### 5.2.2.4 Ruthenium on Alumina-Titania

Catalyst 4966-124 was prepared by a reverse micelle technique on an $Al_2O_3$-$TiO_2$ support (50% each, by weight) in an attempt to develop a catalyst more stable than $Al_2O_3$-supported ruthenium. According to STEM examination ruthenium particles appeared to be in the form of two-dimensional rafts spread over the support particles. These raft-like particles were about 20-25 nm in size.

Catalyst 4966-124 was tested in Runs 39, 41, 42 and 43 at a $H_2$:CO feed ratio = 2, 210°C and 62 atm using different start-up procedures. The selectivities to light hydrocarbons were low, but in each case the catalyst deactivated.

In Run 39, the catalyst was heated from room termperature to 210°C in $H_2$ at 1 atm, followed by a pressure-test at 76 atm of $H_2$. The reactor pressure was then lowered to 62 atm and synthesis gas was introduced at a gas hourly space velocity of 1518 $hr^{-1}$. The results of Run 39 are summarized in Tables 5-39 and 5-40 and Figures 5-232 through 5-238.

The space velocities were higher with the alumina-titania supported catalyst relative to the alumina-supported ruthenium catalysts tested earlier partly because the alumina-titania support was about three times denser than alumina.

Three adjustments were made to the gas hourly space velocity in Run 39: 490 $hr^{-1}$ at 14 hours on stream, 405 $hr^{-1}$ at 23 hours, and 311 $hr^{-1}$ at 37 hours on stream in order to achieve a CO conversion of about 80%, after which no further space velocity change was made. The CO conversion gradually decreased from 82% at 56 hours on stream to 37% by the end of the run at 273 hours on stream.

In Run 41 the reactor was pressure-tested with 76 atm $H_2$ at room temperature. $H_2$ was then depressured and the reactor pressured to 62 atm with synthesis gas. The catalyst was then heated to 210°C under synthesis gas flow (GHSV = 1520 $hr^{-1}$) according to the following schedule:

Table 5-39. Product Distributions in Run 39

| | |
|---|---|
| HYDROCARBON DISTRIBUTION | |
| C1 | 1.261 |
| C2 - C4 | 2.910 |
| C5 - C11 | 14.343 |
| C12 - C18 | 17.150 |
| C19 - C25 | 13.824 |
| C26 PLUS | 50.513 |
| C1 - C44 | 74.361 |
| C45 PLUS | 25.639 |
| RECOVERIES | |
| OVERALL | 85.459 |
| CARBON | 86.454 |
| HYDROGEN | 88.340 |
| ARGON | 82.770 |
| CORRECTED RECOVERIES | |
| OVERALL | 103.248 |
| CARBON | 104.451 |
| HYDROGEN | 106.730 |

| | |
|---|---|
| GAS ANALYSIS, WT% | |
| HYDROGEN | 6.0999 |
| CARBON MONOXIDE | 40.5330 |
| CARBON DIOXIDE | 1.5408 |
| METHANE | 0.2943 |
| ETHANE | 0.0000 |
| ETHYLENE | 0.0000 |
| PROPANE | 0.1342 |
| PROPYLENE | 0.1460 |
| BUTANE | 0.2026 |
| BUTENE | 0.1858 |
| AQUEOUS ANALYSIS, WT% | |
| WATER | 28.2873 |
| ALCOHOLS | |
| C1 | 0.0284 |
| C2 | 0.0584 |
| C3 | 0.0017 |
| C4 | 0.0169 |
| C5 | 0.0404 |
| C6 | 0.0463 |
| C7 | 0.0000 |
| C8 | 0.0000 |
| C9 | 0.0000 |
| C10 | 0.0000 |
| ALDEHYDES | |
| C1 | 0.0000 |
| C2 | 0.0000 |
| C3 | 0.0000 |
| C4 | 0.0000 |
| C5 | 0.0000 |
| C6 | 0.0000 |
| C7 | 0.0000 |
| C8 | 0.0000 |
| C9 | 0.0000 |
| C10 | 0.0000 |
| OTHER OXYGENATES | |
| C1 | 0.0000 |
| C2 | 0.0000 |
| C3 | 0.0000 |
| C4 | 0.0000 |
| C5 | 0.0000 |
| C6 | 0.0000 |
| C7 | 0.0000 |
| C8 | 0.0000 |
| C9 | 0.0000 |
| C10 | 0.0000 |

Table 5-40. Hydrocarbon Distributions in Run 39

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| C1 | 1.2807 | C51 | 0.6338 | C101 | 0.1409 | C151 | 0.0244 | C201 | 0.0014 |
| C2 | 0.0000 | C52 | 0.6178 | C102 | 0.1353 | C152 | 0.0236 | C202 | 0.0013 |
| C3 | 1.2003 | C53 | 0.6085 | C103 | 0.1299 | C153 | 0.0229 | C203 | 0.0013 |
| C4 | 1.7099 | C54 | 0.5933 | C104 | 0.1247 | C154 | 0.0218 | C204 | 0.0012 |
| C5 | 1.6623 | C55 | 0.5787 | C105 | 0.1197 | C155 | 0.0212 | C205 | 0.0012 |
| C6 | 0.5762 | C56 | 0.5645 | C106 | 0.1149 | C156 | 0.0205 | C206 | 0.0011 |
| C7 | 6.1326 | C57 | 0.5421 | C107 | 0.1100 | C157 | 0.0199 | C207 | 0.0011 |
| C8 | 1.5213 | C58 | 0.5288 | C108 | 0.1057 | C158 | 0.0194 | C208 | 0.0000 |
| C9 | 0.9570 | C59 | 0.5158 | C109 | 0.1015 | C159 | 0.0189 | C209 | 0.0000 |
| C10 | 1.4515 | C60 | 0.5029 | C110 | 0.0975 | C160 | 0.0184 | C210 | 0.0000 |
| C11 | 2.0419 | C61 | 0.4981 | C111 | 0.0937 | C161 | 0.0179 | C211 | 0.0000 |
| C12 | 2.5201 | C62 | 0.4852 | C112 | 0.0901 | C162 | 0.0174 | C212 | 0.0000 |
| C13 | 2.7506 | C63 | 0.4722 | C113 | 0.0866 | C163 | 0.0170 | C213 | 0.0000 |
| C14 | 2.6652 | C64 | 0.4594 | C114 | 0.0832 | C164 | 0.0166 | C214 | 0.0000 |
| C15 | 2.5204 | C65 | 0.4468 | C115 | 0.0800 | C165 | 0.0162 | C215 | 0.0000 |
| C16 | 2.1930 | C66 | 0.4302 | C116 | 0.0770 | C166 | 0.0158 | C216 | 0.0000 |
| C17 | 2.2710 | C67 | 0.4182 | C117 | 0.0747 | C167 | 0.0154 | C217 | 0.0000 |
| C18 | 2.2292 | C68 | 0.4066 | C118 | 0.0719 | C168 | 0.0150 | C218 | 0.0000 |
| C19 | 2.1838 | C69 | 0.3953 | C119 | 0.0692 | C169 | 0.0147 | C219 | 0.0000 |
| C20 | 2.1165 | C70 | 0.3844 | C120 | 0.0666 | C170 | 0.0145 | C220 | 0.0000 |
| C21 | 2.0013 | C71 | 0.3724 | C121 | 0.0641 | C171 | 0.0141 | C221 | 0.0000 |
| C22 | 2.0151 | C72 | 0.3624 | C122 | 0.0617 | C172 | 0.0138 | C222 | 0.0000 |
| C23 | 1.9028 | C73 | 0.3527 | C123 | 0.0595 | C173 | 0.0134 | C223 | 0.0000 |
| C24 | 1.8136 | C74 | 0.3433 | C124 | 0.0573 | C174 | 0.0131 | C224 | 0.0000 |
| C25 | 1.7907 | C75 | 0.3342 | C125 | 0.0553 | C175 | 0.0128 | C225 | 0.0000 |
| C26 | 1.7376 | C76 | 0.3252 | C126 | 0.0534 | C176 | 0.0124 | C226 | 0.0000 |
| C27 | 1.6663 | C77 | 0.3205 | C127 | 0.0515 | C177 | 0.0121 | C227 | 0.0000 |
| C28 | 1.6264 | C78 | 0.3118 | C128 | 0.0493 | C178 | 0.0118 | C228 | 0.0000 |
| C29 | 1.5526 | C79 | 0.3032 | C129 | 0.0477 | C179 | 0.0115 | C229 | 0.0000 |
| C30 | 1.5018 | C80 | 0.2947 | C130 | 0.0461 | C180 | 0.0112 | C230 | 0.0000 |
| C31 | 1.4533 | C81 | 0.2864 | C131 | 0.0447 | C181 | 0.0108 | C231 | 0.0000 |
| C32 | 1.4095 | C82 | 0.2782 | C132 | 0.0433 | C182 | 0.0105 | C232 | 0.0000 |
| C33 | 1.3631 | C83 | 0.2676 | C133 | 0.0420 | C183 | 0.0103 | C233 | 0.0000 |
| C34 | 1.3210 | C84 | 0.2597 | C134 | 0.0408 | C184 | 0.0100 | C234 | 0.0000 |
| C35 | 1.2792 | C85 | 0.2519 | C135 | 0.0396 | C185 | 0.0097 | C235 | 0.0000 |
| C36 | 1.2513 | C86 | 0.2442 | C136 | 0.0384 | C186 | 0.0094 | C236 | 0.0000 |
| C37 | 1.2072 | C87 | 0.2366 | C137 | 0.0373 | C187 | 0.0091 | C237 | 0.0000 |
| C38 | 1.1716 | C88 | 0.2291 | C138 | 0.0362 | C188 | 0.0024 | C238 | 0.0000 |
| C39 | 1.1393 | C89 | 0.2216 | C139 | 0.0352 | C189 | 0.0023 | C239 | 0.0000 |
| C40 | 1.1076 | C90 | 0.2155 | C140 | 0.0347 | C190 | 0.0022 | C240 | 0.0000 |
| C41 | 1.0655 | C91 | 0.2082 | C141 | 0.0336 | C191 | 0.0021 | C241 | 0.0000 |
| C42 | 1.0430 | C92 | 0.2009 | C142 | 0.0326 | C192 | 0.0020 | C242 | 0.0000 |
| C43 | 1.0072 | C93 | 0.1937 | C143 | 0.0316 | C193 | 0.0019 | C243 | 0.0000 |
| C44 | 0.9709 | C94 | 0.1866 | C144 | 0.0306 | C194 | 0.0018 | C244 | 0.0000 |
| C45 | 0.7389 | C95 | 0.1796 | C145 | 0.0297 | C195 | 0.0017 | C245 | 0.0000 |
| C46 | 0.7246 | C96 | 0.1728 | C146 | 0.0287 | C196 | 0.0017 | C246 | 0.0000 |
| C47 | 0.7060 | C97 | 0.1662 | C147 | 0.0278 | C197 | 0.0016 | C247 | 0.0000 |
| C48 | 0.6880 | C98 | 0.1590 | C148 | 0.0269 | C198 | 0.0015 | C248 | 0.0000 |
| C49 | 0.6671 | C99 | 0.1527 | C149 | 0.0261 | C199 | 0.0015 | C249 | 0.0000 |
| C50 | 0.6502 | C100 | 0.1467 | C150 | 0.0252 | C200 | 0.0014 | C250 | 0.0000 |

Figure 5-232. Alumina-Titania-Supported Ruthenium Catalyst: Conversions in Run 39 ($H_2$:CO Feed Ratio = 2.0, 210°C at Inlet, 62 atm)

