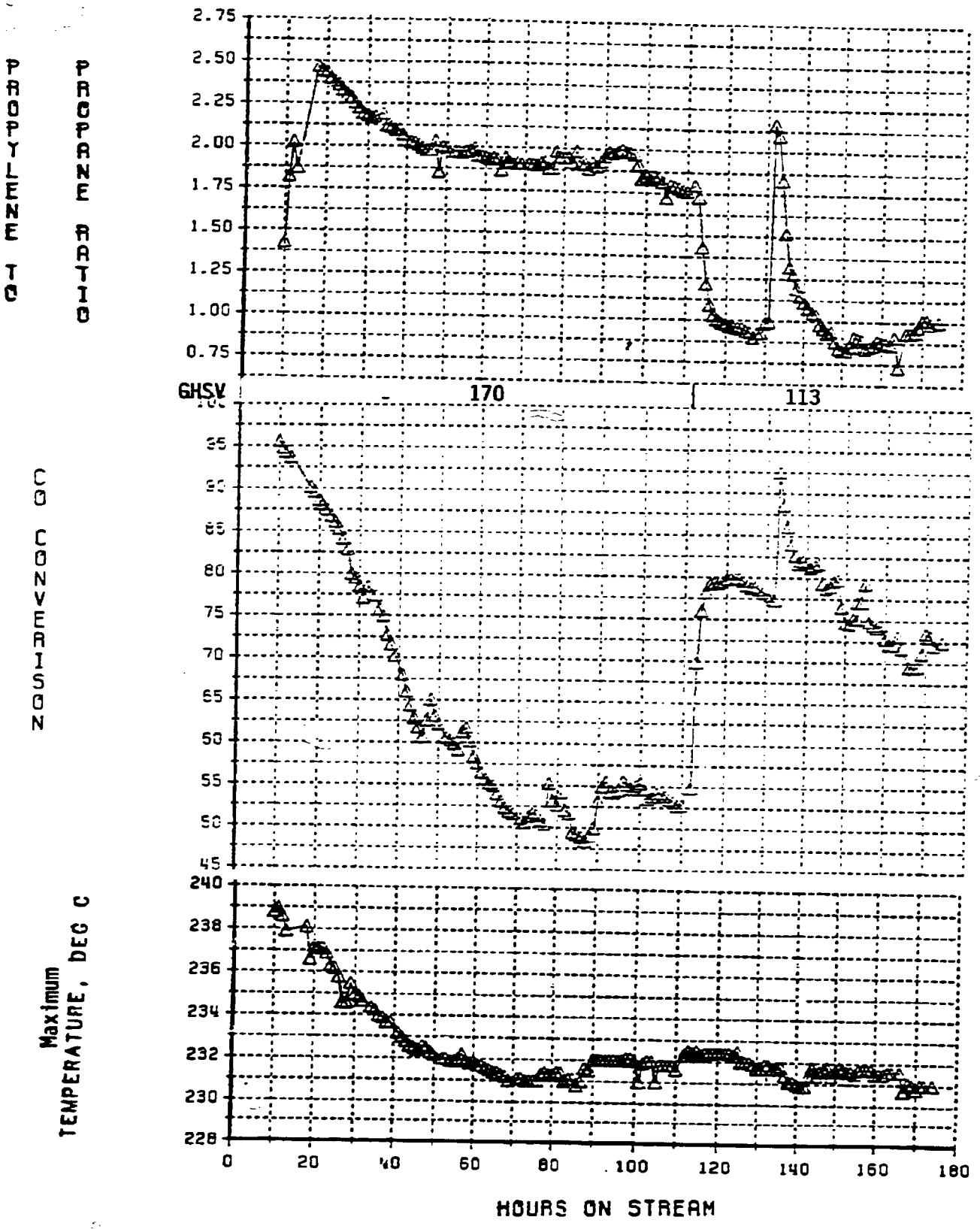


Figure 5-190. Catalyst 4966-119 with Mostly 4-6 nm Ruthenium Particles: Propylene:Propane Ratios in Run 34 (H_2:CO Feed Ratio = 2.0, 225°C at Inlet, 34 atm)



At 112 hours on stream, the gas hourly space velocity was lowered from 170 hr^{-1} to 113 hr^{-1}. The CO conversion increased to 85% and remained above 75% during the next 64 hours. However, a plug occurred in the reactor at 132 hours on stream causing the pressure drop across the reactor to gradually increase from 0.7 atm to 5.8 atm in 44 hours. Accordingly, the run had to be terminated at the end of 176 hours on stream.

The use of 1.9 H_2:CO feed ratio had caused the H_2:CO ratio to decrease across the catalyst bed in Runs 33 and 34. Since this may have accelerated catalyst deactivation, H_2:CO feed rates, no smaller than 2.0, were used in subsequent runs.

In Run 35 the H_2:CO feed ratio was slightly higher than the H_2:CO usage ratio, and therefore the H_2:CO ratio at the catalyst outlet increased above the level in the feed with increase in the conversion level.

In Run 35, the gas hourly space velocity was lowered from 340 hr^{-1} to 113 hr^{-1} during the first 46 hours in order to achieve about 90% CO conversion at 225°C and 35 atm (Figures 5-191 through 5-197). The light hydrocarbon selectivities obtained at different conversion levels between 55 and 106 hours on stream are illustrated in Figure 5-195. The selectivity-conversion relation observed in Run 35 was in agreement with the relation established in Run 33 with another catalyst having similar average size ruthenium particles, although the average H_2:CO ratios in the catalyst beds were slightly different. After 106 hours, the reactor pressure was varied in the following manner:

Hours	Pressure, atm
0-106	35
106-133	25
133-152	30
152-173	40
173-252	49

Figure 5-191. Catalyst 4966-119 with Mostly 4-6 nm Ruthenium Particles: Conversions in Run 35 (H_2:CO Feed Ratio = 2.0, 225°C at Inlet)

