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TITLE: THE DEVELOPMENT OF A SELECTIVE RUTHENIUM CATALYST
FOR FISCHER-TROPSCH SYNTHESIS

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OBJECTIVE: The objective of this program is to identify development needs for a
ruthenium Fischer-Tropsch catalyst with significantly lower light ends make
relative to Sasol's Arge operation ($\sim$8.2% C_1+C_2), with 88% CO+H_2 conversion at
663 gas hourly space velocity and with at least 0.3 year catalyst life.

TECHNICAL APPROACH:

(1) Develop a reverse micelle technique for preparing supported catalysts with
     different size ruthenium particles.

(2) Establish ruthenium particle size and support effects.

(3) Identify developmental needs with the most promising catalyst.

(4) Explore various approaches to improve the catalyst chemistry.

(5) Demonstrate stable operation with the best catalyst.

SIGNIFICANT ACCOMPLISHMENTS:

(1) A micelle technique was developed for preparing supported catalysts with
     different size ruthenium particles.

(2) Ruthenium was stabilized on the support, light ends make was minimized and
     activity was maximized by adjusting the ruthenium particle size and metal-
     support interaction. One of the most promising catalysts consisted of
     4-6 nm ruthenium particles on an alumina support.

(3) Stability improvement was determined to be the major catalyst developmental
     need.

(4) A new ruthenium modifier was identified which improved the catalyst's
     stability.

(5) 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 2.5% C_1+C_2. Activity increase is identified to be the future catalyst developmental need.

INTRODUCTION

Project Background

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 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 diffi- cult 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 increase in 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 the UOP Technical 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 reactions 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) reported for 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 catalyst weight basis the catalyst with 1% Ru may 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].

The 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 3.7 times lower than the selectivity reported for the Arge catalyst [6].

The third year of the program was 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.

During the fourth and fifth years of the program research work focused on establishing the deactivation mechanism and improving catalytic stability. This work is going to be described in this paper.

Fischer-Tropsch Reaction Mechanism

The first step in Fischer-Tropsch synthesis is the dissociative chemisorption of CO (Figure 1). CO dissociation requires several adjacent vacant metal

atom sites. The probability of finding an ensemble of vacant metal atom sites decreases with a decrease in metal particle size. Accordingly, very small particles have low activity.

The metal-carbon bond has to be of intermediate strength for a good Fischer-Tropsch catalyst: strong enough to favor CO dissociation, yet not too strong to prevent subsequent hydrogenation to methyl and methylene species. A very strong metal-carbon bond then implies low activity or rapid deactivation.

Similarly, the metal-oxygen bond has to be of intermediate strength: strong enough to favor CO dissociation, yet not too strong to prevent hydrogenation to form water.

Chain growth is believed to occur by insertion of a methylene species to a metal-methyl bond. Chain termination will occur by hydrogenation of the alkyl species to produce the paraffin or by hydrogen abstraction from the alkyl species to produce the corresponding olefin.

When the concentrations of surface carbon and surface methylene species are high, relative to the concentration of surface hydrogen, chain growth will most likely be favored over chain termination and methane + ethane selectivity will be low. This, then, indicates that under conditions which favor chain growth a high carbon concentration may exist on the surface of the catalyst.

At least two criteria are needed for stable catalyst performance:

1. The coverage of active sites by the active carbon species should not indefinitely increase. This carbon species may form via CO dissociation on vacant active sites. This, then, implies that catalytic stability may be improved when the catalyst is modified in a manner that balances the CO dissociation rate relative to the hydrogenation rate of this active carbon into methyl and methylene species.

2. The hydrocarbons on the surface should not be converted into polynuclear aromatic (PNA) compounds. Therefore, a modifier which suppresses the dehydrogenation/cyclization reaction of hydrocarbons into PNA's may improve catalytic stability.

EXPERIMENTAL

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:

$$CO \text{ Conversion, } \% = \frac{(\frac{CO}{Ar})_{feed} - (\frac{CO}{Ar})_{product}}{(\frac{CO}{Ar})_{feed}} \times 100$$

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

$$C_n \text{ Selectivity, } \% = \frac{(\frac{C_n}{Ar})_{product} \times n}{(\frac{CO}{Ar})_{feed} - (\frac{CO}{Ar})_{product}} \times 100$$

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

Establishment of Deactivation Mechanism

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, 62 atm with a $2H_2$:1CO feed gas at a CO conversion level of about 75-85% in a fixed bed reactor for 800 hours. This catalyst was not stable and accordingly, the gas hourly space velocity had to be continuously decreased between 40 hours and 530 hours on stream from 500 hr^{-1} to 147 hr^{-1} in order to maintain 75-85% conversion. After 530 hours 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. Characterization of the used catalyst showed a high coke level. There was no change in the ruthenium particle size which remained at 4-6 nm during the 800 hour-test. It was, therefore, tentatively concluded that deactivation was through coking.

