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TECHNICAL PROGRESS REPORT

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ABSTRACT

A new ruthenium modifier has been identified which improves the catalyst's stability. The modified catalyst with 2.8% Ru achieved 80% conversion at 150 gas hourly space velocity and is expected to have at least 1 year catalyst life with no more than 6.6% C_1-C_4 selectivity. Activity increase is identified to be the future catalyst developmental need. Work during the next quarter will focus on writing the final report for the program.

OBJECTIVE

The objective of this program is to identify developmental needs for a ruthenium Fischer-Tropsch catalyst with significantly lower light ends make relative to Sasol Arge operation (20% C_1-C_4), with 88% CO+H_2 conversion at 663 gas hourly space velocity and with at least 0.3 year catalyst life.

INTRODUCTION

Fischer-Tropsch synthesis products, with current catalyst systems, obey the Anderson-Schulz-Flory polymerization law by which the probability of chain growth is independent of carbon number. This polymerization law imposes strict maxima to the

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selectivity toward desirable liquid fuel products. Accordingly, light olefins have to be oligomerized and waxes have to be hydrocracked in order to increase the overall yield of liquid fuels. Light paraffins are more difficult to upgrade: methane and ethane may be recycled back to a steam reforming unit to make more synthesis gas along with carbon oxides, while propane and butane may be sold as LPG. There is a great incentive to develop catalysts by which the overall yield of liquid fuels will be enhanced.

This program aims at developing a supported ruthenium Fischer-Tropsch catalyst with improved selectivity relative to state-of-the-art precipitated iron catalysts. Performance of supported ruthenium catalysts has been shown to vary with metal particle size [1-5]. While it is generally agreed that, with catalysts prepared on alumina, the turnover frequency increases with increasing ruthenium metal particle size, the effect of ruthenium metal particle size on selectivity has not been clarified. Reverse micelle-derived catalysts with regulated ruthenium particle sizes were used in order to clarify the effects of metal particle size on selectivity in Fischer-Tropsch synthesis. According to the reverse micelle technique that was developed at Allied Signal Engineered Materials Research Center, the ruthenium particle size on the support is determined by the concentration of ruthenium in the water core of the reverse micelle and by the size of the water core. Narrow size distribution of ruthenium particles on the support can be obtained because water cores that are used as precursors for metal particles typically have a narrow size distribution in reverse micelle solutions.

Two approaches for improving catalyst selectivity have been investigated in this program:

The first approach aimed at minimizing the formation of waxes. During the first two years of the program the validity of literature reports of hydrocarbon cutoff of high molecular weight products by the use of small metal particles was investigated. It was determined that cutoff was not effected with an alumina-supported catalyst

having 3 nm average size ruthenium particles. Also a Y-type zeolite-supported catalyst having 1.5 nm average size ruthenium particles and a titania-supported catalyst having smaller than 1.5 nm ruthenium particles did not show cutoff [6].

The second approach aimed at enhancing the overall liquid fuel yield by developing a catalyst with the Anderson-Schulz-Flory distribution of products and with minimal selectivity to light ends. The large amount of wax produced by this catalyst may then be efficiently hydrocracked to liquid fuels with minimal light ends production [6].

Under the second approach, during the second year, several ruthenium catalysts with different size ruthenium particles in the range 0.8 nm to 5 nm were compared. It was determined that CO undergoes three different types of reaction during Fischer-Tropsch synthesis: 1) CO can react with Ru to form ruthenium carbonyl; 2) CO can react with H_2 to make hydrocarbons and H_2O; and 3) CO can react with H_2O to form H_2. Specifically, it was found that ruthenium particles smaller than 4 nm agglomerated on alumina during Fischer-Tropsch synthesis via the formation of the volatile ruthenium carbonyl species, while larger particles were stable. On the other hand, small ruthenium particles were stable on titania and on Y-type zeolite. Larger ruthenium particles on alumina gave higher turnover frequencies for Fischer-Tropsch synthesis. Highly dispersed alumina-supported ruthenium showed water gas shift activity while larger ruthenium particles did not. The ratio of olefinic to paraffinic products and the chain growth probability increased with an increase in metal particle size for alumina-supported ruthenium catalysts [7].

Based on the work done under the second approach, one of the most suitable catalysts was identified as having about 1% ruthenium with mostly 5 nm ruthenium particles on alumina. This catalyst was further evaluated under Arge-type conditions of 225°C, $2H_2$:1CO, 35 atm and at various conversion levels.

The ruthenium catalyst initially possessed one-quarter of the activity (per unit catalyst volume) of the Arge precipitated iron catalyst [8]. It is important, however,

to note that the ruthenium catalyst had an apparent bulk density of 0.3 g/cc, possibly 3-4 times less dense than the Arge catalyst. Accordingly, on a catalyst weight basis the catalyst with 1% Ru seems to have comparable activity relative to the Arge catalyst. Direct comparison of the intrinsic activity between the two catalysts is not currently possible because of the differences in the catalyst particle sizes [6].

Lowest light ends selectivity was obtained at 87% $CO+H_2$ conversion where the selectivity to C_1-C_4 paraffins and olefins was approximately 5 times lower relative to the selectivity reported for the Arge catalyst [6].

The third year of the program aimed at establishing the developmental needs with the most promising ruthenium catalysts identified under the second approach. It was then determined that stability improvement was the major catalyst developmental need. Ruthenium catalysts with different modifiers were evaluated in order to develop a more stable catalyst.