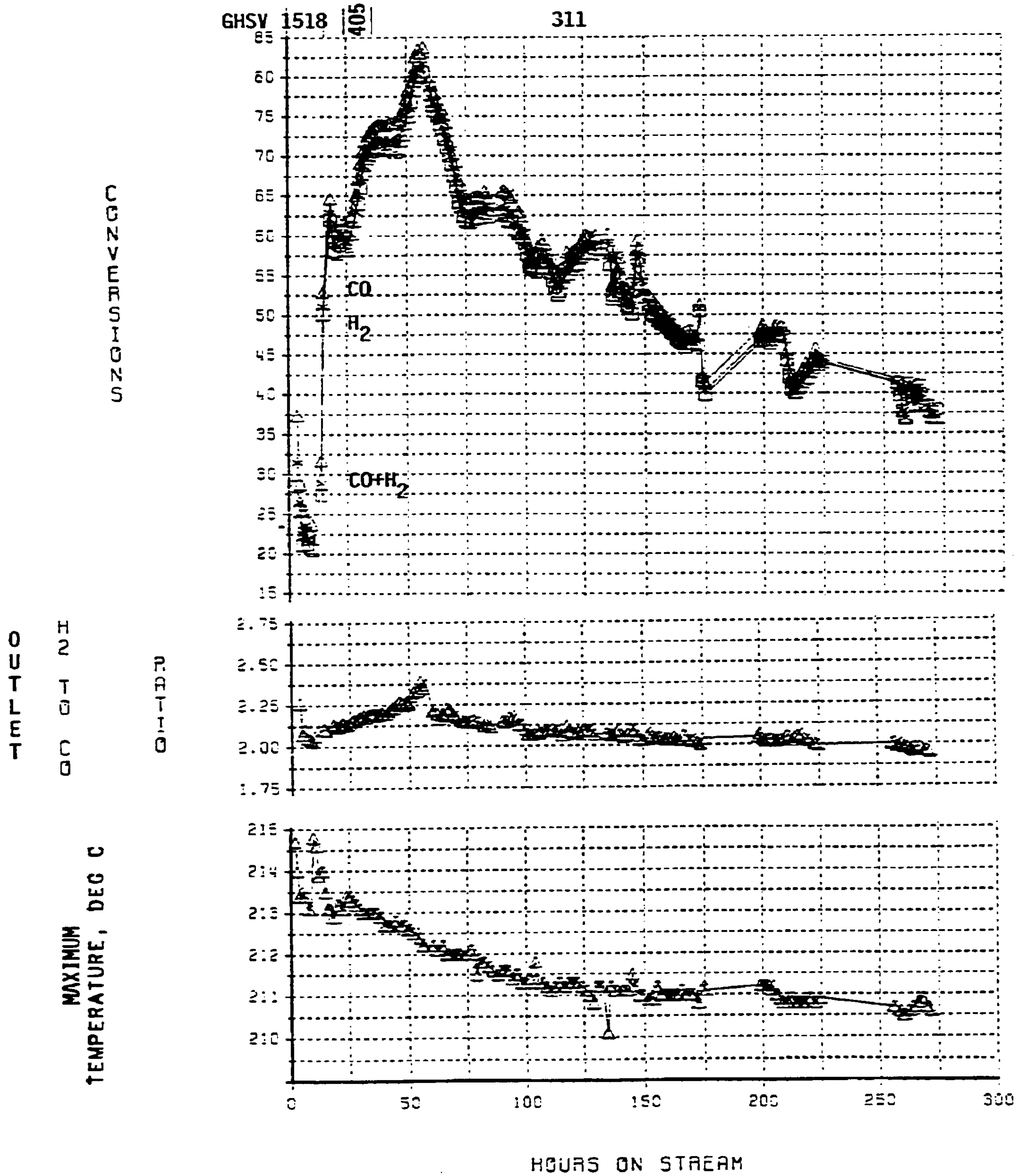


Figure 5-233. Alumina-Titania-Supported Ruthenium Catalyst: Water Gas Shift Activity in Run 39 ($H_2$:CO Feed Ratio = 2.0, 210°C at Inlet, 62 atm)

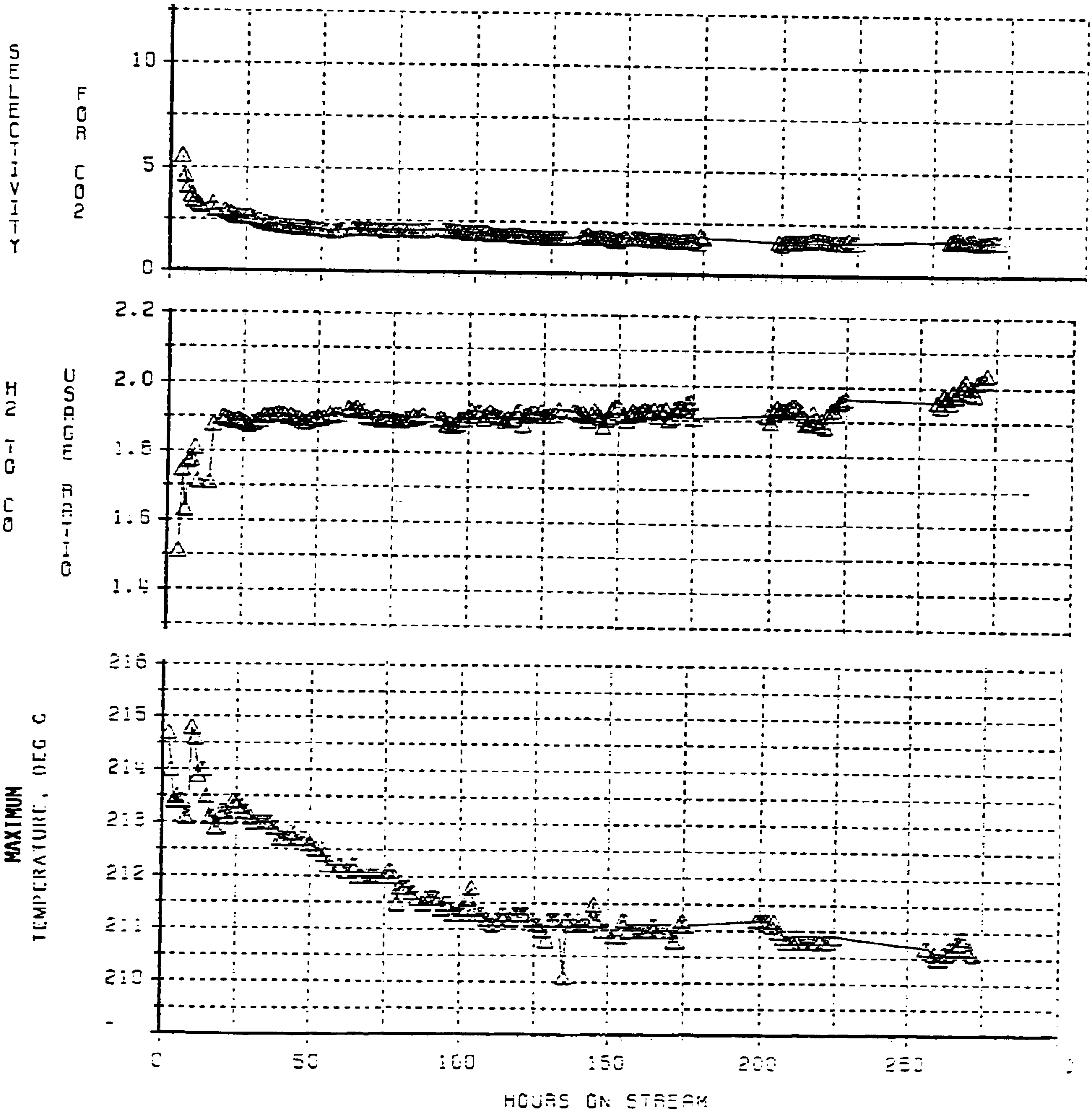


Figure 5-234. Alumina-Titania-Supported Ruthenium Catalyst: $C_1$ and $C_2$ Selectivities in Run 39 ($H_2$:CO Feed Ratio = 2.0, 210°C at Inlet, 62 atm)

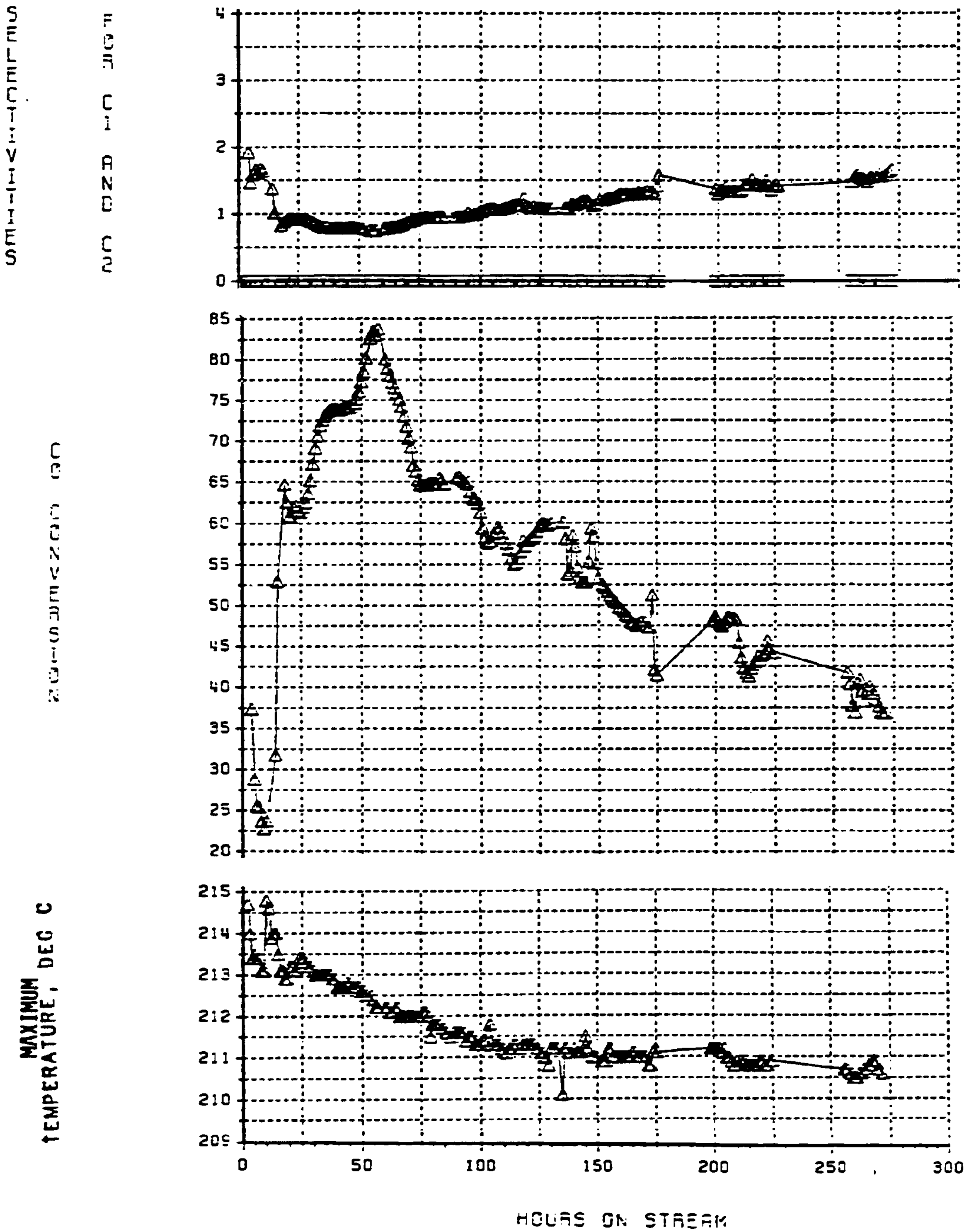


Figure 5-235. Alumina-Titania-Supported Ruthenium Catalyst: $C_3$ and $C_4$ Selectivities in Run 39 ($H_2$:CO Feed Ratio = 2.0, 210°C at Inlet, 62 atm)

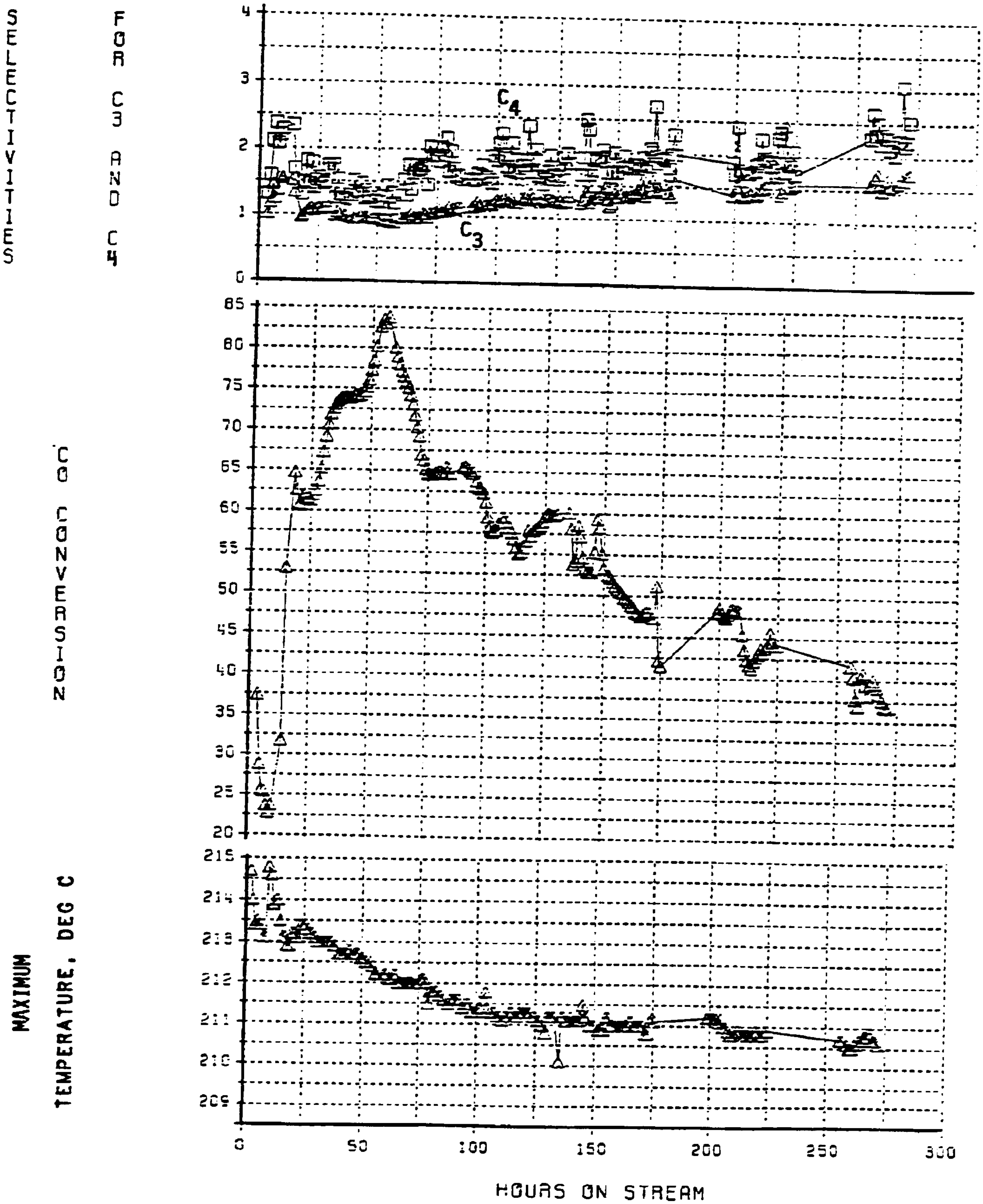


Figure 5-236. Alumina-Titania-Supported Ruthenium Catalyst: Propylene:Propane Ratios in Run 39 ($H_2$:CO Feed Ratio = 2.0, 210°C at Inlet, 62 atm)