Development of a Stable Ruthenium Catalyst

Several ruthenium modifiers were tested which might regulate the relative rates for CO dissociation and carbon hydrogenation or which might suppress the formation of polynuclear aromatic comopunds, and therefore improve catalytic stability. A modified catalyst showed lower initial activity but better stability than the unmodified catalyst. The performance of this catalyst is summarized in Figure 2.

The modified 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 causes of this activity increase are not

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currently known. 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.

The modified catalyst did not show any sign of deactivation at 208-210°C and at about 80% conversion after the initial activity loss (Figure 3). It was, therefore, concluded that the loss in conversion was less than 0.0002%/hour. The methane + ethane selectivity was 1.5% with the modified ruthenium catalyst, much less than that reported for the Sasol Arge high pressure process, which is 8.2%.

In an attempt to measure the catalyst deactivation rate, the severity of operation was increased after 825 hours, by increasing, in parallel, the temperature to 224°C and the space velocity to 205 hr^{-1}. Under these new conditions and at 70% conversion, a deactivation rate of 0.016%/hour was measured. The methane + ethane selectivity was now higher but still much less than that reported for the high pressure Arge process (Figure 3).

There are not presently enough data for calculating the life of this 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 for the Fischer-Tropsch synthesis reaction. The catalyst would then have to be regenerated.

Finally, an assessment was made of the economic impact of the new stable and selective ruthenium catalyst. It was assumed that the performance of the catalyst under commercial process conditions would match the pilot plant performance. Our preliminary analysis indicates that a 20% increase in catalytic activity may make this new ruthenium catalyst commercially attractive. Widespread use of the ruthenium catalyst, however, would require that the ruthenium level in the catalyst be lowered. This may be achieved by replacing a portion of ruthenium with another metal active in Fischer-Tropsch synthesis.

Characterization of Modified and Unmodified Ruthenium Catalysts

In order to gain insight into the role of the ruthenium modifier, the modified ruthenium catalyst and the catalyst without the modifier were characterized by X-ray photoelectron spectroscopy (XPS), which showed that the ruthenium binding energy was slightly higher with the modified catalyst. This indicates that the ruthenium electron density may have been slightly lowered by the modifier. This decrease in ruthenium's electron density is consistent with the attenuation of ruthenium's initial activity by the modifier. Improved catalytic stability may be explained if attenuation of the ruthenium initial activity is caused by a decrease in the rate of CO dissociation.

We have also characterized the coke on the used catalysts. By XPS two types of carbon were observed. A small fraction of the carbon was associated with oxygen, while the majority of the carbon was not associated with oxygen. The first type of carbon appears like an oxygenated hydrocarbon.

In an attempt to gain further insight into the coke chemistry some of the coke was removed from the used catalysts by soxhlet extraction and examined by mass spectroscopy (MS) and X-ray fluorescence. MS analysis confirmed the presence of two types of coke.

One type of coke was composed of long chain olefinic or cyclic oxygenates. These oxygenates could be acids, esters, and/or alcohols. There was also some minor amount of aromatic oxygenates. Both catalysts showed the presence of these oxygenated compounds.

The second type of coke did not contain oxygen and was of an aromatic nature. Alkyl aromatics and naphthalenes were detected by MS. Polynuclear aromatics with 3 or more rings were detected by X-ray fluorescence. These aromatic and polynuclear aromatic compounds were detected only on the ruthenium catalyst without the modifier.

These results seem to indicate that by modifying the chemical properties of ruthenium the chemistry of coke was altered, which may also explain the stability improvement that was observed.