EXPERIMENTAL

In each experiment, 6.5 g reduced catalyst (170-200 mesh) was mixed with 29.6 g alumina powder (170-200 mesh) and loaded into a glass-lined fixed-bed reactor under N_2. The reactor was then pressurized with He to 1200 psig for a pressure test. After a successful pressure test, the reactor was depressured to 0 psig and then pressured up to 900 psig with $2H_2$:1CO ratio feed gas. The temperature was then raised under synthesis gas flow to 208°C. The liquid and solid hydrocarbon products were collected during the test in the product receivers which were kept at low temperature. These products, along with the wax extracted from the catalyst, were analyzed by gel permeation and gas chromatography at the end of the run to determine the carbon number distribution in the C_5-C_{200} range. C_1-C_{10} hydrocarbons, alcohols and aldehydes were analyzed with on-line GC along with CO, CO_2, H_2 and Ar. Argon was used as an internal standard to determine conversions and light hydrocarbon selectivities during the test according to the following expressions:

$$\text{CO Conversion, \% } = \frac{\left[\dfrac{CO}{Ar}\right]_{feed} - \left[\dfrac{CO}{Ar}\right]_{product}}{\left[\dfrac{CO}{Ar}\right]_{feed}} \times 100$$

The $CO+H_2$ conversion was calculated in a similar manner.

$$C_n \text{ Selectivity, \% } = \frac{\left[\dfrac{C_n}{Ar}\right]_{product} \times n}{\left[\dfrac{CO}{Ar}\right]_{feed} - \left[\dfrac{CO}{Ar}\right]_{product}} \times 100$$

where n is the number of carbon atoms in one molecule of hydrocarbon C_n. The calculation of selectivity of CO to CO_2 is similar to the calculation of selectivity to methane for which $n = 1$.

RESULTS AND DISCUSSION

A micelle-derived 2.8% Ru on Al_2O_3 catalyst had a narrow size distribution of ruthenium particles in the 4-6 nm size range. This catalyst was tested at an inlet temperature of 208°C, 900 psig with a $2H_2:1CO$ feed gas at a CO conversion level of about 75-85% in a fixed bed reactor for 700 hours. This catalyst was not stable and accordingly, the gas hourly space velocity was lowered from an initial value of 500 hr^{-1} to 147 hr^{-1} during the first 530 hours on stream, after which no further space velocity change was made. The inlet temperature was increased to 210°C between 700 hours and 825 hours on stream. The CO conversion was about 72% at the end of the test (Figure 1).

In an attempt to improve stability, the micelle technique was used to prepare a modified ruthenium catalyst with the same ruthenium level as the ruthenium-only-catalyst. The first modifier resulted in a catalyst with no activity. The second modified-catalyst, while consisting mostly of 4-6 nm ruthenium particles, had also some 10-20% of the ruthenium in the 3-4 nm and 6-40 nm size range (Figure 2). This catalyst was tested under the same conditions as the ruthenium-only-catalyst. The initial activity of this catalyst was lower. The catalyst showed deactivation during the first 20 hours from about 60% to about 30% CO conversion. The gas hourly space velocity was lowered from 500 hr^{-1} to 125 hr^{-1} during the first 20 hours in order to achieve high conversion. The CO conversion increased to approximately 90%, followed by a decrease. The catalyst activity then gradually increased to achieve a CO conversion level of about 85% at 375 hours on stream, after which the gas hourly space velocity was gradually increased to 150 hr^{-1} by 595 hours to prevent the conversion from exceeding 85%. The catalyst temperature was increased by 2°C after 700 hours on stream in order to compensate for some of the space velocity increase which was apparently done too rapidly (Figure 3).

The activities of the ruthenium catalysts with and without the modifier as a function of time are compared in Figure 4 which shows the global reaction rates, moles $CO+H_2$ converted/hour-moles ruthenium, with the two catalysts during the first 700 hours on stream. The results indicate that the modifier attenuated ruthenium's initial activity by about 50%. The catalyst without the modifier deactivated at a rate which decreased with time on stream. The modified catalyst lost activity during the first 20 hours, after which it gradually gained activity. After 525 hours on stream the modified catalyst's activity was equal to or better than the catalyst without the modifier.

The methane selectivities of the two catalysts are compared in Figure 5. During the first 500 hours the methane selectivity with the modified catalyst was higher than the catalyst without the modifier. After 500 hours the two catalysts showed

essentially the same methane selectivity, between 1.3% and 1.4%. The methane selectivity increase with both catalysts, after 700 hours on stream, is caused by 2°C temperature increase in the catalyst bed. The unmodified catalyst has 10% lower conversion at the end of the run relative to the modified catalyst. The lower conversion accounts for the unmodified catalyst's higher methane selectivity (0.4% higher).

Other selectivity data with the modified catalyst are summarized in Figures 6 and 7. After 500 hours line-out at 208°C inlet temperature and 80% conversion there was essentially no C_2 formation ($\leq 0.2\%$), while the C_3 and C_4 selectivities were 1.3 and 1.9%, respectively, giving an overall C_1-C_4 selectivity of no more than 4.8%. The H_2:CO usage and feed ratios were equal since there was essentially no water gas shift activity.

Since the modified catalyst did not show any sign of deactivation at 208°C and 80% conversion after the initial activity loss during the first 20 hours, the severity of operation was increased during the second part of the test in order to determine the catalytic stability (Figure 8). Between 825 and 933 hours the temperature and space velocity were increased in parallel from 210°C to 224°C and from 150 hr^{-1} to 205 hr^{-1}, respectively, in order to maintain about 80% conversion. During the temperature increase period some deactivation occurred. Assuming an apparent activation energy of about 25 kcal/mole, a higher space velocity increase would have been expected had the catalyst not deactivated between 825 and 933 hours on stream. We believe deactivation occurred possibly because a conversion level of 80% was too severe a condition at the high temperature. The catalyst deactivated to 70% conversion during the following 200 hours, after which it maintained constant conversion for the next 400 hours. The conversion decreased to 60% between 1542 and 1574 hours and showed no further activity loss until 1618 hours. Between 1618 and 1700 hours, which is the end of the run, there were operational problems which caused difficulties in interpreting the data. From the activity loss between 933 hours on stream to 1542 hours, a deactivation rate of about

0.016%/hour can be calculated at 224°C.