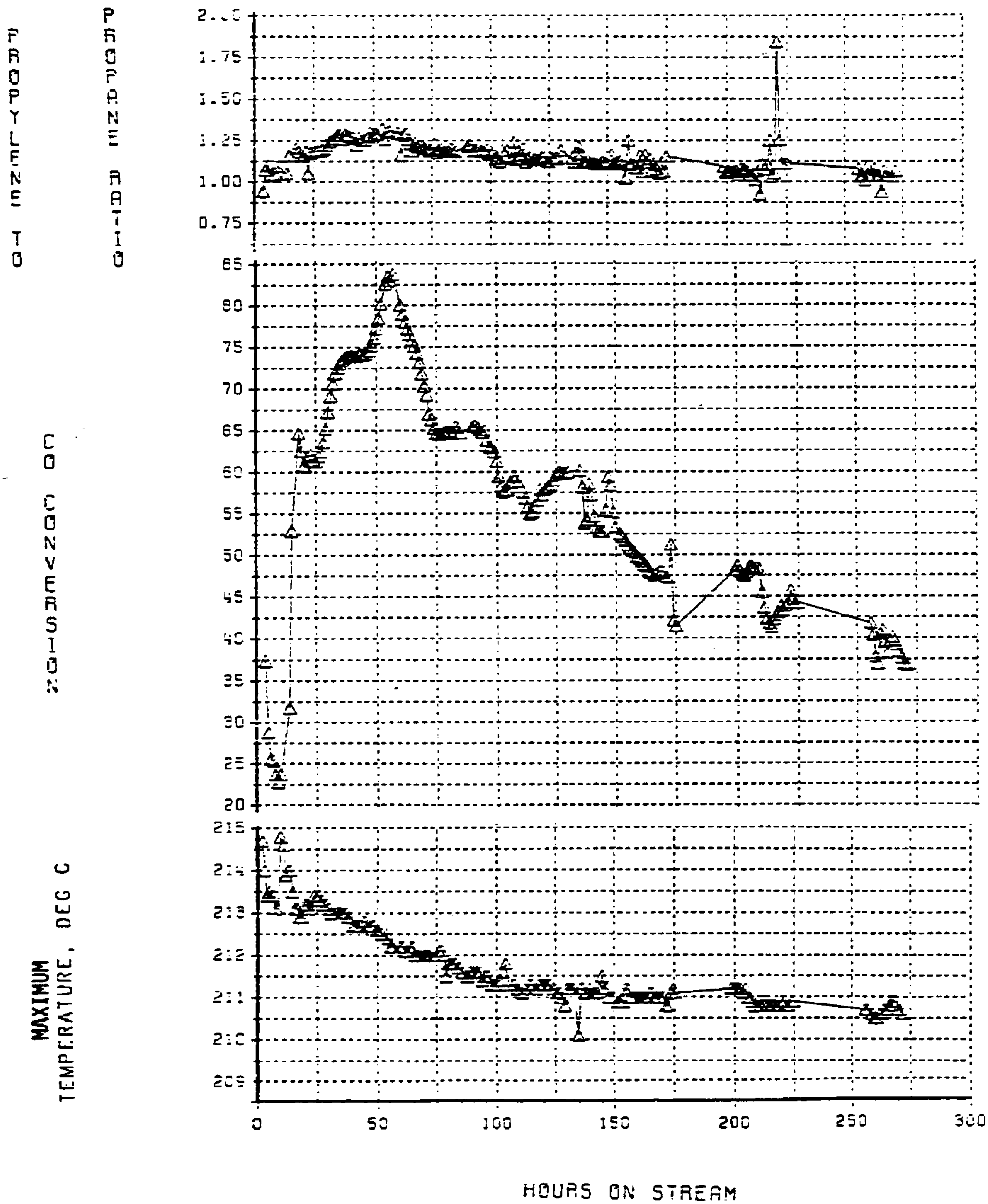


Figure 5-237. Anderson-Schulz-Flory Distribution with Alumina-Titania-Supported Ruthenium Catalyst in Run 39 (Hydrocarbons Only; $C_1$-$C_{44}$)

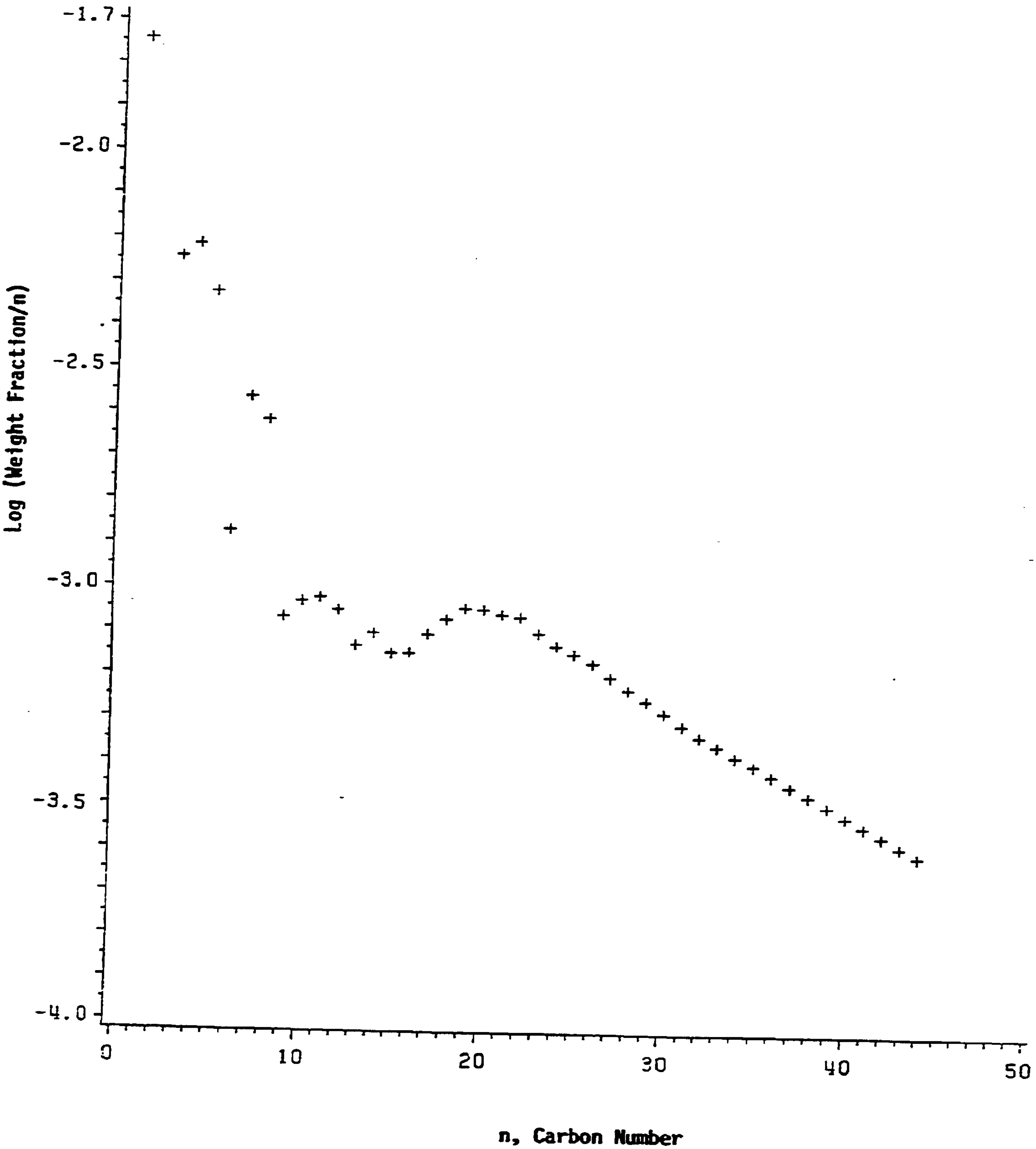
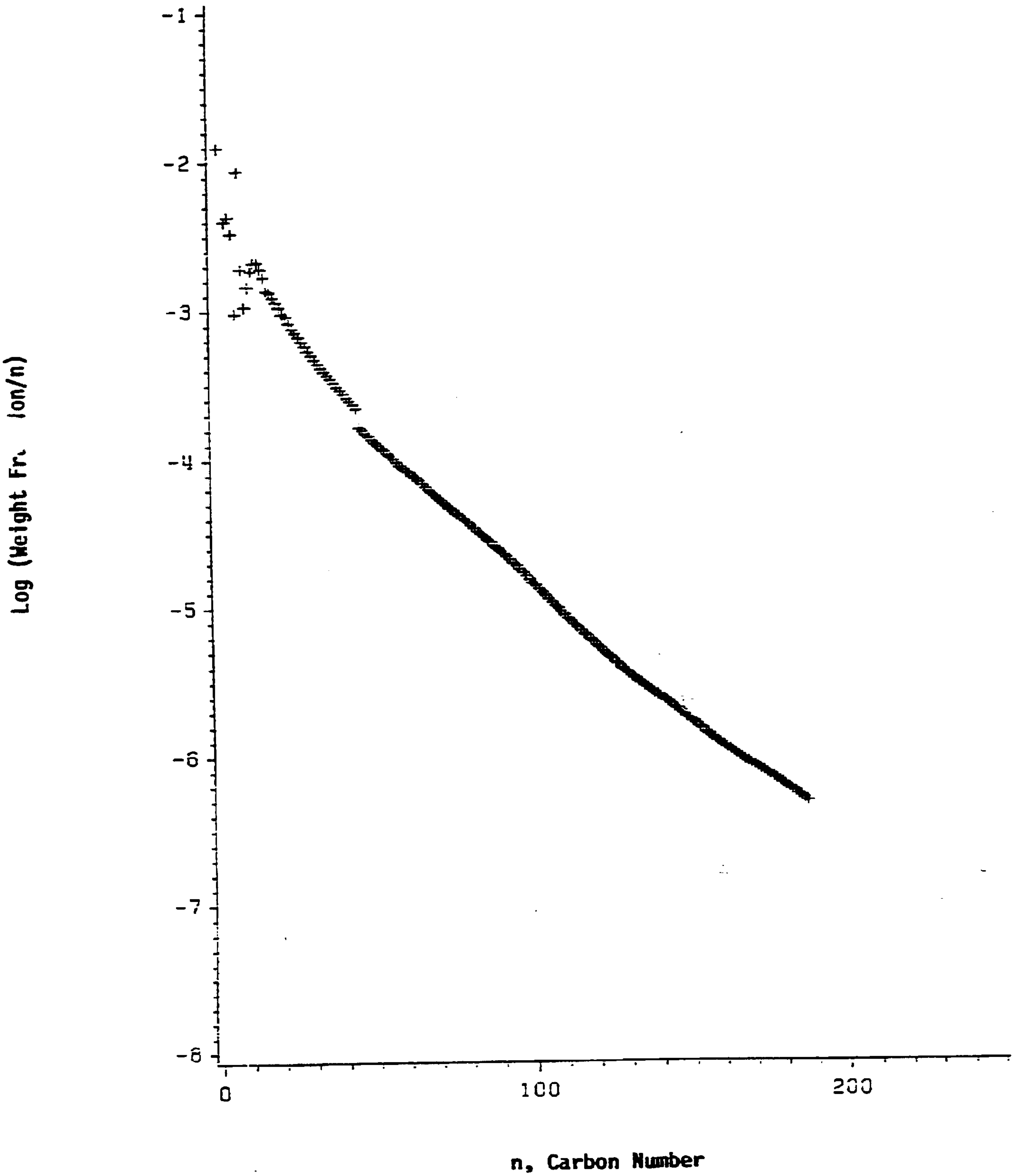


Figure 5-238. Anderson-Schulz-Flory Distribution with Alumina-Titania-Supported Ruthenium Catalyst in Run 39 (Hydrocarbons Only; $C_1$-$C_{250}$)



| Heat to °C | in, hrs | and maintain, hrs |
|---|---|---|
| 100 | 2 | 4 |
| 120 | 2 | 4 |
| 140 | 2 | 4 |
| 150 | 1 | 4 |
| 160 | 1 | 4 |
| 170 | 1 | 4 |
| 180 | 1 | 4 |
| 190 | 1 | 4 |
| 200 | 1 | 4 |
| 210 | 1 | 4 |

The results obtained in Run 41 are summarized in Figures 5-239 through 5-243. The reaction temperature was reached after 53 hours on stream. The gas hourly space velocity was adjusted to 540 $hr^{-1}$ at 40 hours on stream and finally to 205 $hr^{-1}$ at 64 hours. The CO conversion never exceeded 65% during the run and declined to 42% by 175 hours on stream (Figure 5-239). It, now, appears that, relative to Run 39, the start-up procedure used in Run 41 had an adverse effect on catalytic stability.