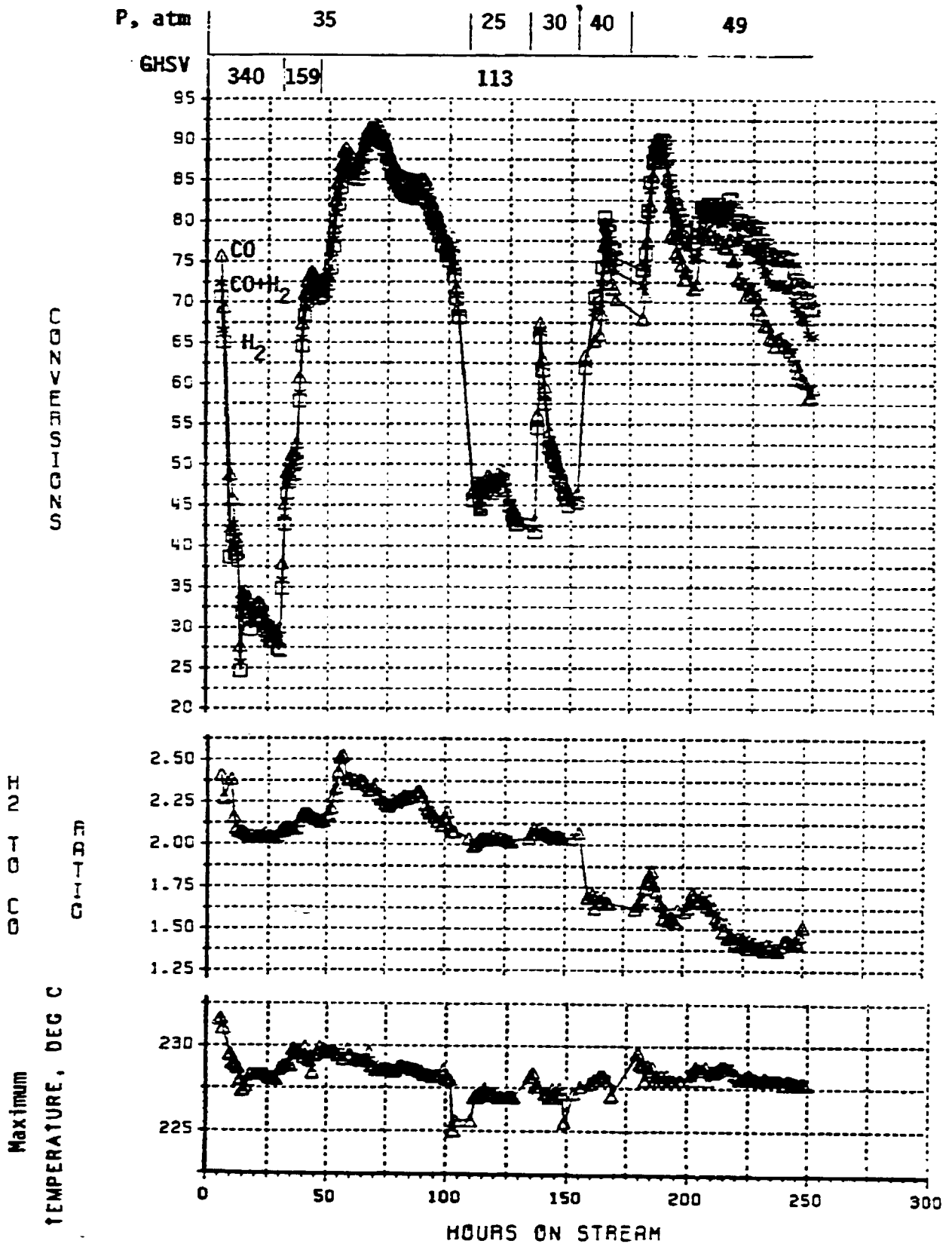


Figure 5-192. Catalyst 4966-119 with Mostly 4-6 nm Ruthenium Particles: Water Gas Shift Activity in Run 35 (H_2:CO Feed Ratio = 2.0, 225°C at Inlet)