There are not presently enough data for calculating the life of the modified-ruthenium catalyst. Since there was no apparent deactivation at 208°C, half of the deactivation rate at 224°C was roughly estimated to be an upper limit to the average deactivation rate between 208°C and 224°C. A commercial run with beginning and end of run temperatures of 208°C and 224°C, respectively, would then result in about 1 year catalyst life at 70-80% CO conversion, given an apparent activation energy of about 25 kcal/mole. The catalyst would then have to be regenerated.

The average light-ends selectivity between 208°C and 224°C would then be an upper limit to the yearly average light ends selectivity. The selectivities at 80% CO conversion and 208°C were described above. The selectivities at 224°C are illustrated in Figures 9 and 10. The increases in light ends selectivities between 825 hours and about 1050 hours are mostly due to the temperature increase from 210°C and 224°C between 835 and 933 hours on stream. Further increases in light ends selectivities later in the run are mostly due to decreases in the conversion level to below 80%. The selectivities at about 1050 hours are then taken to represent the 224°C performance. They are: 3.2% C_1, $\leq$0.2% C_2, 2.1% C_3, and 2.9% C_4. The upper limit to the yearly average selectivities are then estimated to be: 2.3% C_1, $\leq$0.2% C_2, 1.7% C_3, and 2.4% C_4.

FUTURE PLAN

Work during the next quarter will focus on writing the final report for the program.