The initial part of the start-up procedure used for Run 42 was similar to that used in Run 41, except the catalyst temperature was raised to 210°C within 1 hour instead of 53 hours. The results obtained in Run 42 are summarized in Figures 5-244 through 5-248. High conversion was achieved initially; however the catalyst rapidly deactivated. The gas hourly space velocity was then lowered from 490 $hr^{-1}$ to 360 $hr^{-1}$ at 29 hours or stream in order to achieve a CO conversion level of about 85%. The catalyst conversions again continued to decrease, however, this time at a slower rate.

Figure 5-239. Alumina-Titania-Supported Ruthenium Catalyst 4966-124: Conversions in Run 41 ($H_2$:CO Feed Ratio = 2.0, 210°C at Inlet, 62 atm)

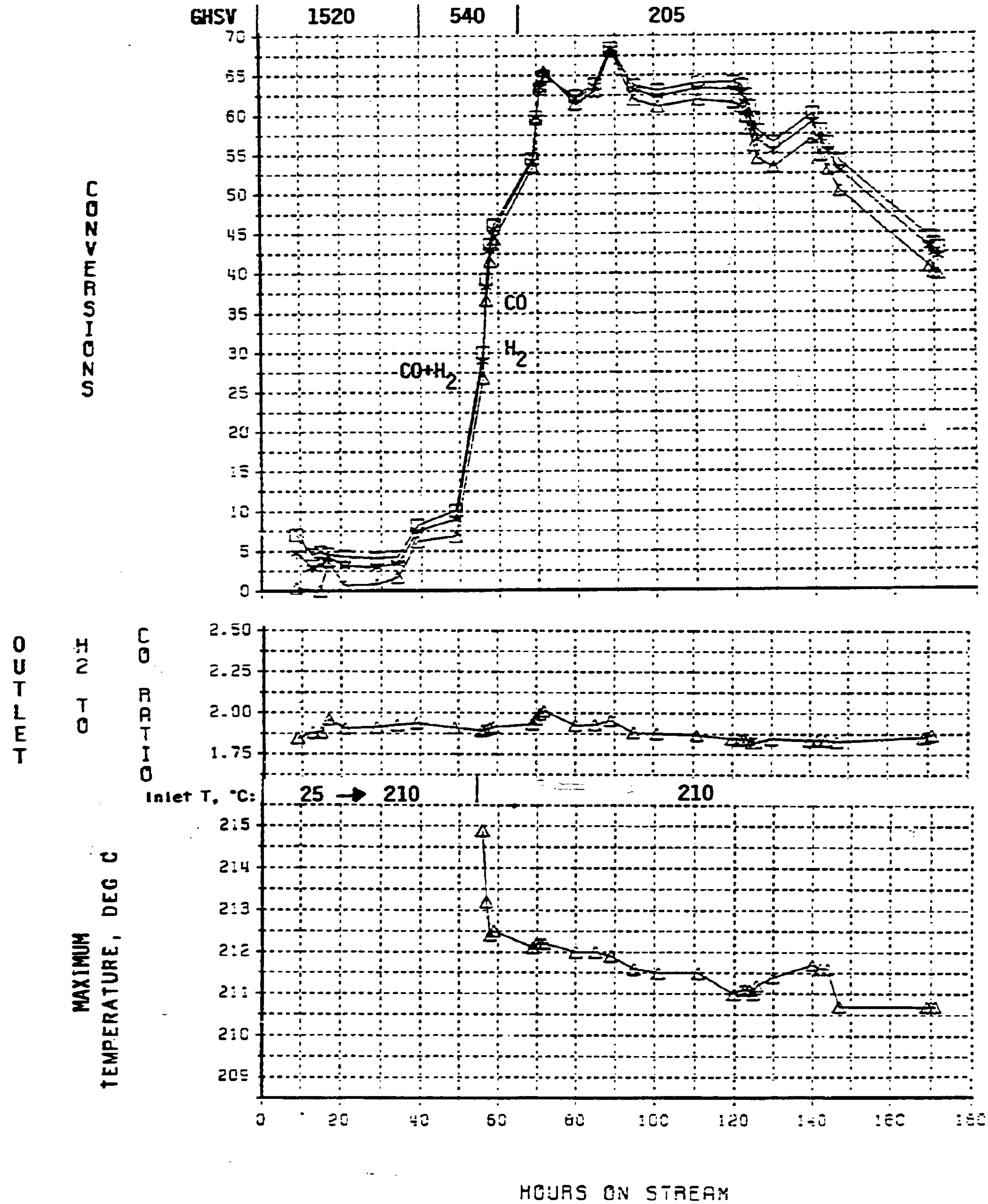


Figure 5-240. Alumina-Titania-Supported Ruthenium Catalyst 4966-124;Water Gas Shift Activity in Run 41 ($H_2$:CO Feed Ratio = 2.0, 210°C at Inlet, 62 atm)

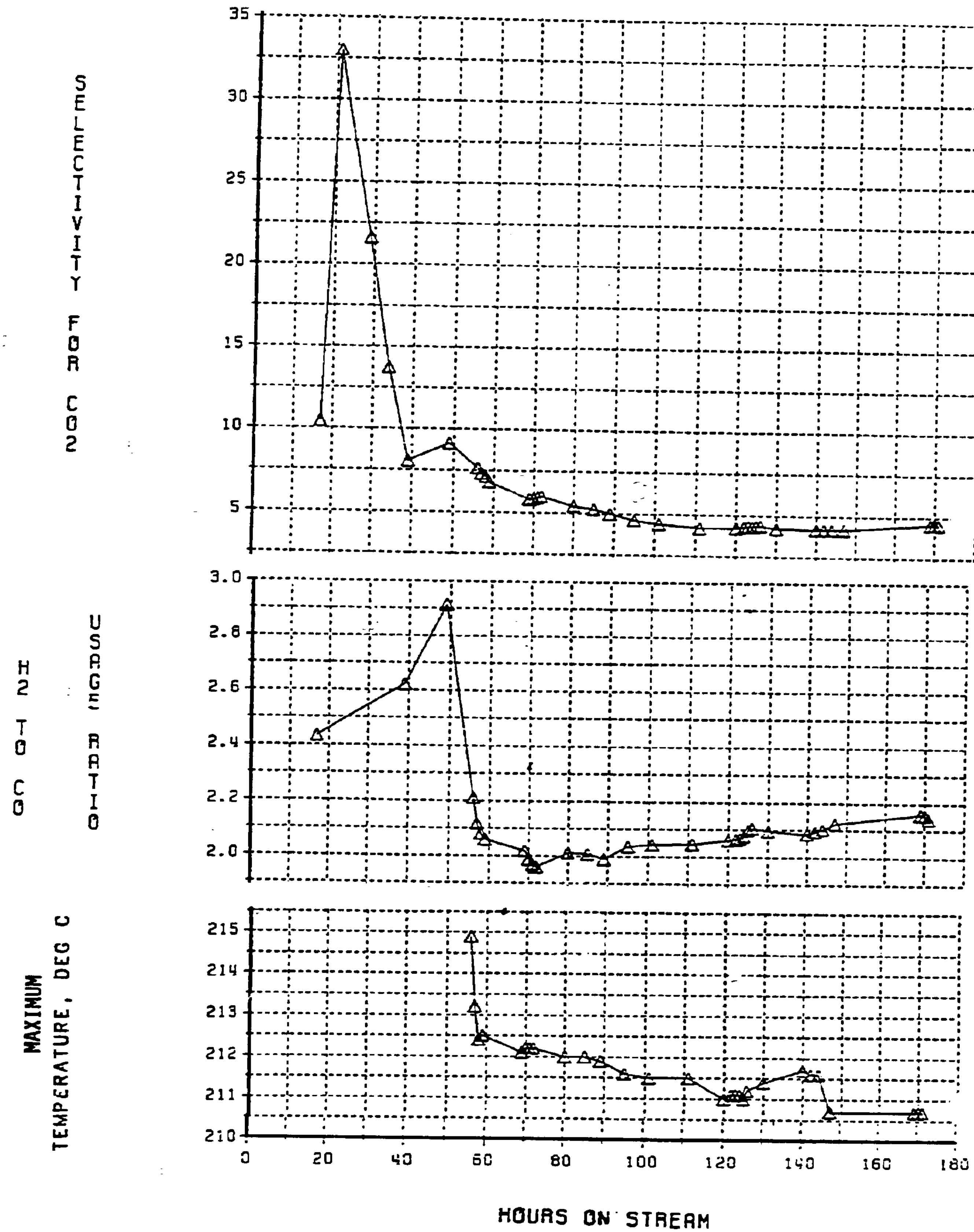


Figure 5-241. Alumina-Titania-Supported Ruthenium Catalyst 4966-124: $C_1$ and $C_2$ Selectivities in Run 41 ($H_2$:CO Feed Ratio = 2.0, 210°C at Inlet, 62 atm)

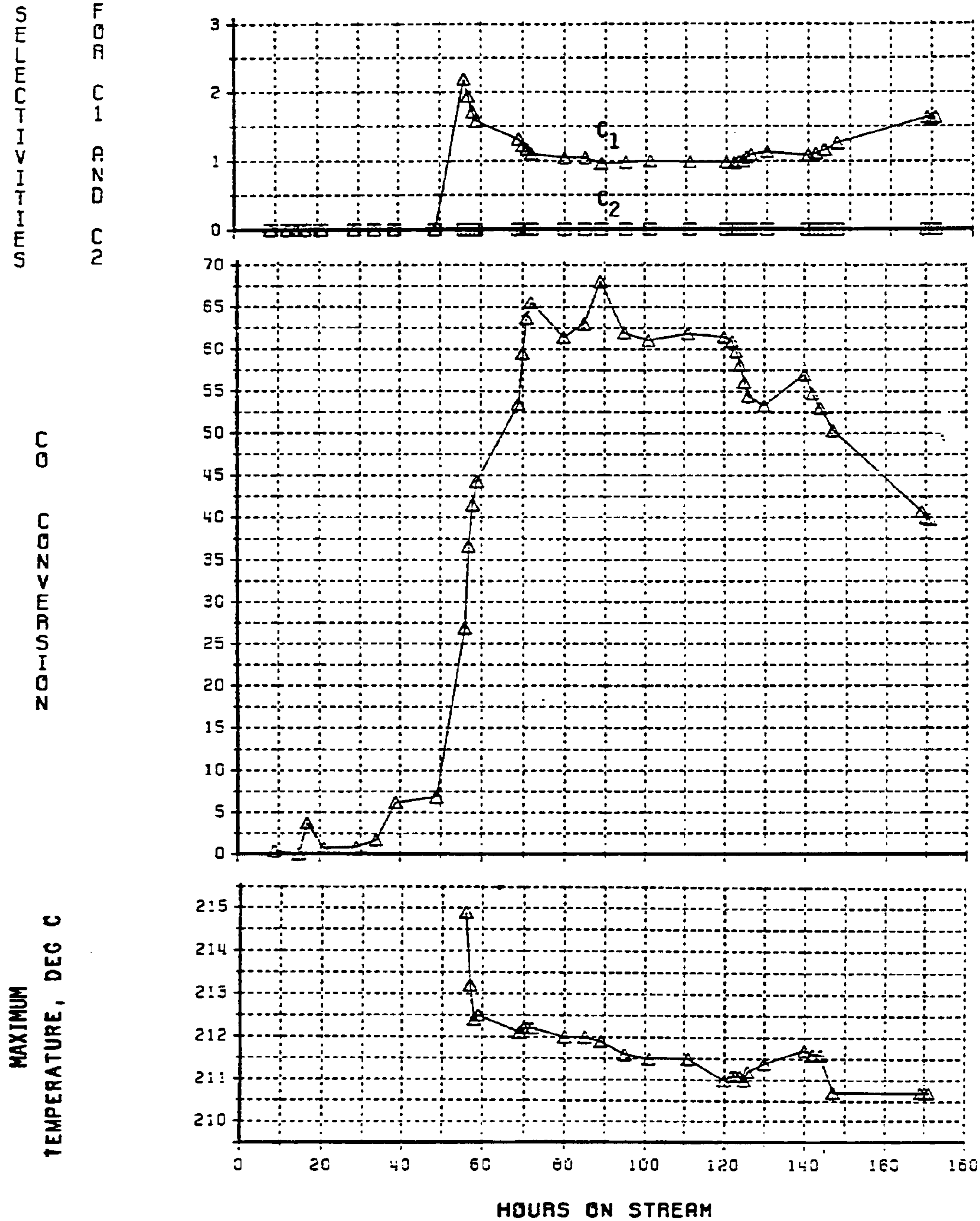


Figure 5-242. Alumina-Titania-Supported Ruthenium Catalyst 4966-124: $C_3$ and $C_4$ Selectivities in Run 41 ($H_2$:CO Feed Ratio = 2.0, 210°C at Inlet, 62 atm)