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FIGURE 1
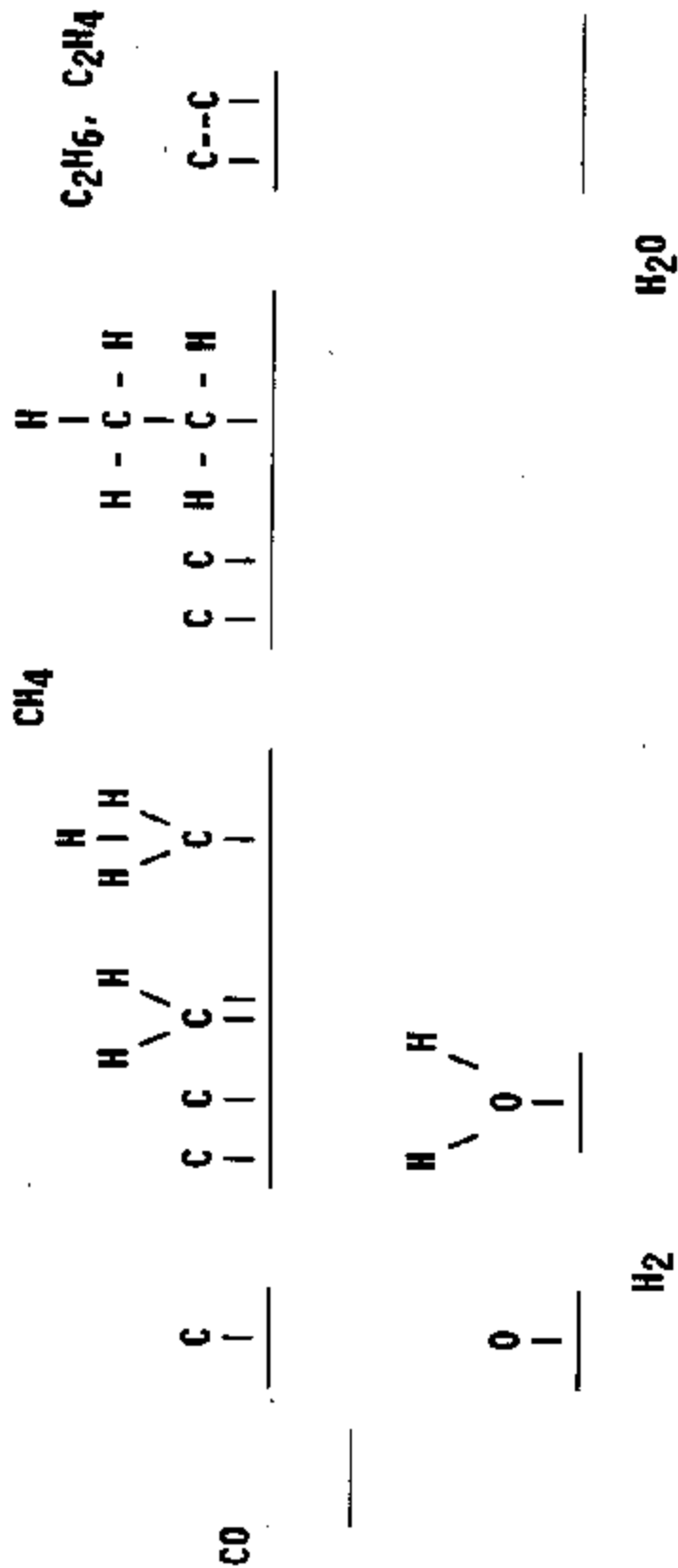
FISCHER–TROPSCH REACTION MECHANISM