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DISCLAIMER

Figure 1

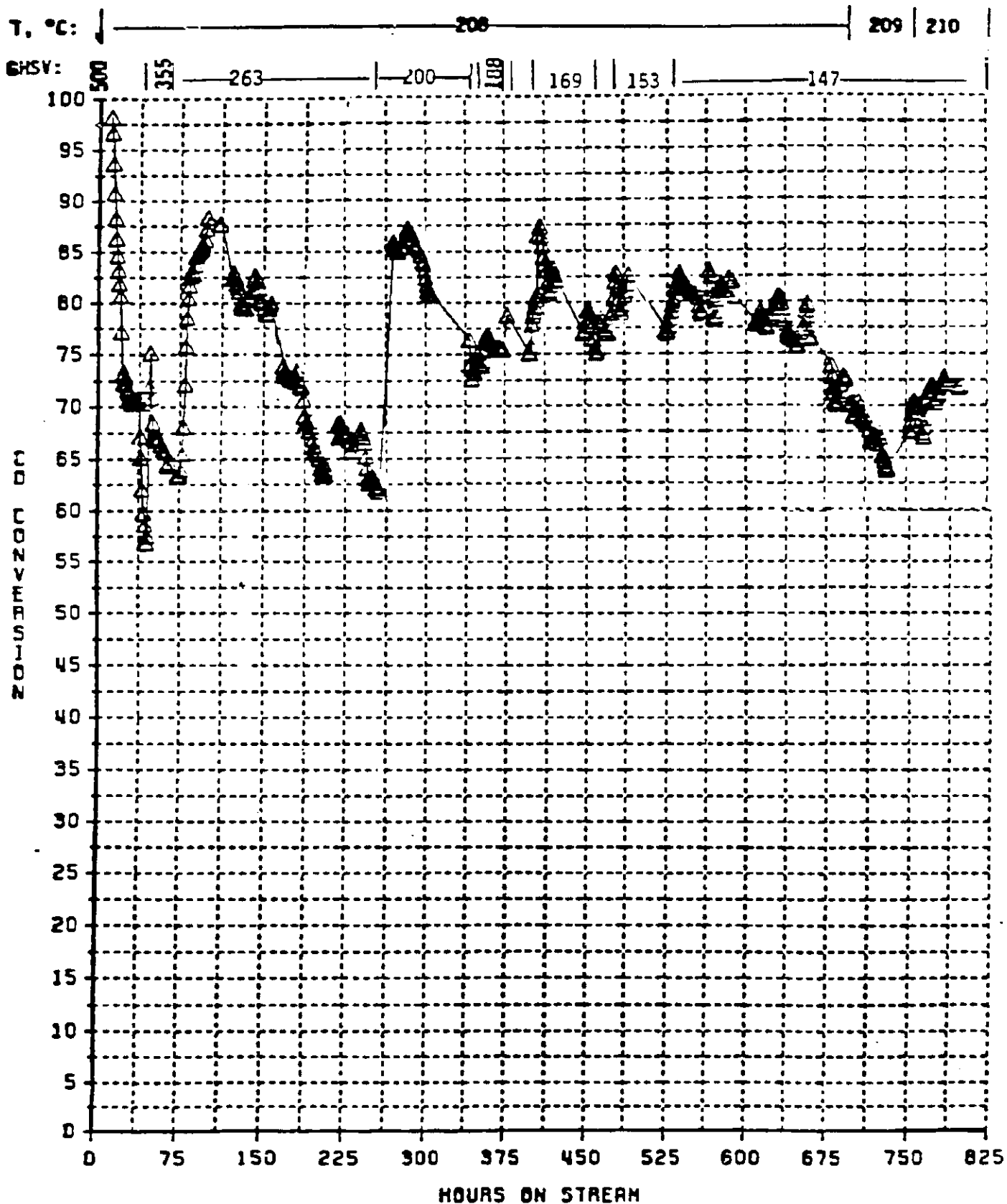MODIFIED Ru CATALYST
TABILITY EVALUATION