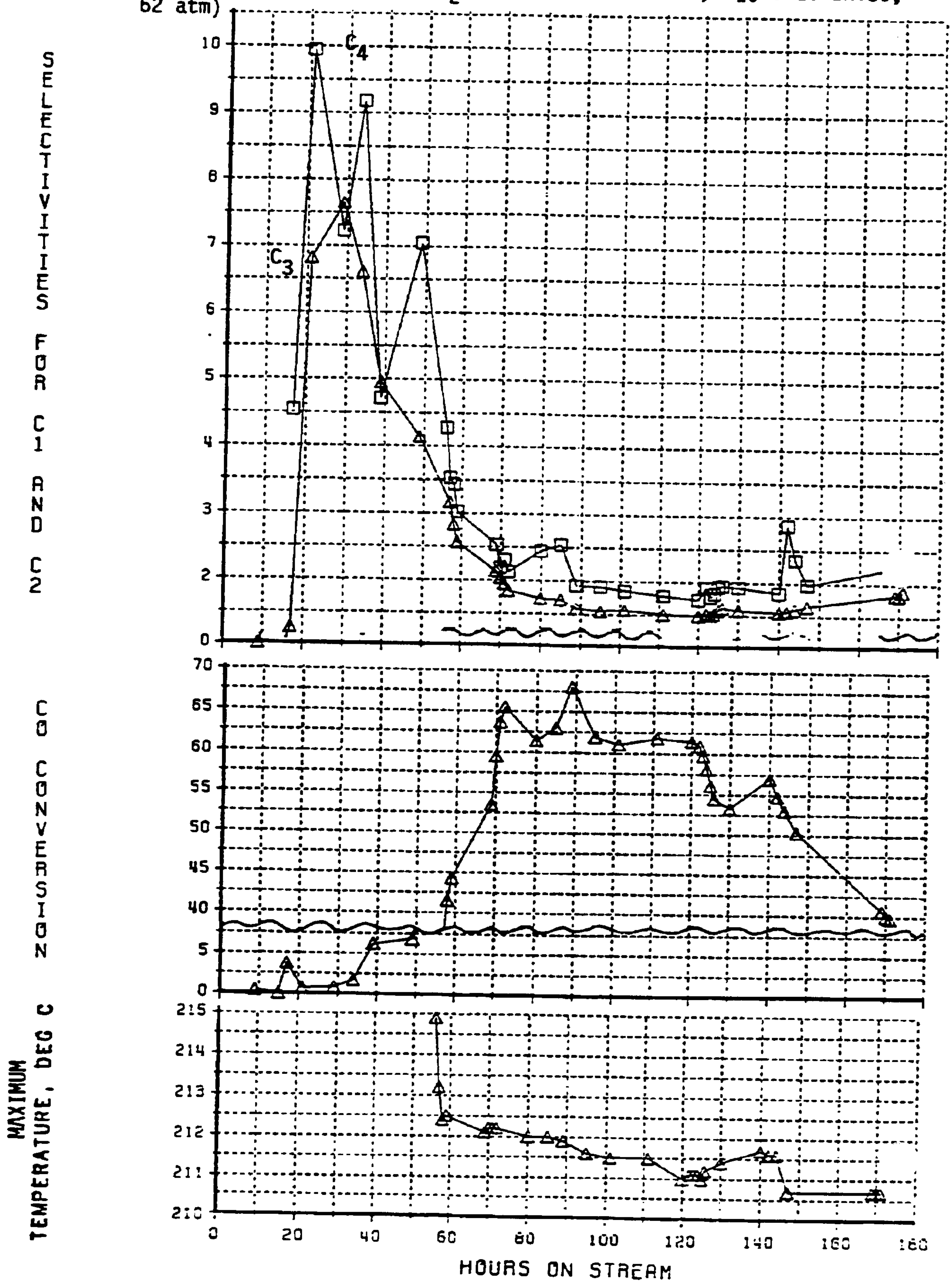


Figure 5-243. Alumina-Titania-Supported Ruthenium Catalyst 4966-124: Propylene: Propane Ratios in Run 41 ($H_2$:CO Feed Ratio = 2.0, 210°C at Inlet, 62 atm)

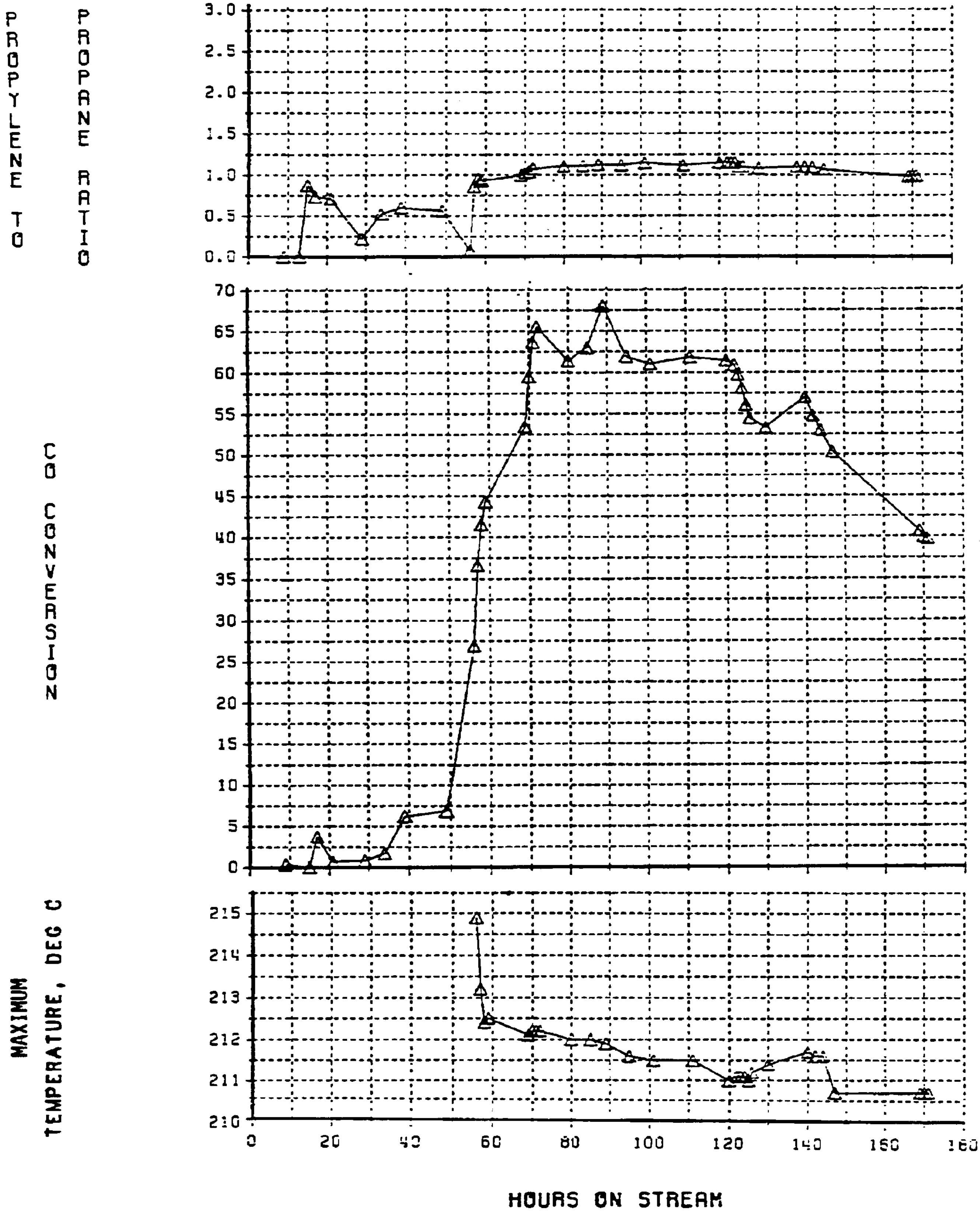


Figure 5-244. Alumina-Titania-Supported Ruthenium Catalyst 4966-124: Conversions in Run 42 ($H_2$:CO Feed Ratio = 2.0, 210°C at Inlet, 62 atm)

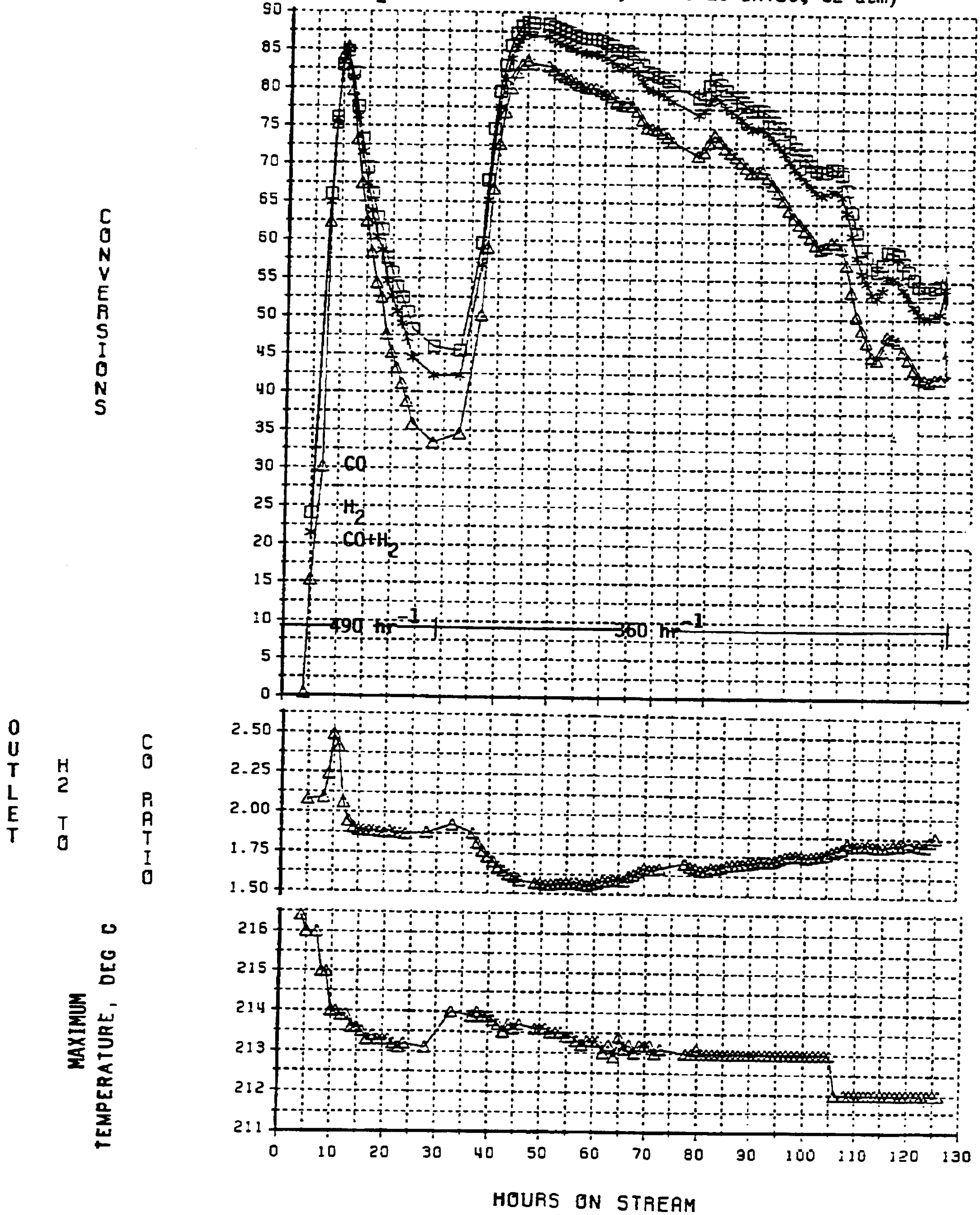


Figure 5-245. Alumina-Titania-Supported Ruthenium Catalyst 4966-124: Water Gas Shift Activity in Run 42 ($H_2$:CO Feed Ratio = 2.0, 210°C at Inlet, 62 atm)