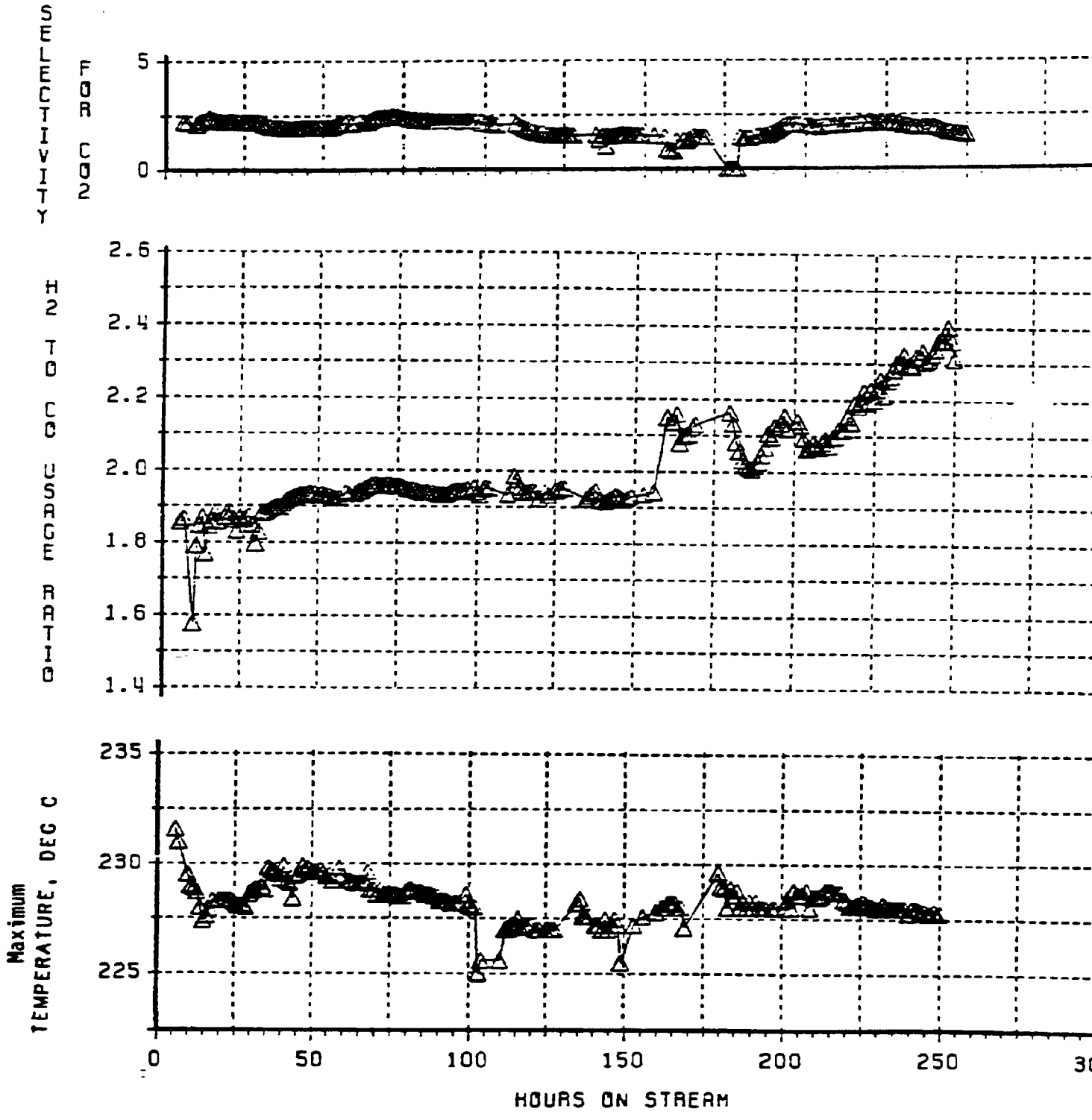


Figure 5-193. Catalyst 4966-119 with Mostly 4-6 nm Ruthenium Particles: C_1 and C_2 Selectivities in Run 35 (H_2:CO Feed Ratio = 2.0, 225°C at Inlet)

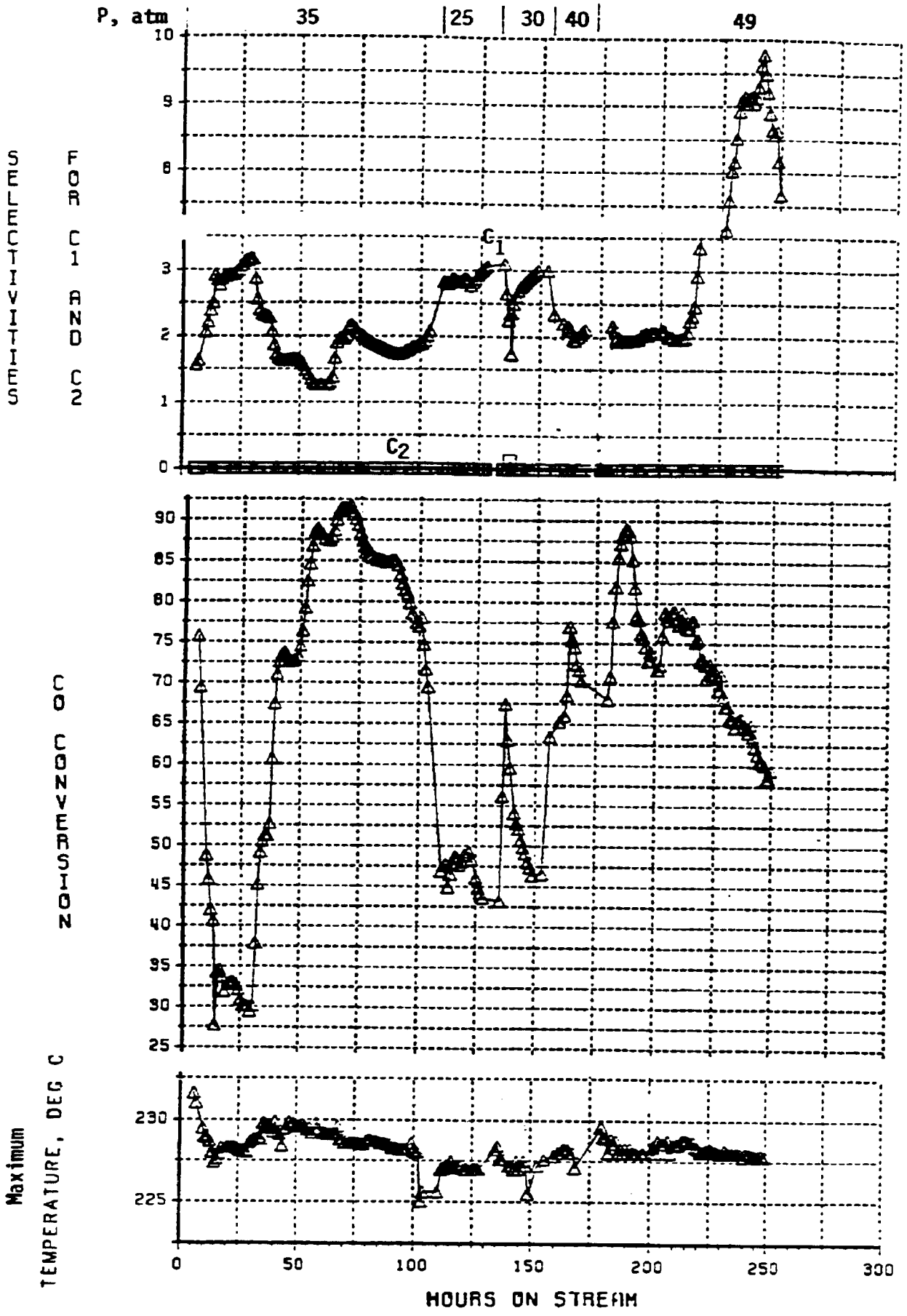


Figure 5-194. Catalyst 4966-119 with Mostly 4-6 nm Ruthenium Particles: C_3 and C_4 Selectivities in Run 35 (H_2:CO Feed Ratio = 2.0, 225°C at Inlet)