RUN 46, PLANT 700, 2H₂:1CO, 62 ATM
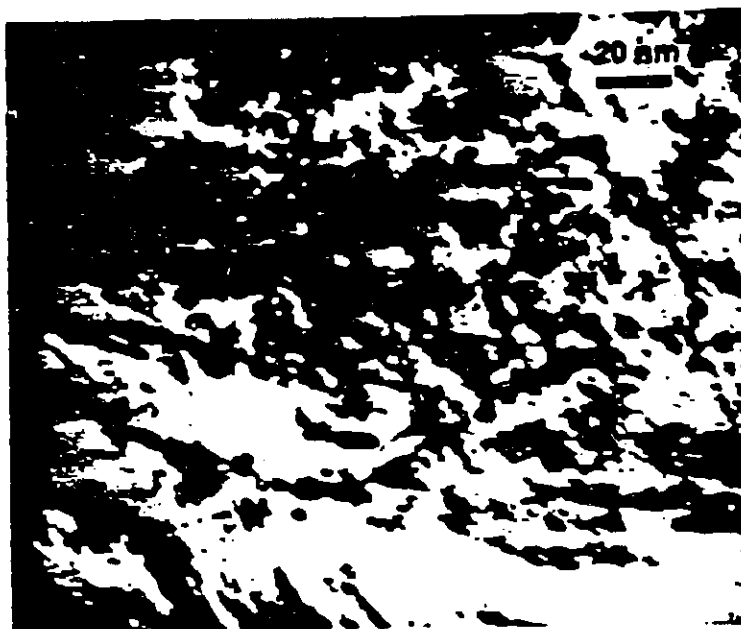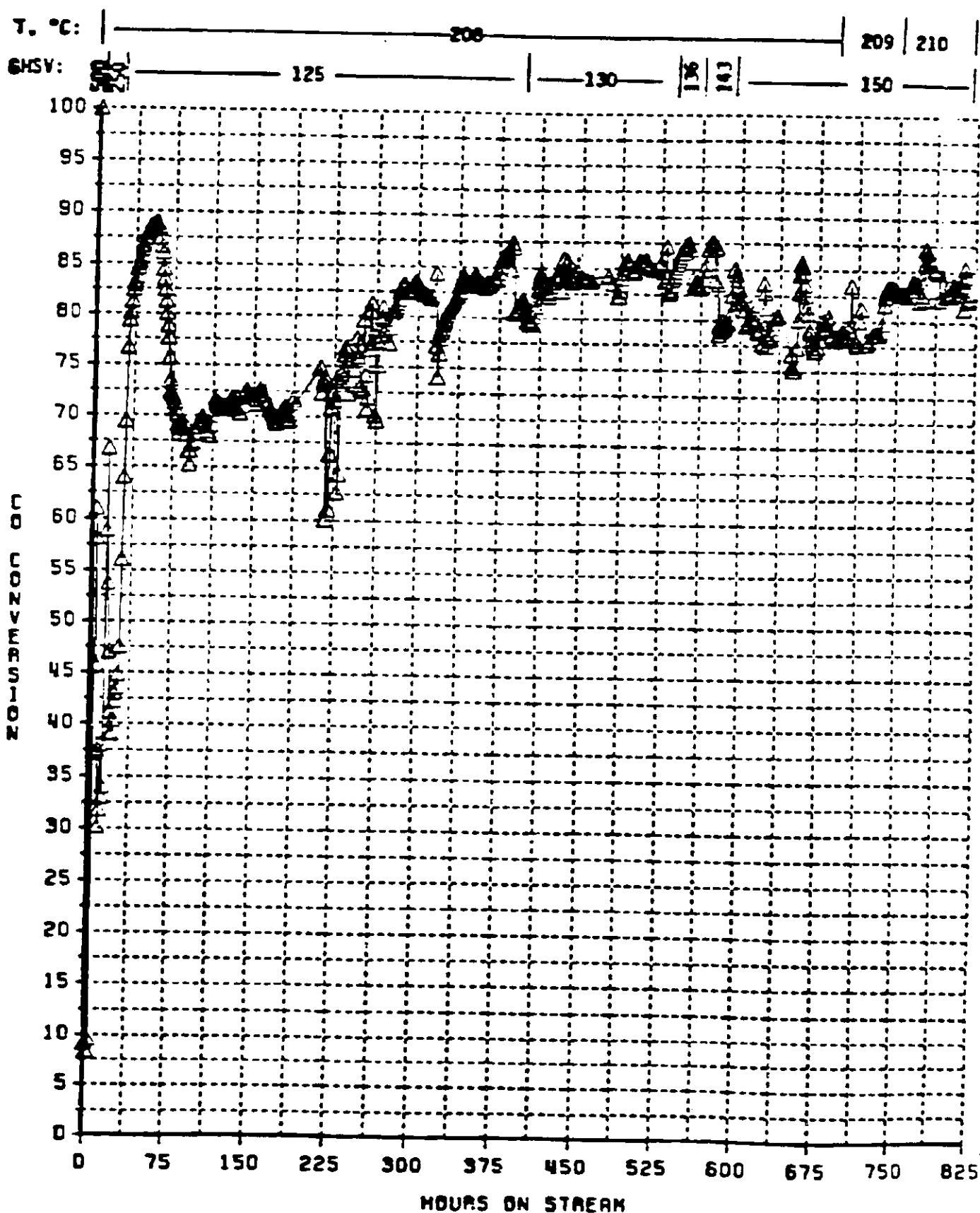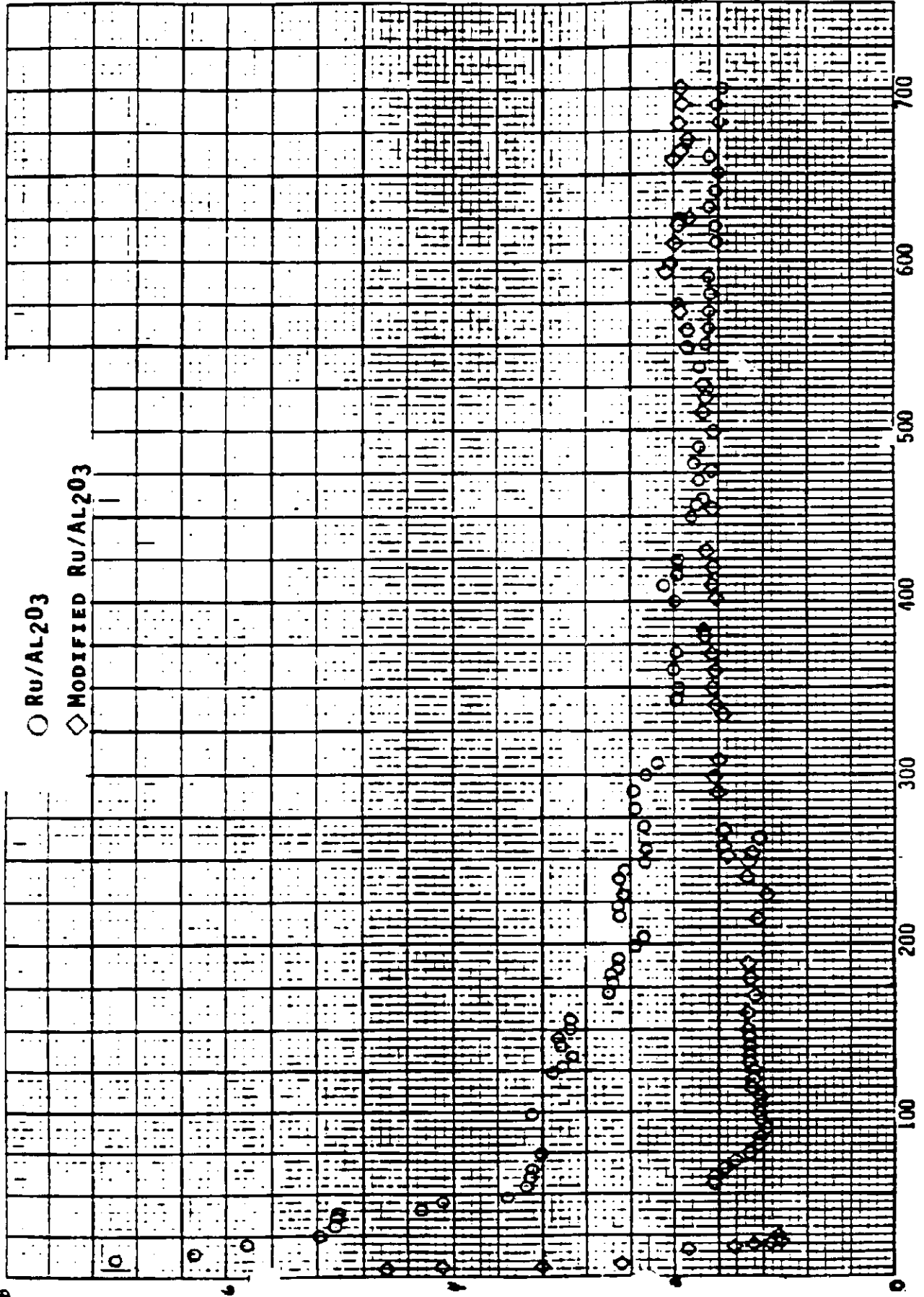
Figure 2