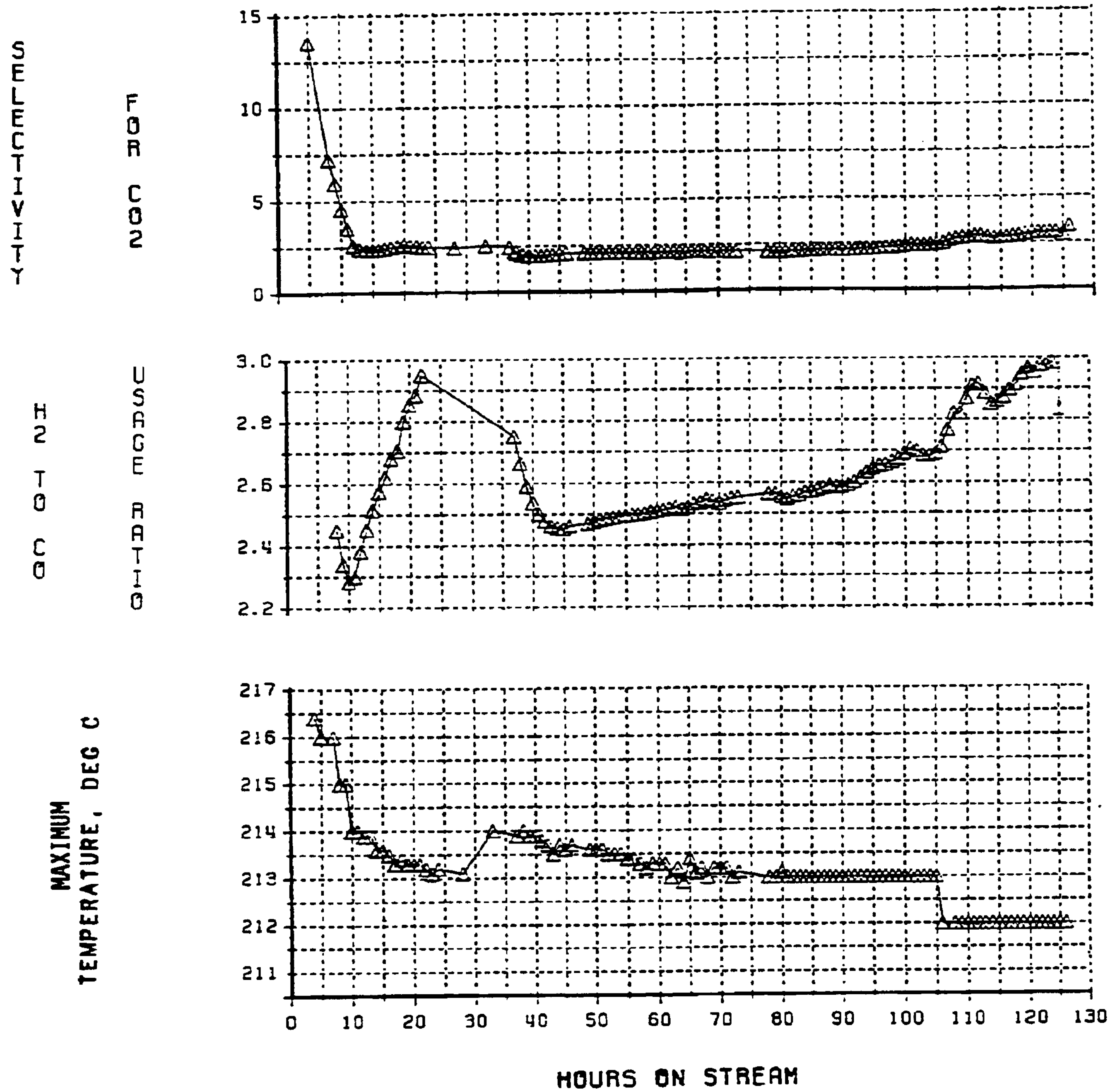


Figure 5-246. Alumina-Titania-Supported Ruthenium Catalyst 4966-124:$C_1$ and $C_2$ Selectivities in Run 42 ($H_2$:CO Feed Ratio = 2.0, 210°C at Inlet, 62 atm)

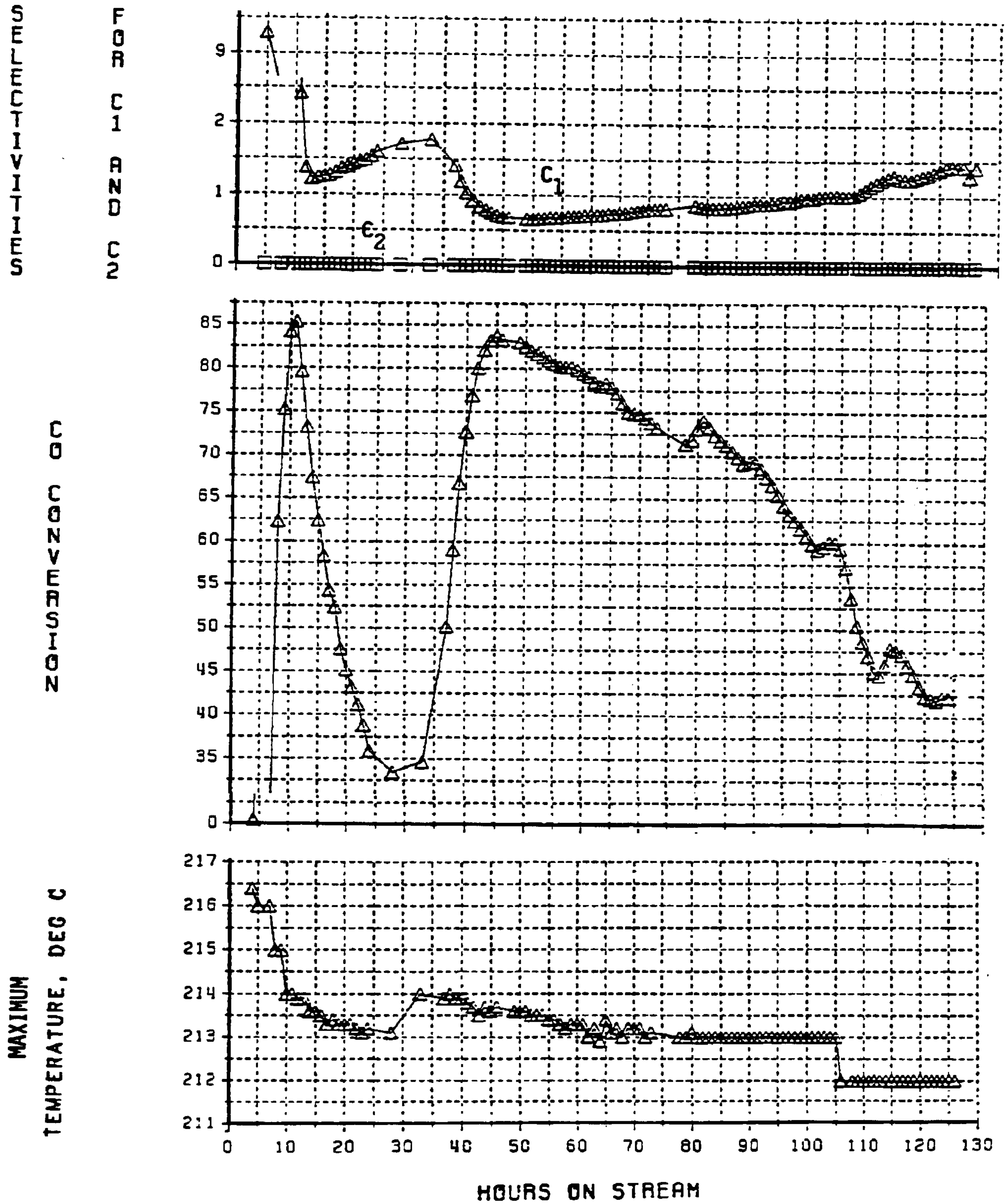


Figure 5-247. Alumina-Titania-Supported Ruthenium Catalyst 4966-124:$C_3$ and $C_4$ Selectivities in Run 42 ($H_2$:CO Feed Ratio = 2.0, 210°C at Inlet, 62 atm)

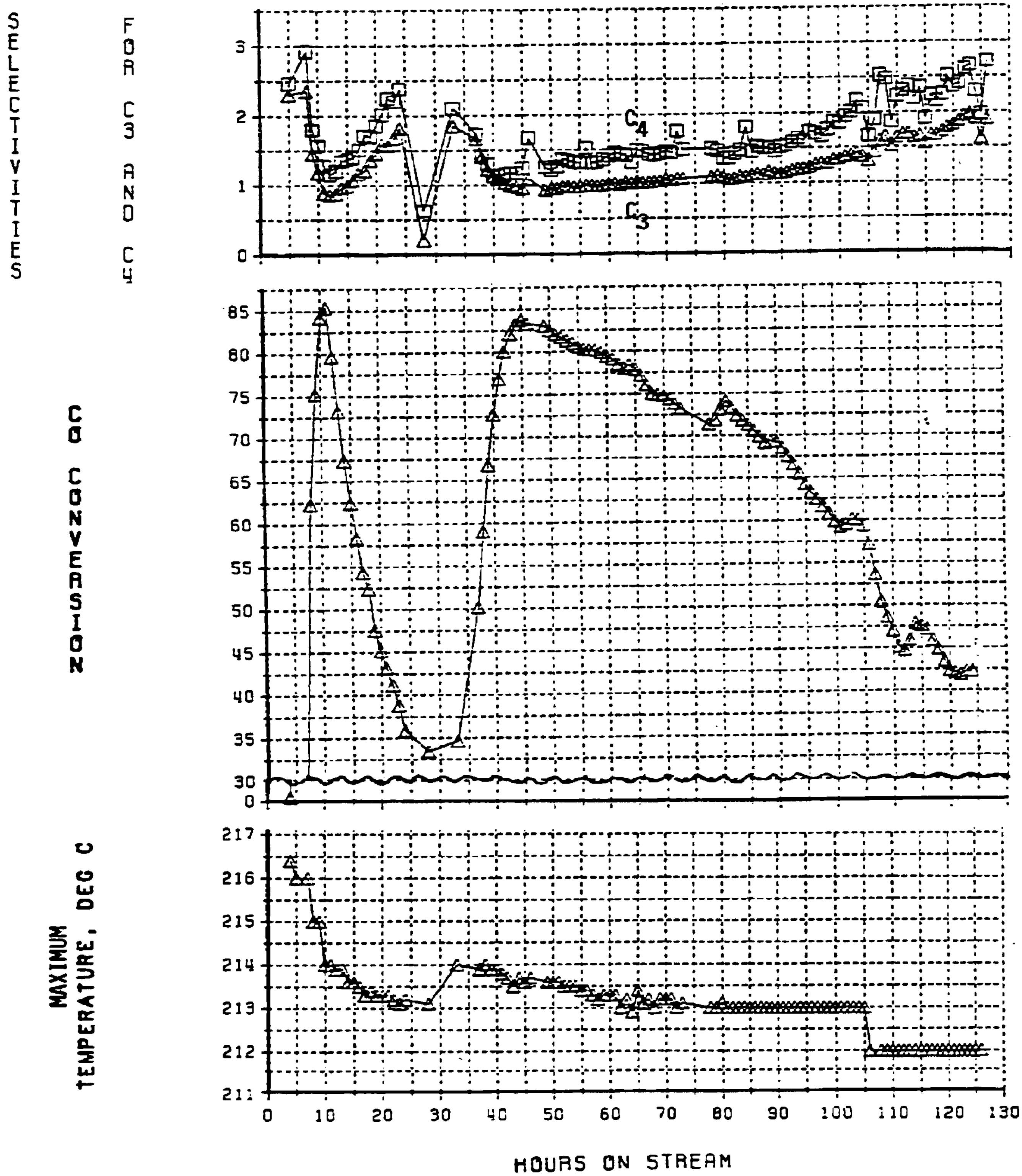
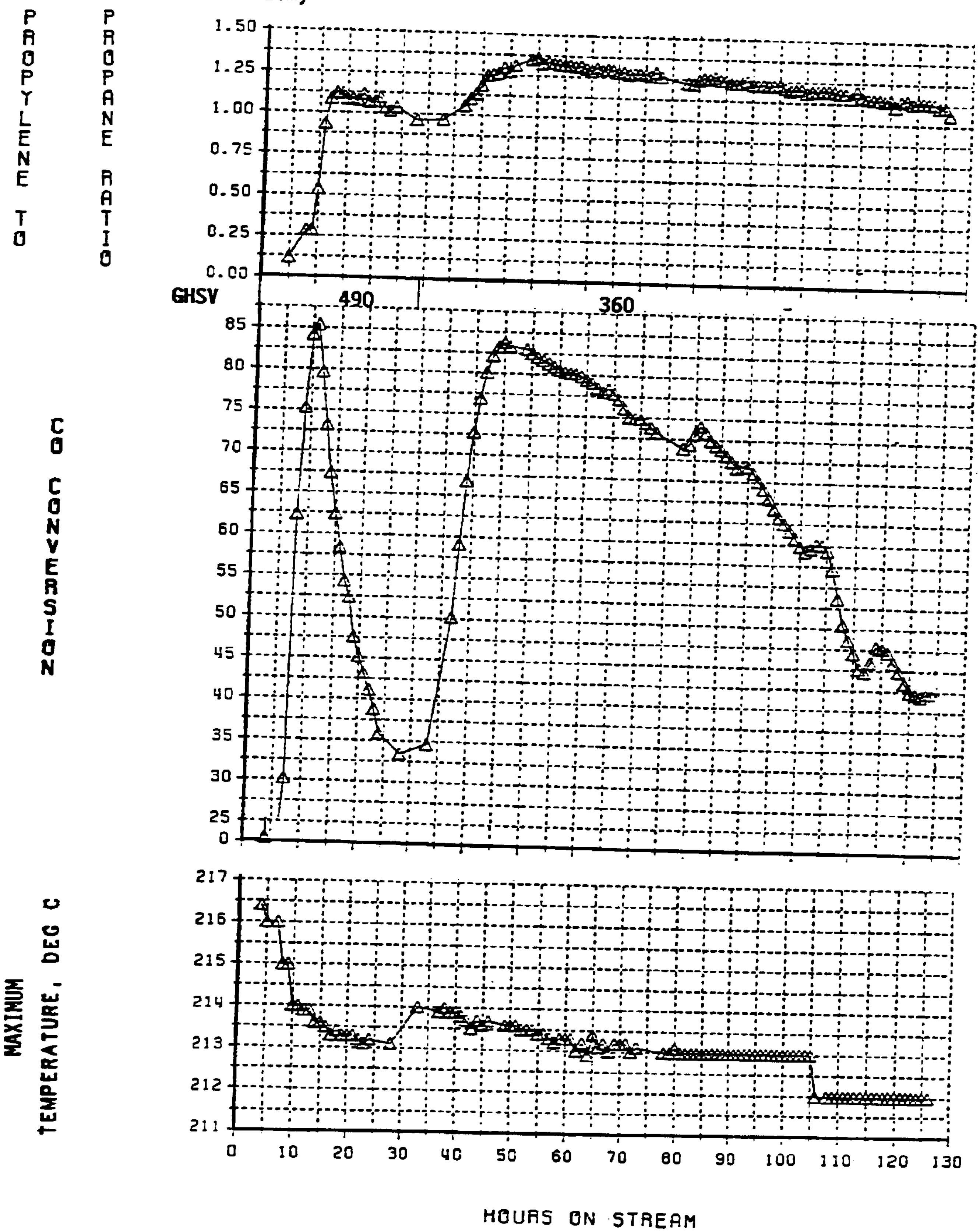


Figure 5-248. Alumina-Titania-Supported Ruthenium Catalyst 4966-124:Propylene: Propane Ratios in Run 42 ($H_2$:CO Feed Ratio = 2.0, 210°C at Inlet, 62 atm)



The activity *vs*. time on stream performance in Run 42 revealed, in a pronounced manner, a feature that was common to most other ruthenium catalyst tests described so far in this work. The catalysts typically showed, during the first 15 hours, high conversion at high space velocities, but then rapidly deactivated to very low conversion levels in a matter of hours. The deactivation rates were significantly slower when space velocities were adjusted to raise the conversion levels after the initial rapid deactivation periods. In an attempt to lower the catalyst's initial activity and prevent the initial rapid deactivation the reduced Catalyst 4966-124 was recalcined under air at the same temperature that was used for the initial calcination before being tested in Run 43. The start-up procedure in Run 43 was, otherwise, similar to that in Run 42.