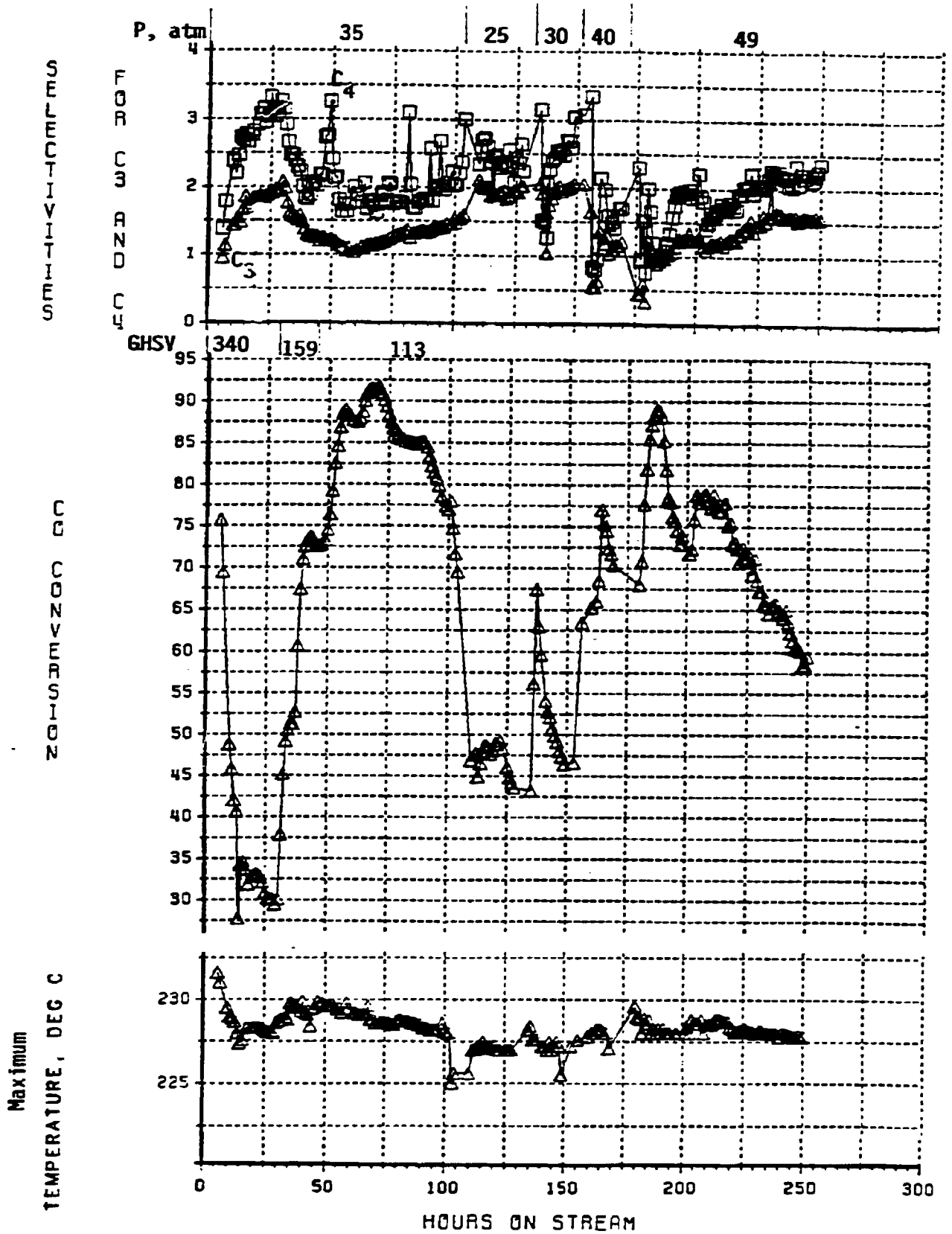
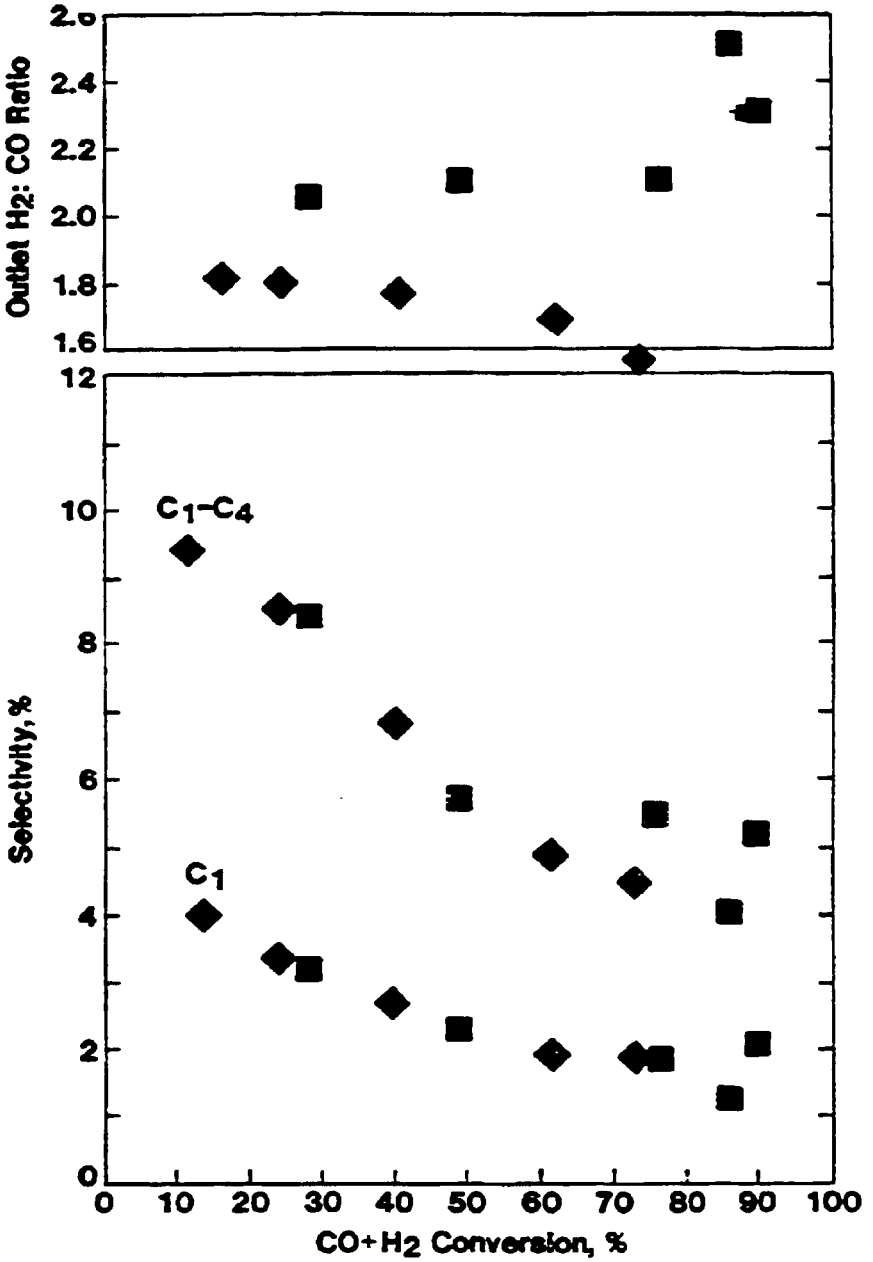


Figure 5-195. Effect of Conversion Level on Light Hydrocarbon Selectivities with Catalysts Having ~5 nm Ruthenium Particles at 225°C at Inlet and 35 atm

