

CONTRACT IDENTIFICATION: THE DEVELOPMENT OF A SELECTIVE RUTHENIUM CATALYST	REPORTING PERIOD: 10/1/87 - 12/31/87	CONTRACT NUMBER: DE-AC22-84PC70023
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TECHNICAL PROGRESS REPORT

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ABSTRACT

A micelle technique was developed for preparing supported catalysts with different size ruthenium particles. Ruthenium was stabilized on the support, light ends make was minimized and activity was maximized by adjusting the ruthenium particle size and the metal-support interaction. The most promising catalysts consisted of 10-15 nm ruthenium particles on an alumina-titania support and 4-6 nm ruthenium particles on an alumina support. Stability improvement was determined to be the major catalyst developmental need. Work during the next quarter will focus on the development of a stable ruthenium catalyst.

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% C₁-C₄), with 88% CO+H₂ 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

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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 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 (Figure 1). 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 affected 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 H₂ to make hydrocarbons and H₂O; and 3) CO can react with H₂O to form H₂. 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 (Figures 1 and 2) [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, 2H₂:1CO, 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.

Lowest light ends selectivity was obtained at 87% CO+H₂ conversion where the selectivity to C₁-C₄ 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.

EXPERIMENTAL

The catalysts were loaded into a glass-lined fixed-bed reactor in reduced form under N₂ (Figure 3). For alumina-supported catalysts (40-200 mesh), the volumes were either 30 cc or 60 cc, while for zeolite and titania-supported catalysts they were less, 3 cc and 17 cc, respectively. The temperature was then raised under H₂ flow at 1 atm to reaction temperature. Unless otherwise specified, the reactor was then pressurized with He to 14 atm above the reaction pressure for a 1-hour pressure test; then, the pressure was lowered to reaction pressure and the synthesis gas introduced. Temperatures in the range 200-225°C, pressures in the range 14-62 atm, H₂:CO feed ratios

in the range 0.9-3, and testing times from one-half day to 10 days were used. For some tests the catalysts were diluted with quartz sand or alumina powder to control the catalyst bed temperature within about 5°C from the temperature at the catalyst inlet. The liquid and solid hydrocarbon products were collected during the test in the product receivers which were kept at a 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 C₅-C₂₀₀ range. C₁-C₁₀ hydrocarbons, alcohols and aldehydes were analyzed with on-line GC along with CO, CO₂, H₂ and Ar. Argon was used as an internal standard to determine conversions and light hydrocarbon selectivities during the test according to the following expressions:

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

The CO+H₂ conversion was calculated in a similar manner.

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

where n is the number of carbon atoms in one molecule of hydrocarbon C_n. The calculation of selectivity of CO to CO₂ is similar to the calculation of selectivity to methane for which n = 1.

RESULTS AND DISCUSSION

The 1% Ru catalyst, with mostly 5 nm ruthenium particles, prepared on an Al₂O₃ support with 0.3 g/cc apparent bulk density was further evaluated and was found to be unstable at 210-225°C, 34-62 atm and 2H₂:1CO feed ratio.

Another 1% Ru catalyst, with 10-15 nm ruthenium particles, prepared on a mixed alumina-titania support with an apparent bulk density equal to 0.9 g/cc was similarly unstable at 210°C, 62 atm and 2H₂:1CO feed ratio, as is indicated in Figure 4. The gas hourly space velocity (GHSV) during the first 20 hours of the test was adjusted to 310 in order to achieve a CO+H₂ conversion level of about 85%. The catalyst then deactivated to a conversion level of about 45% in 120 hours. The lowest light ends (C₁-C₄ paraffins and olefins) selectivity was equal to 2.4 and was obtained at the highest conversion level. The light ends selectivity then increased with time, mostly because of the decrease in the conversion level. The conversion level indirectly influences the product selectivity probably by virtue of directly influencing the partial pressures of reactants and products.