The results obtained in Run 43 are summarized in Figures 5-249 through 5-255. In Run 43, the gas hourly space velocity was lowered from 1518 $hr^{-1}$ to 490 $hr^{-1}$ at 11 hours, and finally to 310 $hr^{-1}$ at 18 hours. Initially in Run 43, the catalyst did not achieve high conversion at high space velocity as it did in Run 42. Nevertheless, the catalyst in Run 43 deactivated in a similar manner to the catalyst in Run 42.

Figure 5-249. Alumina-Titania-Supported Ruthenium Catalyst 4966-124:Conversions in Run 43 ($H_2$:CO Feed Ratio = 2.0, 210°C at Inlet, 62 atm)

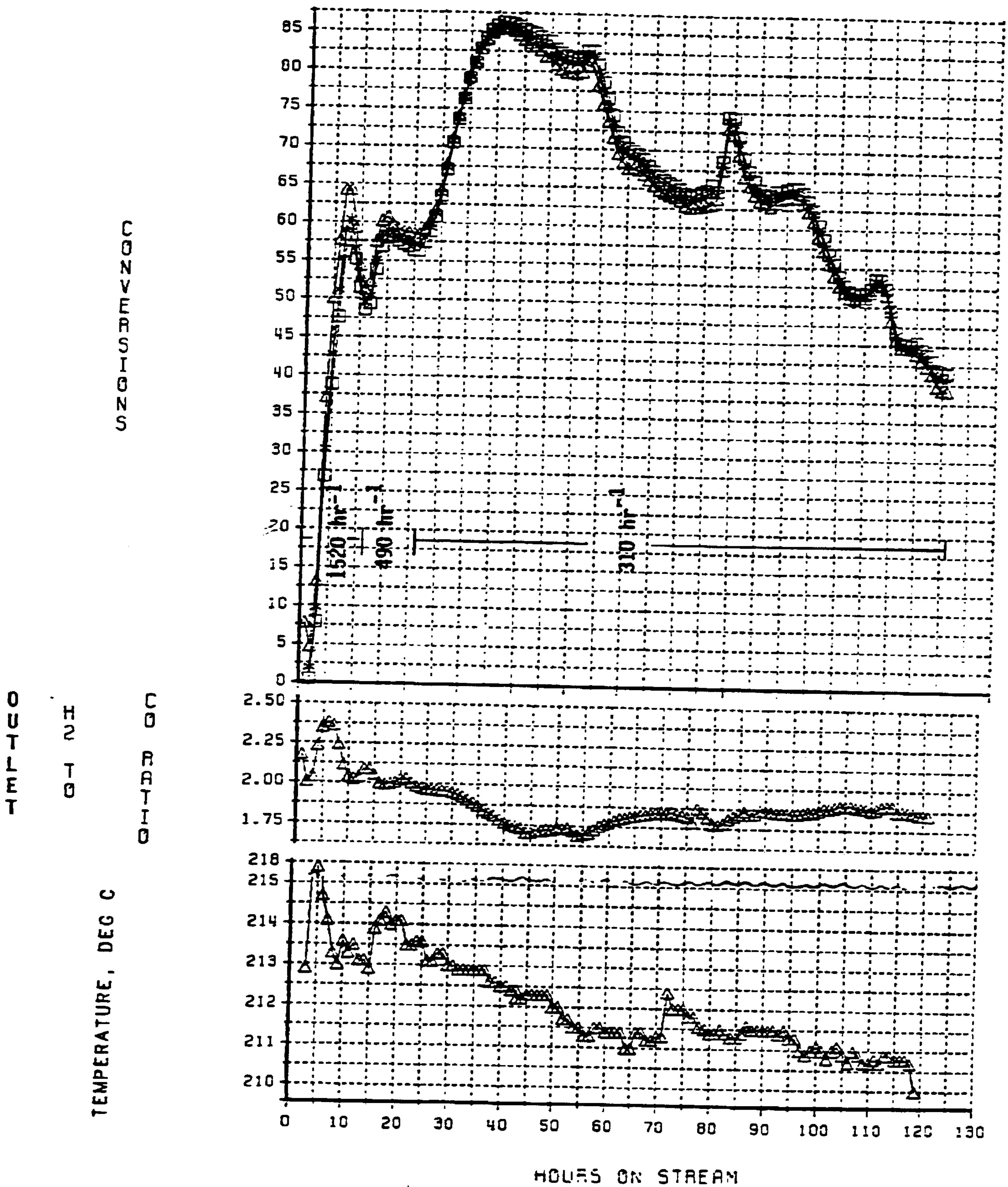


Figure 5-250. Alumina-Titania-Supported Ruthenium Catalyst 4966-124: Water Gas Shift Activity in Run 43 ($H_2$:CO Feed Ratio = 2.0, 210°C at Inlet, 62 atm)

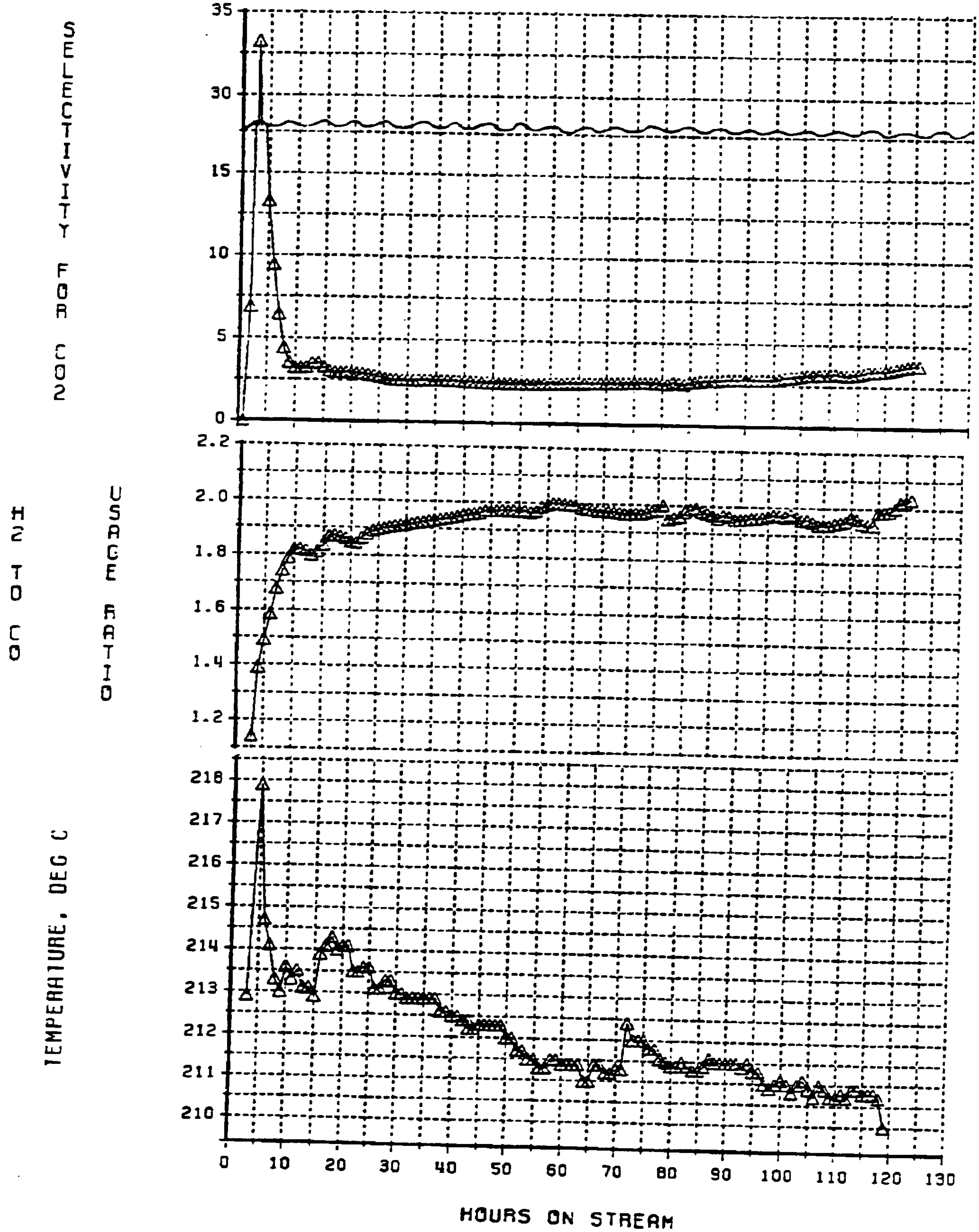


Figure 5-251. Alumina-Titania-Supported Ruthenium Catalyst 4966-124: $C_1$ and $C_2$ Selectivities in Run 43 ($H_2$:CO Feed Ratio = 2.0, 210°C at Inlet, 62 atm)

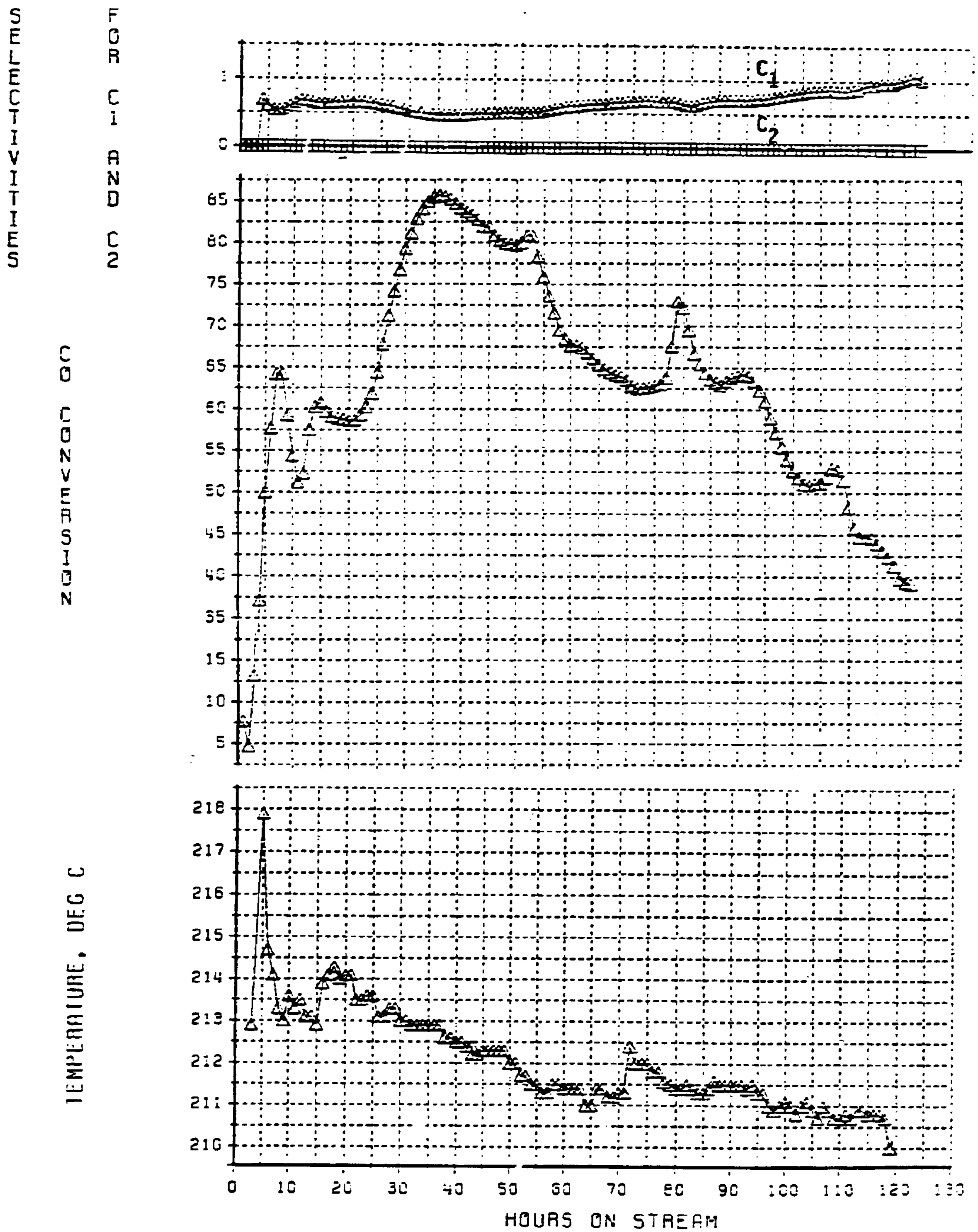


Figure 5-252. Alumina-Titania-Supported Ruthenium Catalyst 4966-124:$C_3$ and C
Selectivities in Run 43 ($H_2$:CO Feed Ratio = 2.0, 210°C at Inle
62 atm)