Run	H_2:CO Feed Ratio
◇ 33	1.9
□ 35	2.0



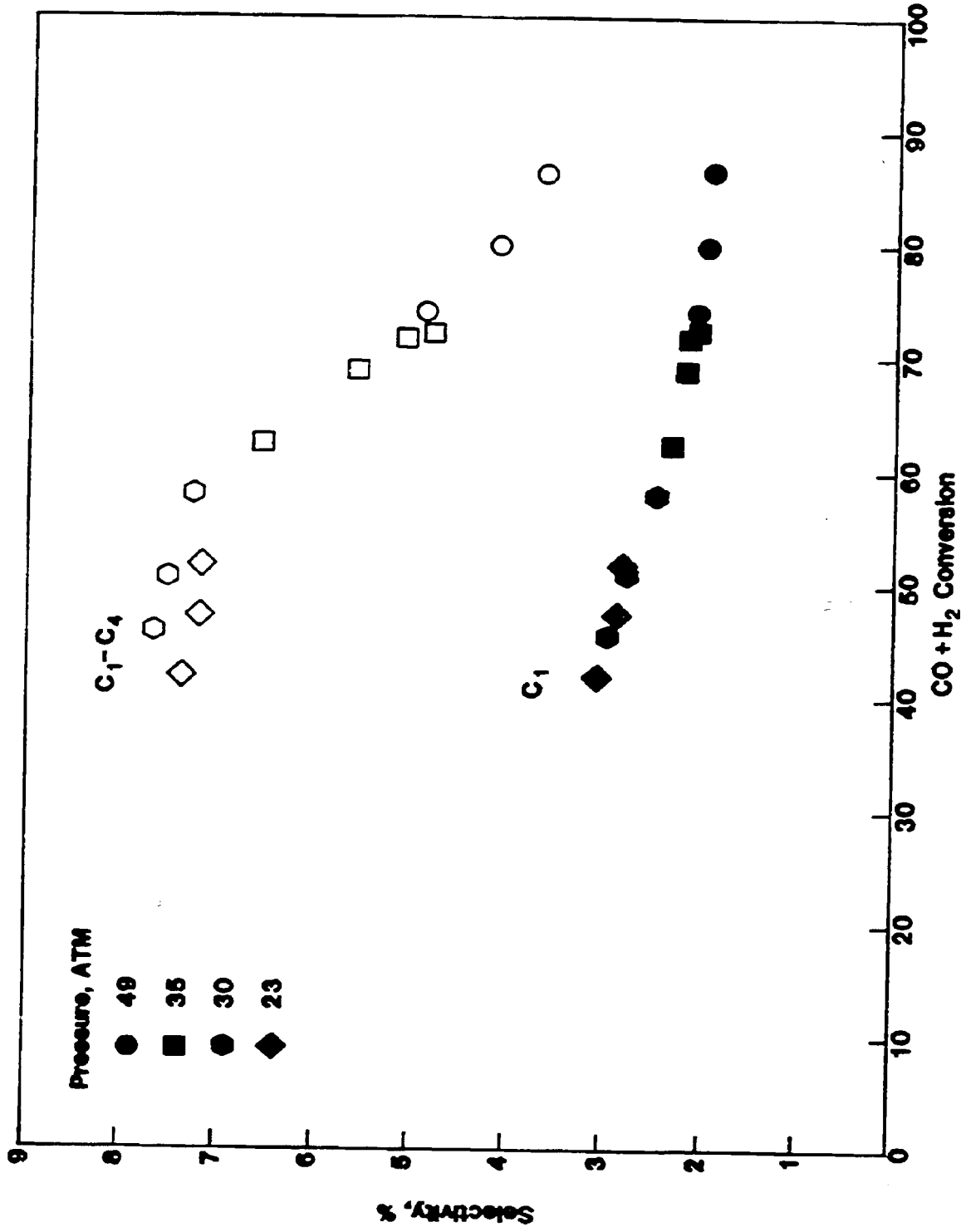
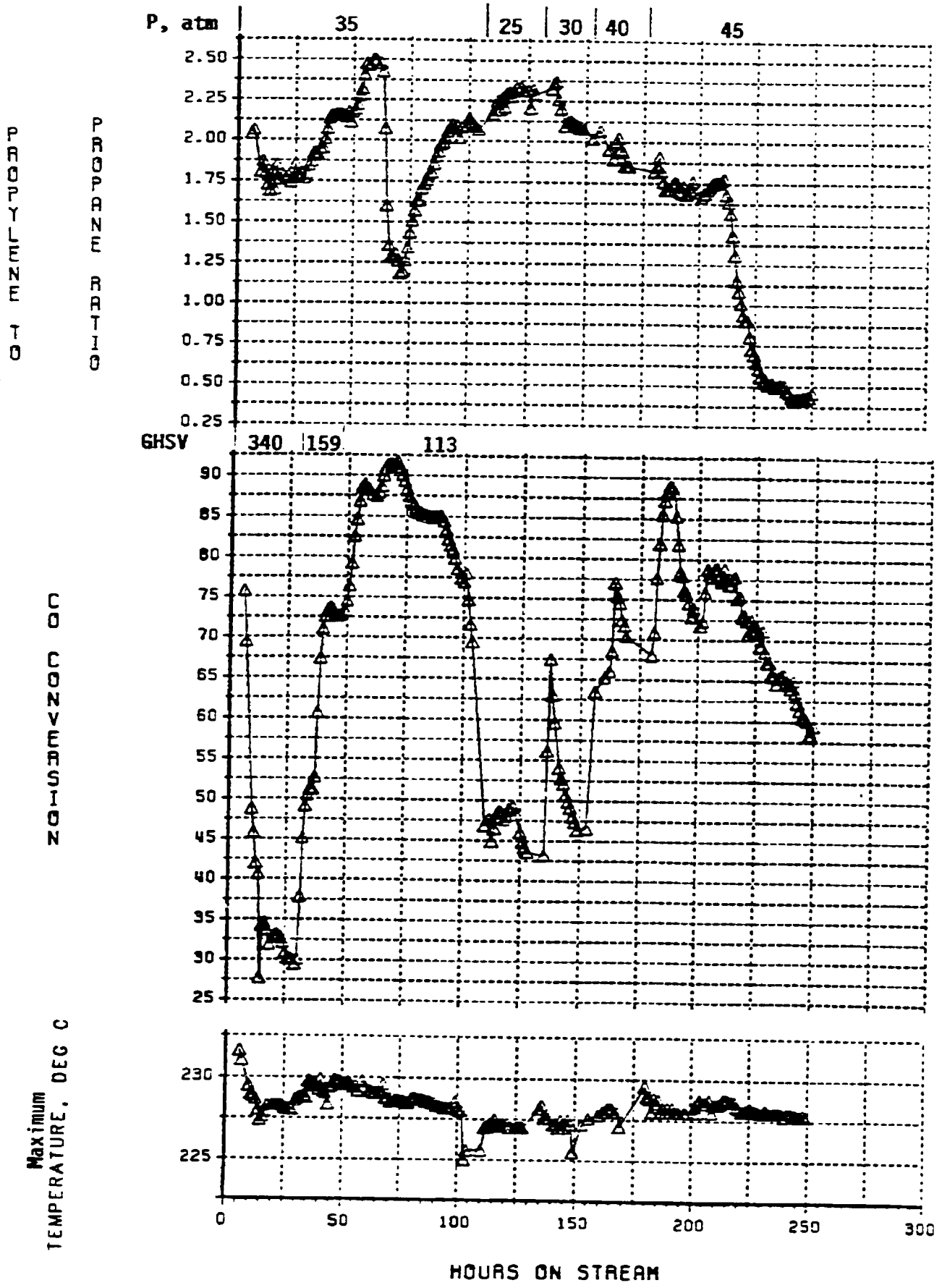