The concentrations of C₁-C₁₀ paraffins, olefins, alcohols and aldehydes in the effluent gas with the Ru/Al₂O₃-TiO₂ catalyst at 65% CO+H₂ conversion are shown in an Anderson-Schulz-Flory type distribution in Figure 5. A high chain growth probability of 0.85 was obtained from the slope of the Anderson-Schulz-Flory line drawn from paraffins + olefins. The chain growth probability at higher carbon numbers was previously shown to be even higher with typical ruthenium catalysts [9]. The results summarized in Figure 5 indicate that the light ends selectivity with the ruthenium catalyst was low not only because of the high chain growth probability but also because light hydrocarbons were made with selectivities significantly below the Anderson-Schulz-Flory prediction.

Evaluation of ruthenium catalysts prepared on Al₂O₃ and on Al₂O₃-TiO₂ clearly indicated that stability improvement was the major developmental need.

FUTURE PLAN

This research program was originally scheduled to end on March 31, 1987, but was recently extended until November 30, 1988. During this extension period various approaches to improve the catalyst chemistry will be explored. Since catalyst deactivation appears to have occurred mostly through coking, a ruthenium modifier which will suppress coking reactions will be identified.

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FIGURE 1

Ru PARTICLE SIZE EFFECTS WITH Al_2O_3 SUPPORTED CATALYSTS

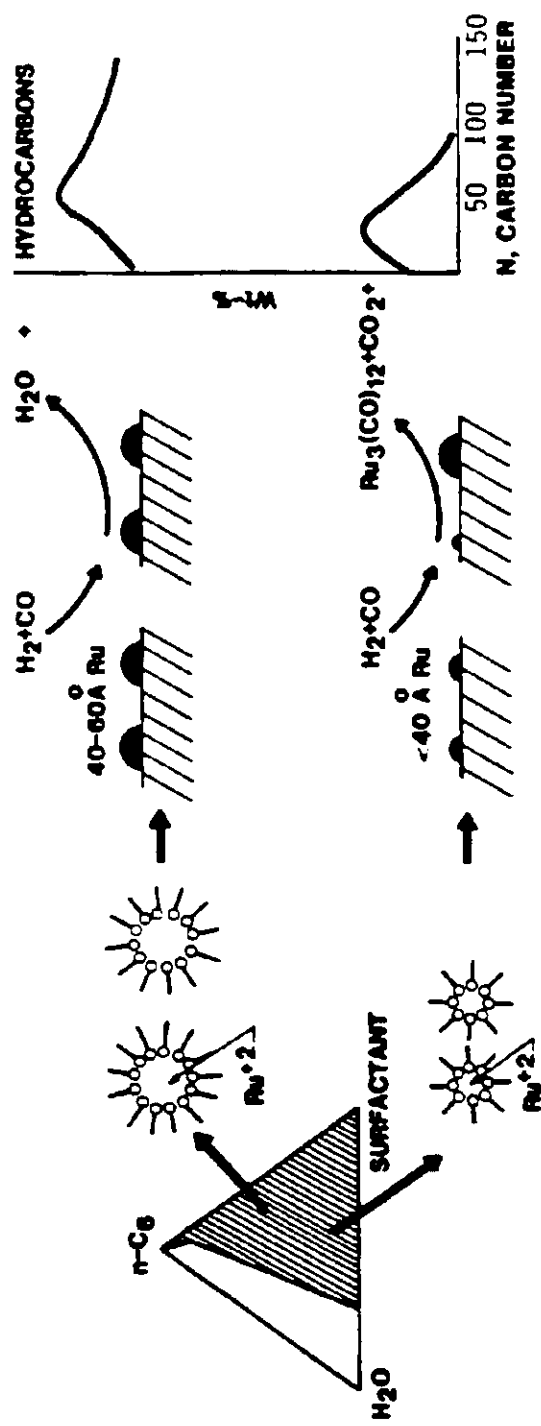


FIGURE 2

SUMMARY OF PARTICLE SIZE AND SUPPORT EFFECTS WITH Ru CATALYSTS

	Ru Agglomeration and Loss Under CO/H ₂ Via Carbonyl	Initial Activity (By Volume)	Light Ends Selectivity
<4nm Ru / Al ₂ O ₃	YES		
<4nm, Ru/TiO ₂ or Y-Zeolite	NO		
4-6 nm Ru / Al ₂ O ₃ (0.3 g/cc; 1 wt. % Ru)	NO	50% of Target	LOW
10-15 nm Ru / Al ₂ O ₃ -TiO ₂ (0.9 g/cc; 1 wt. % Ru)	NO	Target	LOW