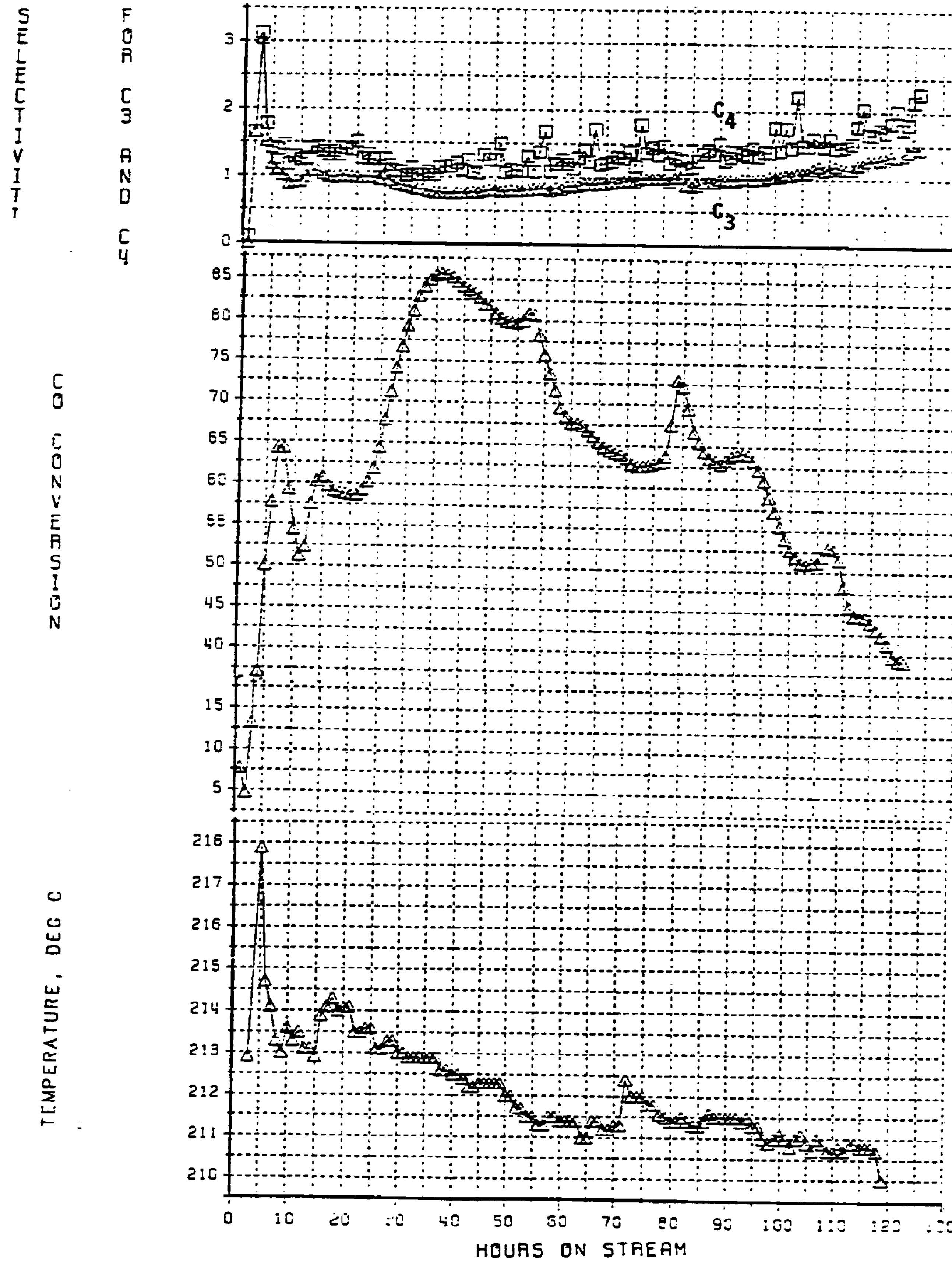


Figure 5-253. Alumina-Titania-Supported Ruthenium Catalyst 4966-124: Propylene to Propane Ratios in Run 43 ($H_2$:CO Feed Ratio = 2.0, 210°C at Inlet, 62 atm)

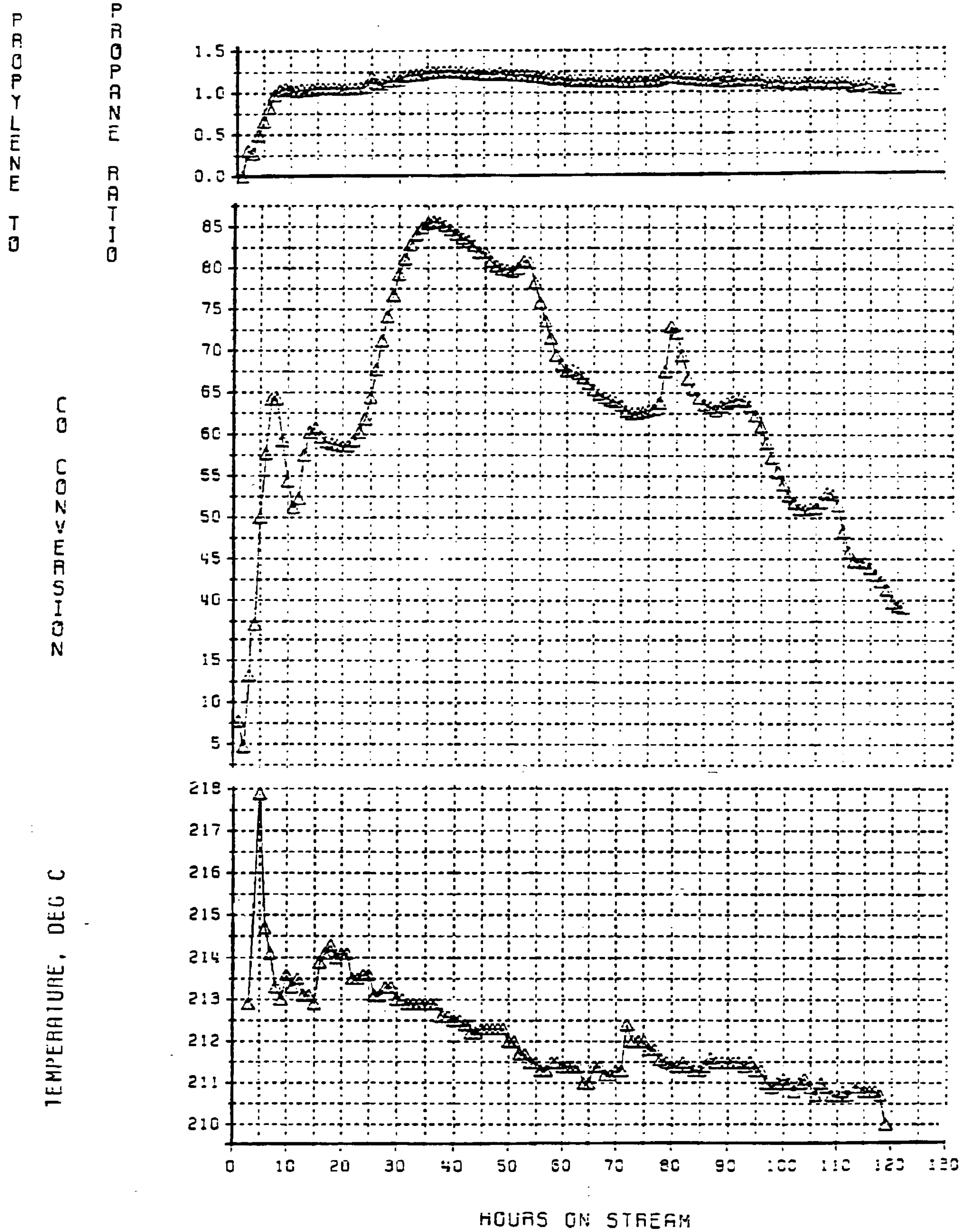


Figure 5-254. Light Hydrocarbon Selectivities with the Alumina-Titania-Supported Ruthenium Catalyst in Run 43 ($H_2$:CO Feed Ratio = 2.0, 210°C at Inlet, 62 atm)

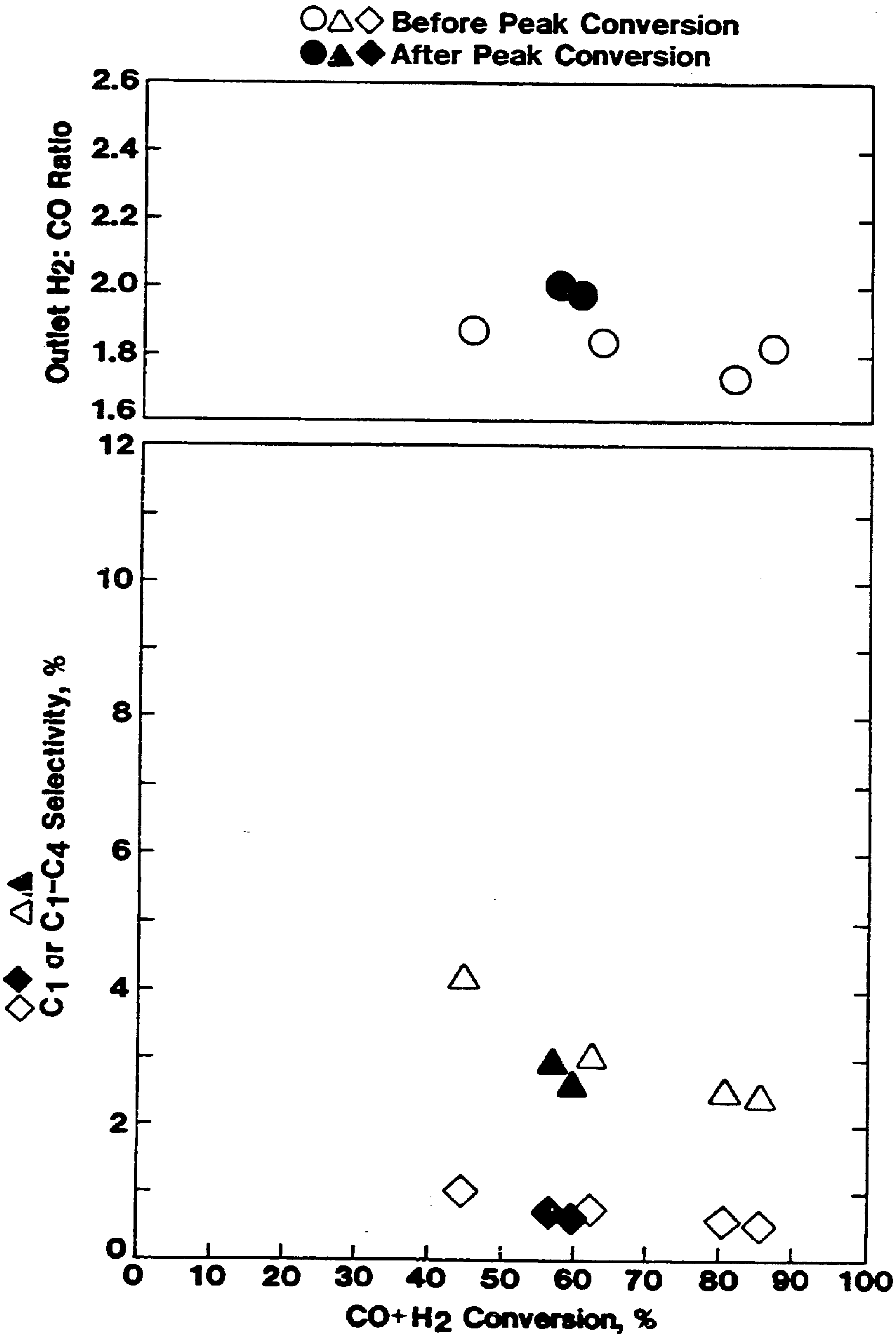


Figure 5-255

**ANDERSON-SCHULZ-FLORY-TYPE DISTRIBUTION FOR $Ru/Al_2O_3$-$TiO_2$**

210°C, 900 psig, $2H_2$:1CO feed, 65% CO + $H_2$ Conversion