Figure 5-196. Effect of Conversion Level on Light Hydrocarbon Selectivities with Catalyst 4966-119 Having Mostly 4-6 nm Ruthenium Particles at Various Pressures in Run 35 (H_2:CO Feed Ratio = 2.0, 225°C at Inlet)

Figure 5-197. Catalyst 4966-119 with Mostly 4-6 nm Ruthenium Particles : Propylene:Propane Ratios in Run 35 (H_2:CO Feed Ratio = 2.0, 225°C at Inlet



There was a direct relation between the conversion level and the total pressure. The olefin to paraffin ratios decreased with increase in pressure. The light hydrocarbon selectivities were not noticeably affected by the total reactor pressure (Figure 5-196). Once again, the conversion level was the major factor determining the selectivities. The catalyst was not stable under any set of conditions studied. After 210 hours on stream, there was a rapid increase in selectivity to methane, accompanied by a rapid decrease in the olefin to paraffin ratio.

Catalyst 4966-119 was retested in Run 36 with a H_2:CO feed ratio = 2.0 at 225°C at inlet and 35 atm (Figures 5-198 through 5-202).

During Run 36, the gas hourly space velocity was gradually decreased from 500 hr^{-1} initially to 130 hr^{-1} at 228 hours on stream in order to achieve a CO conversion of about 80% (Figure 5-198). However, the catalyst was not stable under these conditions, as it is apparent from the rapidly declining CO conversion, declining olefin to paraffin ratios and from the rapid increase in light hydrocarbon selectivities at the end of the run.

Figure 5-198. Catalyst 4966-119 with Mostly 4-6 nm Ruthenium Particles: Conversions in Run 36 (H_2:CO Feed Ratio = 2.0, 225°C at Inlet, 35 atm)

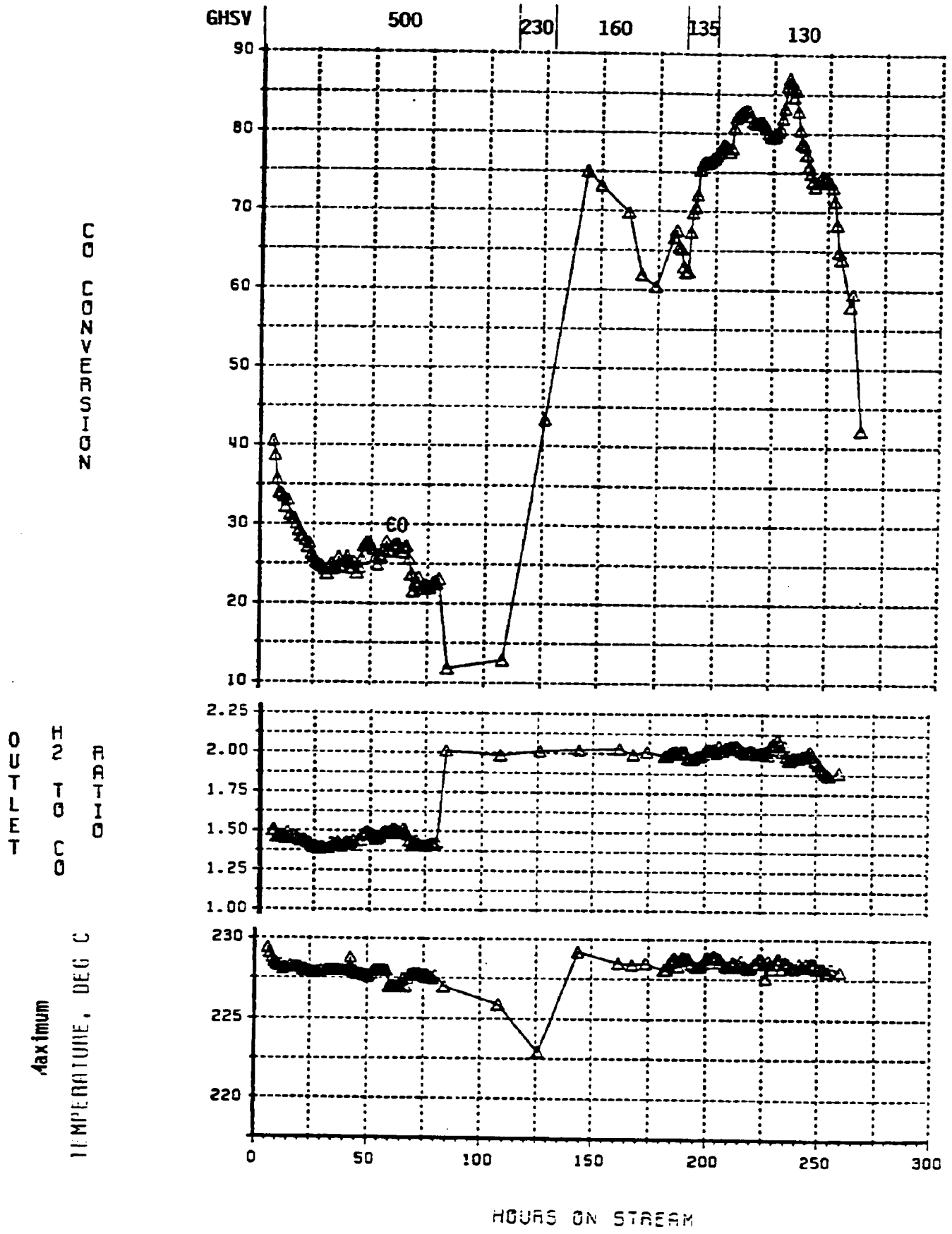


Figure 5-199. Catalyst 4966-119 with Mostly 4-6 nm Ruthenium Particles:Water Gas Shift Activity in Run 36 (H_2:CO Feed Ratio = 2.0, 225°C at Inlet, 35 atm)