STEM MICROGRAPHS OF MODIFIED Ru CATALYST

Figure 3

MODIFIED Ru CATALYST
STABILITY EVALUATION

RUN 46, PLANT 700, 2H₂:1CO, 62 ATM

Figure 4

COMPARISON OF Ru AND
MODIFIED Ru CATALYSTS
208°C, 62 ATM, 2H2:1CO

○ Ru/Al2O3
◇ Modified Ru/Al2O3

10⁻⁸ Moles CO+H₂ Converted/sec-mole Ru

Figure 5

COMPARISON OF RU AND
MODIFIED Ru CATALYSTS
62 ATM, 2H$_2$:1CO

△ Ru/AL$_2$O$_3$

◻ MODIFIED Ru/AL$_2$O$_3$
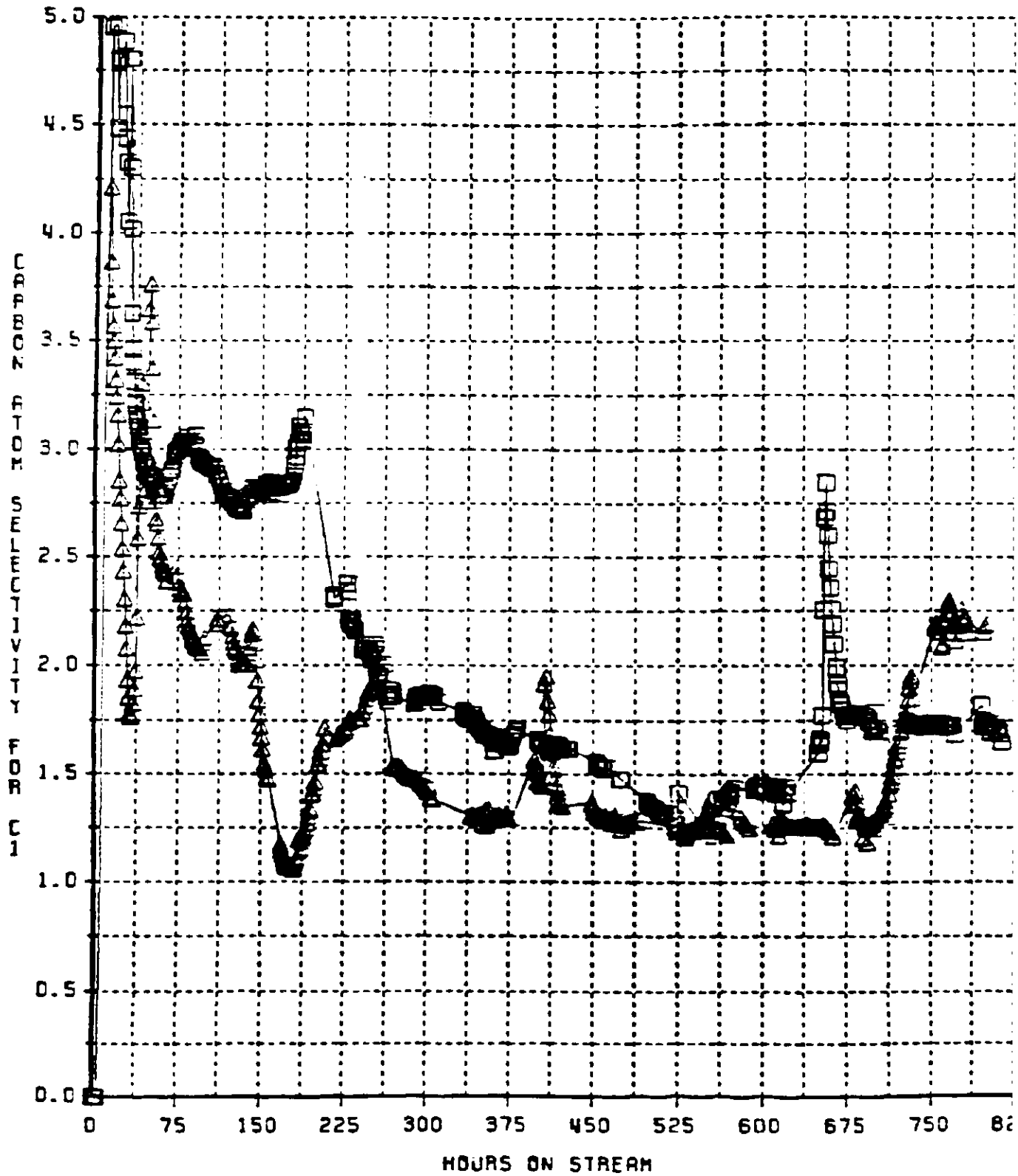
Figure 6

MODIFIED Ru CATALYST