FIGURE 2
MODIFIED Ru CATALYST
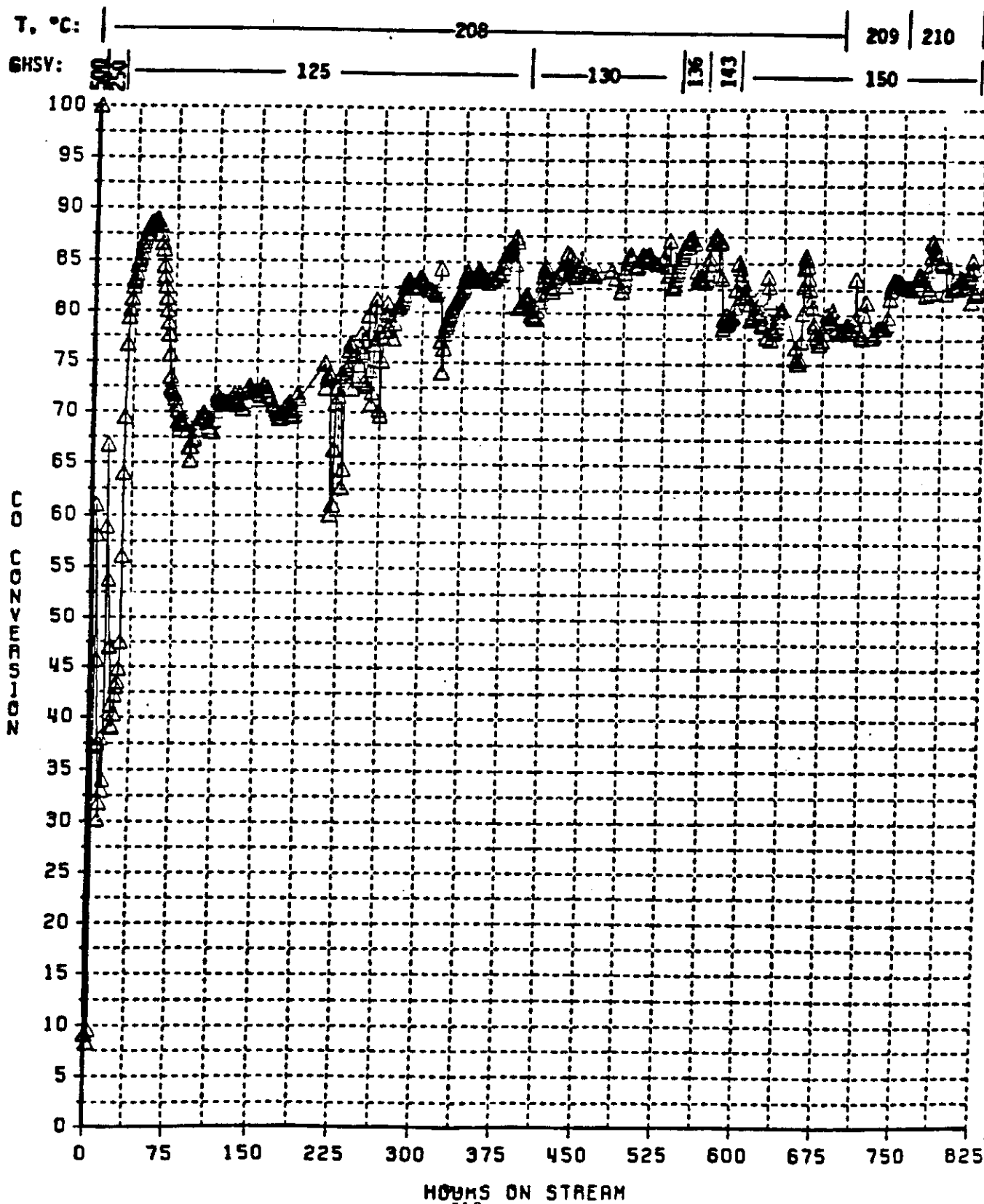# STABILITY EVALUATION
RUN 46, PLANT 700, 2H$_2$:1CO, 62 ATM

T, °C: | 208 | 209 | 210 |

GHSY: | 125 | 130 | 136 | 143 | 150 |

CO CONVERSION

HOURS ON STREAM

FIGURE 3

PERFORMANCE OF MODIFIED-Ru/AL$_2$O$_3$ CATALYST

	MODIFIED-Ru/AL$_2$O$_3$		SASOL ARGE
INLET TEMPERATURE, $^\circ$C	208	224	225
PRESSURE, ATM	~62	~62	~45
H$_2$:CO FEED RATIO, MOLAR	2.0	2.0	1.7
GHSV	150	205	663
CO + H$_2$ CONVERSION	80	70	88
C$_1$ + C$_2$ %	1.5	3.4	8.2
% CONVERSION LOSS/HOUR	<0.0002	0.016	?
PREDICTED CATALYST LIFE, YEAR	~1		?

ELUCIDATION OF THE ROLE OF MODIFIER FOR RUTHENIUM FISCHER-TROPSCH CATALYSTS

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CATALYST FEATURE	CATALYST FRESH OR USED	(A) MODIFIED-Ru/Al$_2$O$_3$	(B) Ru/Al$_2$O$_3$
Ru3p^3 (XPS)	FRESH	461.32-461.47 eV	461.22 eV
SOXHLET EXTRACTED COKE (MS)	USED	<------ $C_NH_{2N-0,6}O_2$ ------>	
		<------ $C_NH_{2N-6,8}O$ ------>	
			$C_NH_{2N-6,8,10,12}$
(X-RAY FLUORESCENCE)		NO PNA's	3-5 RING PNA's
CARBON ANALYSIS (XPS)	USED		
OXYGENATED CARBON		3%	1.0%
CARBON WITH NO OXYGEN		17%	22.8%

(A): 1600 Hours At 208 - 224°C
(B):   825 Hours At 208 - 210°C

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