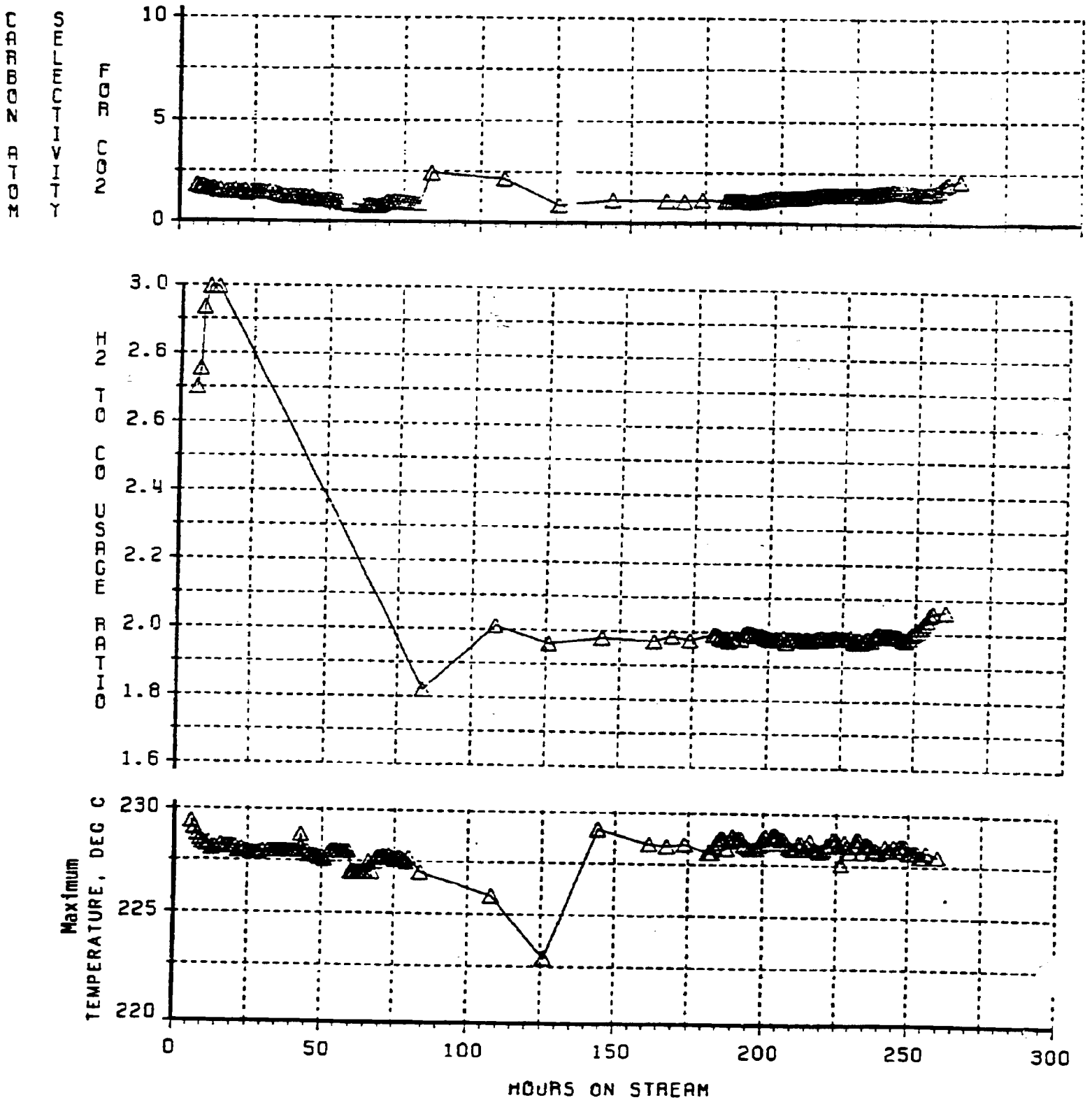


Figure 5-200. Catalyst 4966-119 with Mostly 4-6 nm Ruthenium Particles: C_1 and C_2 Selectivities in Run 36 (H_2:CO Feed Ratio = 2.0, 225°C at Inlet, 35 atm)