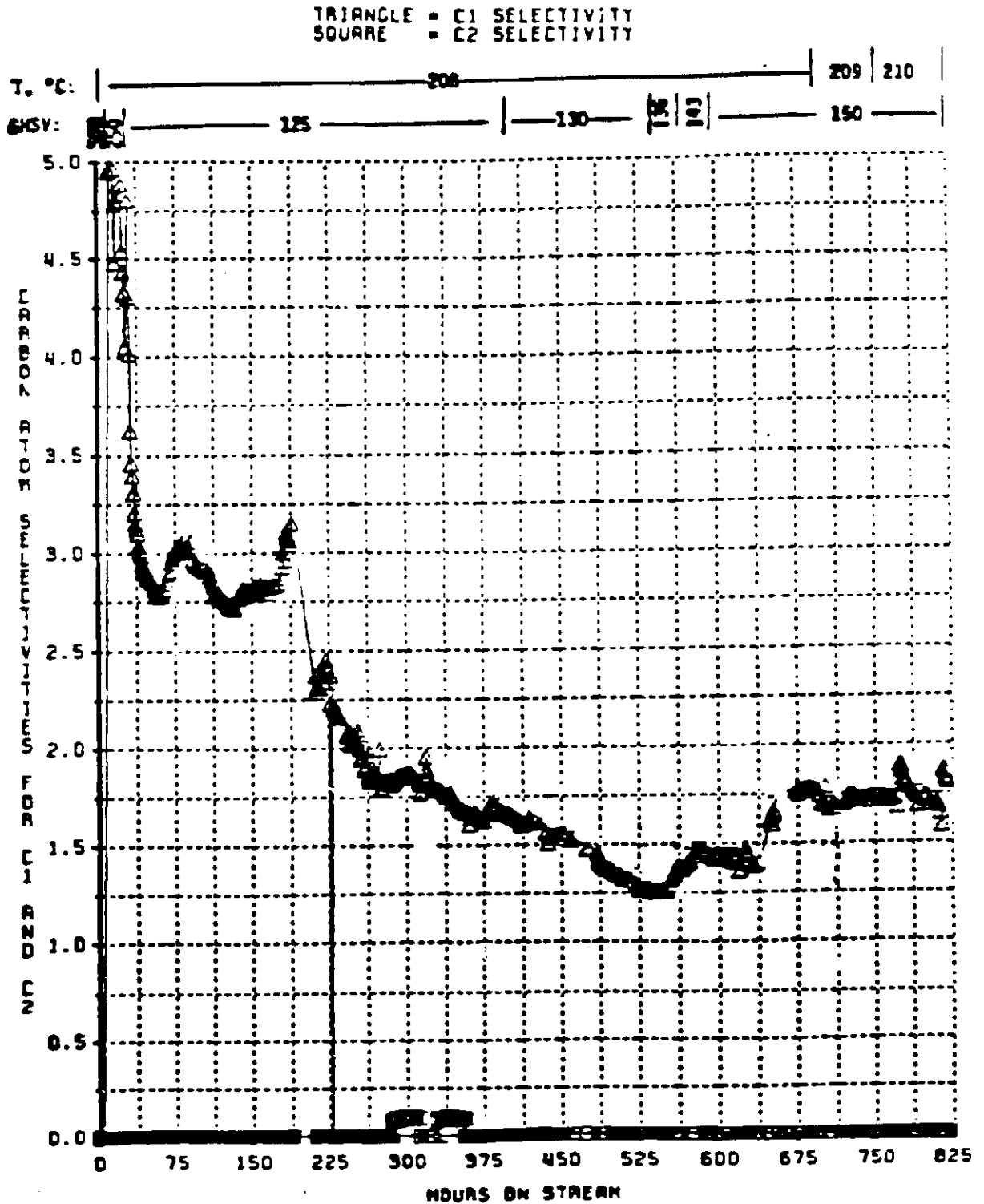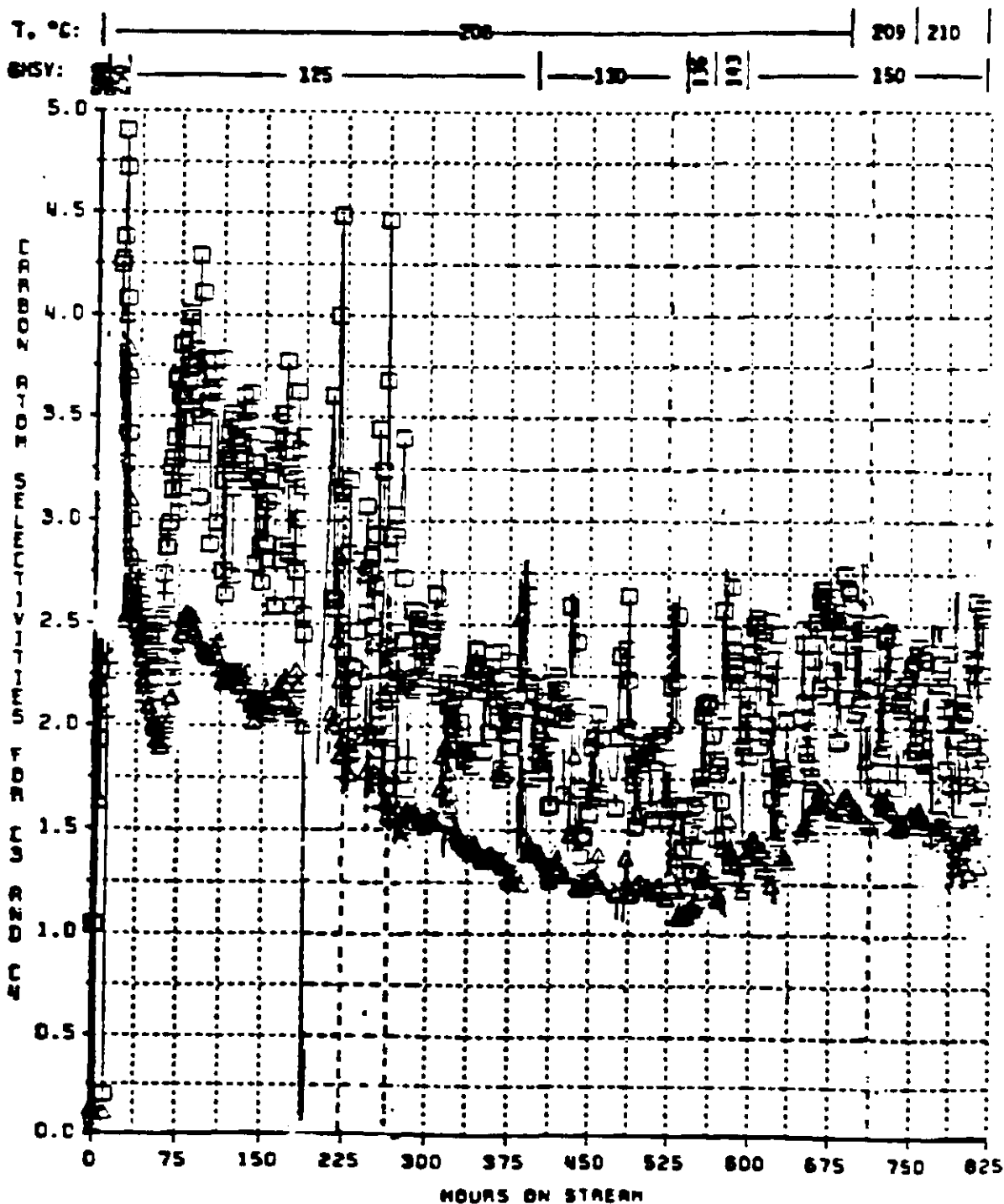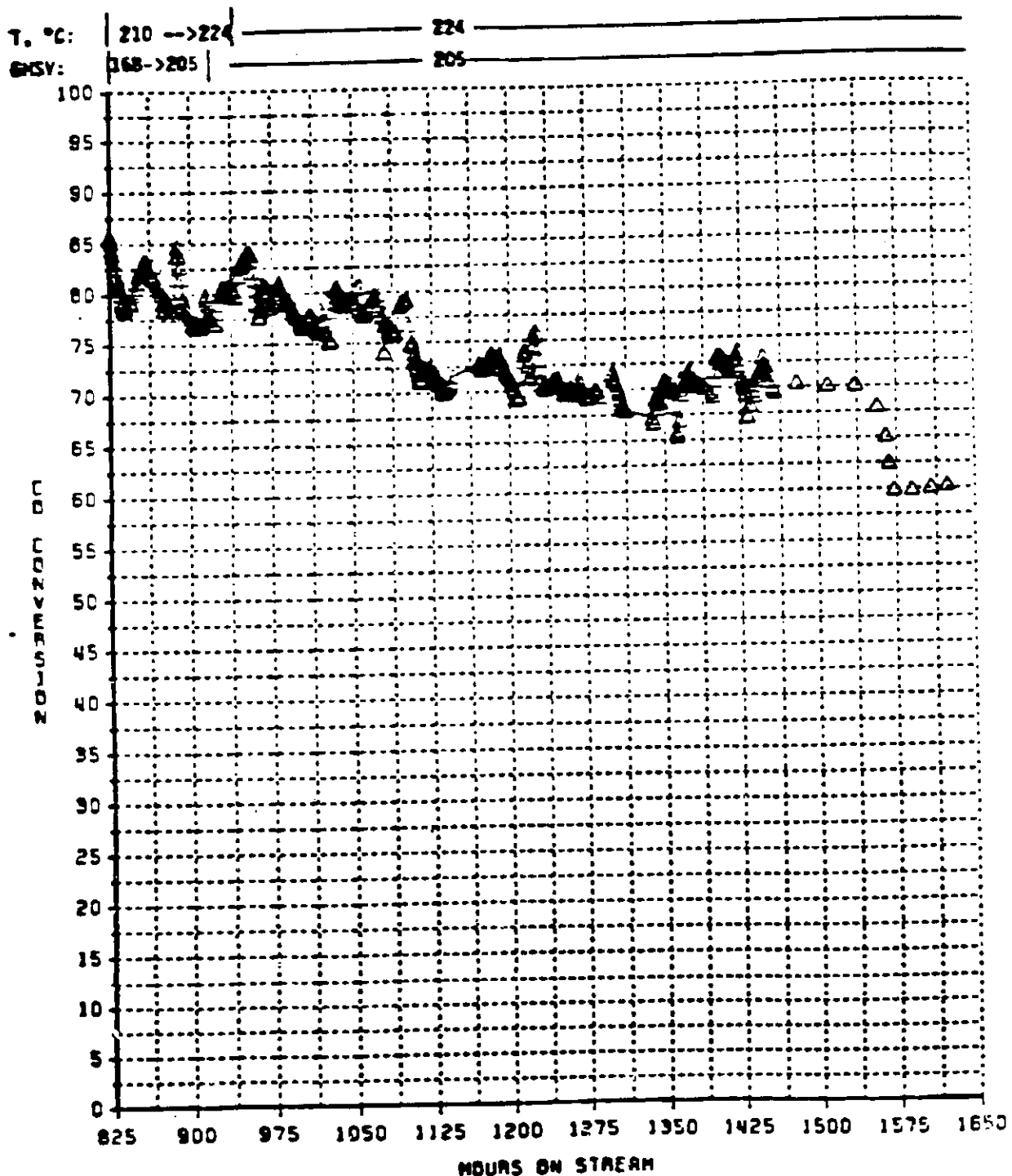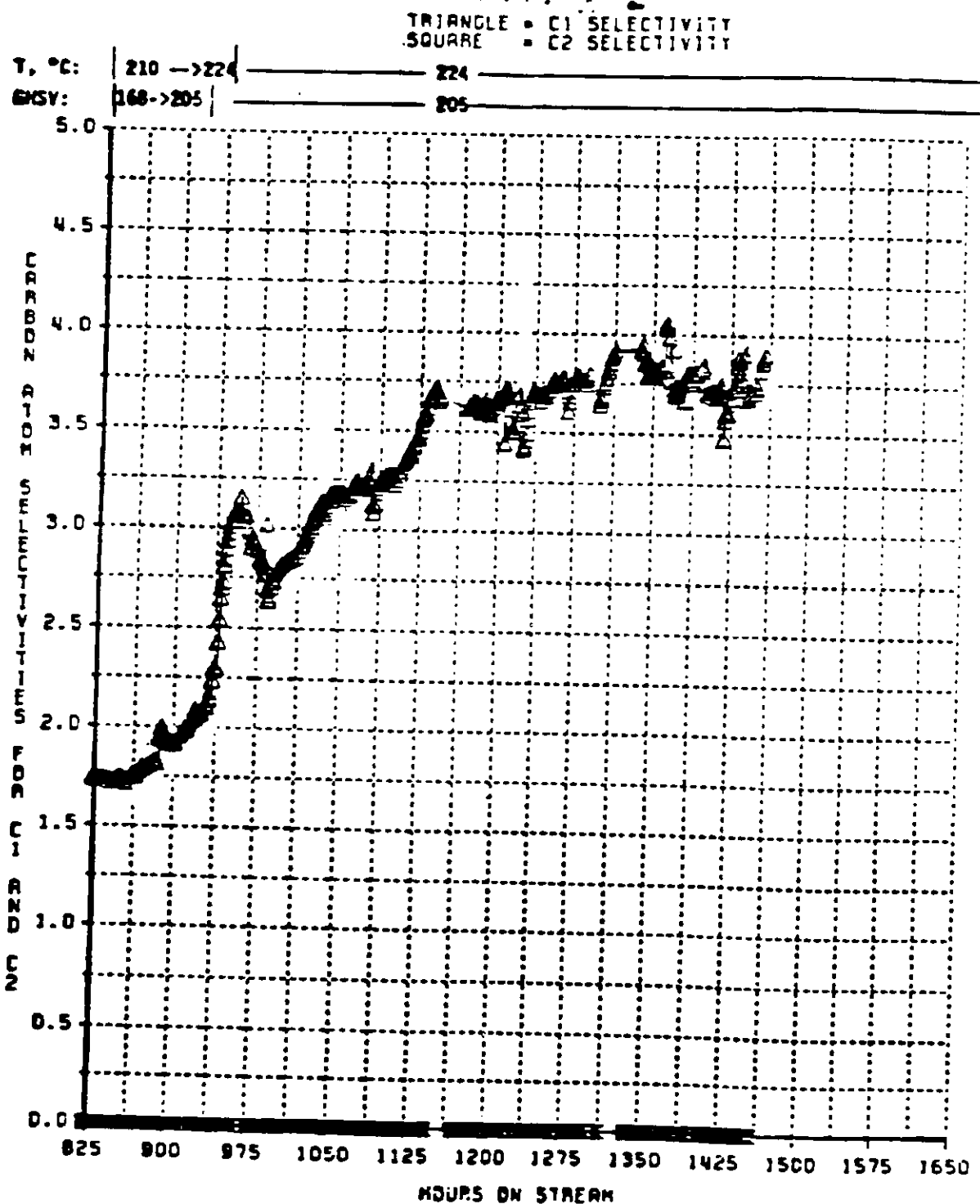STABILITY EVALUATION

RUN 46, PLANT 700, 2H$_2$:1CO, 62 ATM

Figure 7

MODIFIED Ru CATALYST
STABILITY EVALUATION

RUN 46, PLANT 700, $2H_2$:1CO, 62 ATM

TRIANGLE = C3 SELECTIVITY (Lower limit of
SQUARE = C4 SELECTIVITY fluctuations is correct)

Figure 8

MODIFIED Ru CATALYST
STABILITY EVALUATION

RUN 46, PLANT 700, $2H_2:1CO$, 62 ATM

Figure 9

MODIFIED Ru CATALYST
STABILITY EVALUATION

RUN 46, PLANT 700, 2H$_2$:1CO, 62 ATM

TRIANGLE = C1 SELECTIVITY
SQUARE = C2 SELECTIVITY

Figure 10

MODIFIED Ru CATALYST
STABILITY EVALUATION

RUN 46, PLANT 700, 2H$_2$:1CO, 62 ATM

TRIANGLE = C3 SELECTIVITY (Lower bound of
SQUARE = C4 SELECTIVITY fluctuations is correct)

T. °C: | 210 -->224 | ———————— 224 ————————
GHSV: | 168->205 | ——————————— 205 ————————————

HOURS ON STREAM