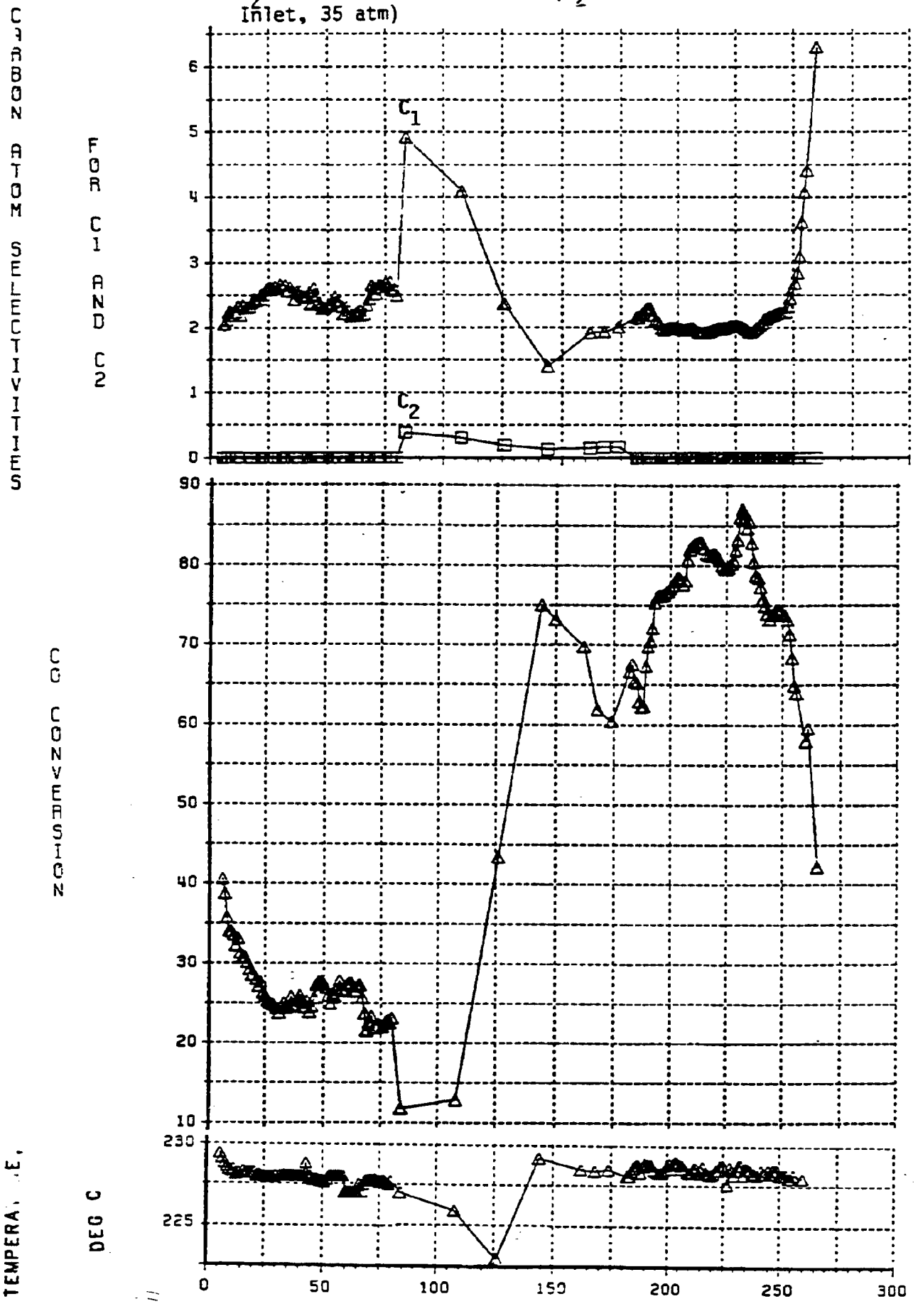


Figure 5-201. Catalyst 4966-119 with Mostly 4-6 nm Ruthenium Particles: C_3 and C_4 Selectivities in Run 36 (H_2:CO Feed Ratio = 2.0, 225°C at Inlet, 35 atm)

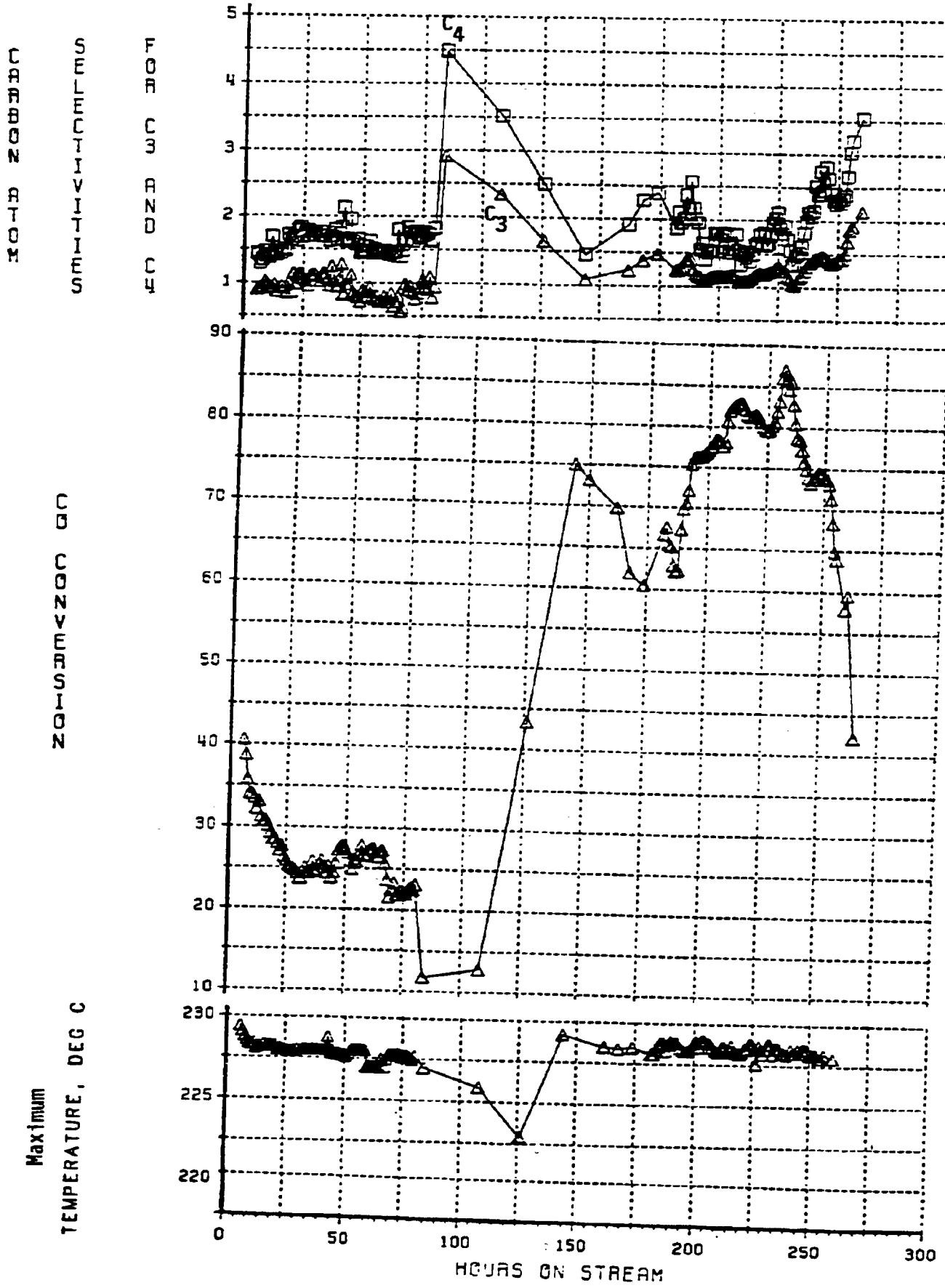


Figure 5-202. Catalyst 4966-119 with Mostly 4-6 nm Ruthenium Particles: Propylene:Propane Ratios in Run 36 (H_2:CO Feed Ratio = 2.0, 225 at Inlet, 35 atm)