Most Promising

FIGURE 3

CATALYST TESTING PROCEDURE

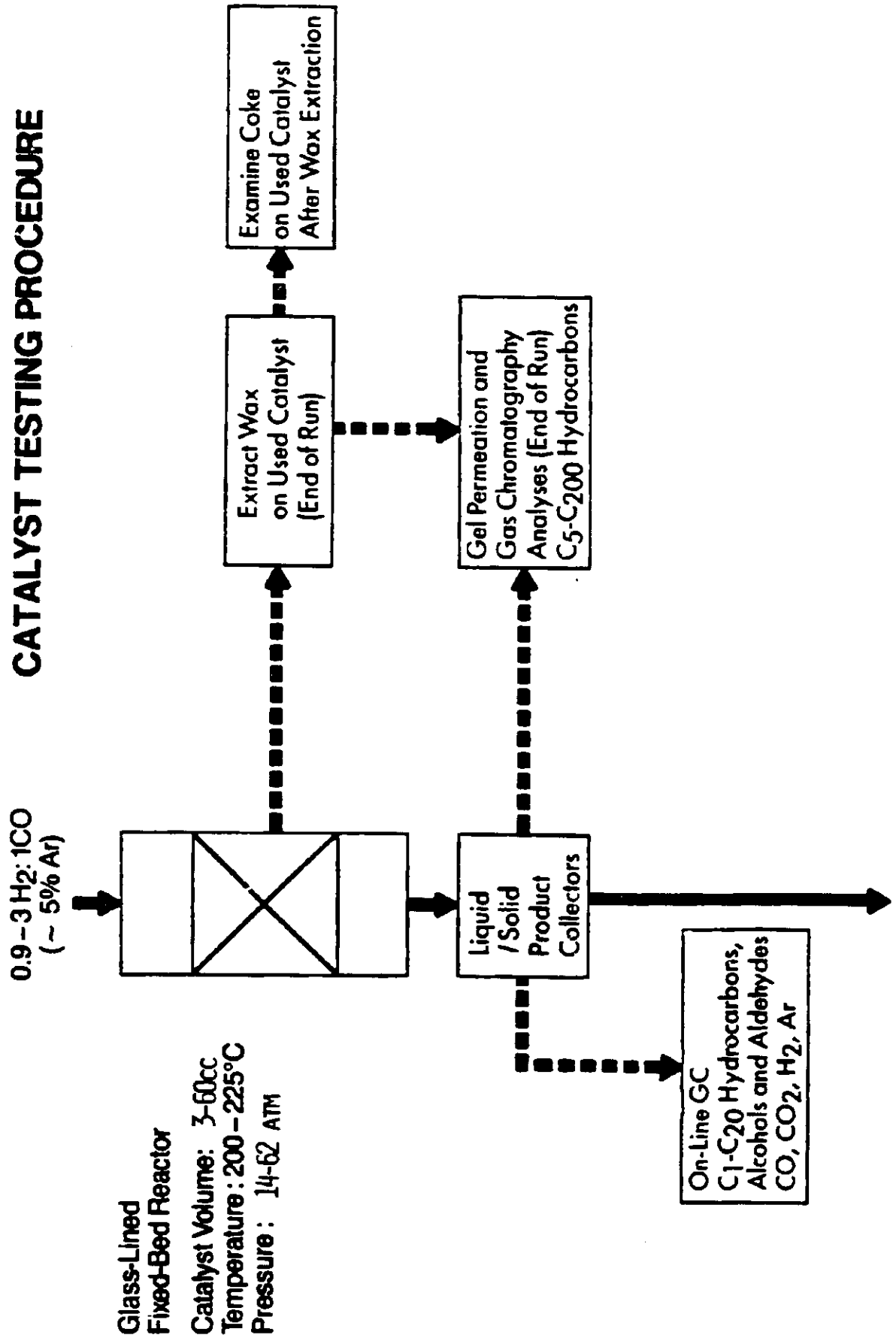


FIGURE 4

Ru/Al₂O₃ - TiO₂ STABILITY EVALUATION
210°C, 900 psig, 2H₂:1CO FEED
2.4% C₁ - C₄ at 37 HOURS

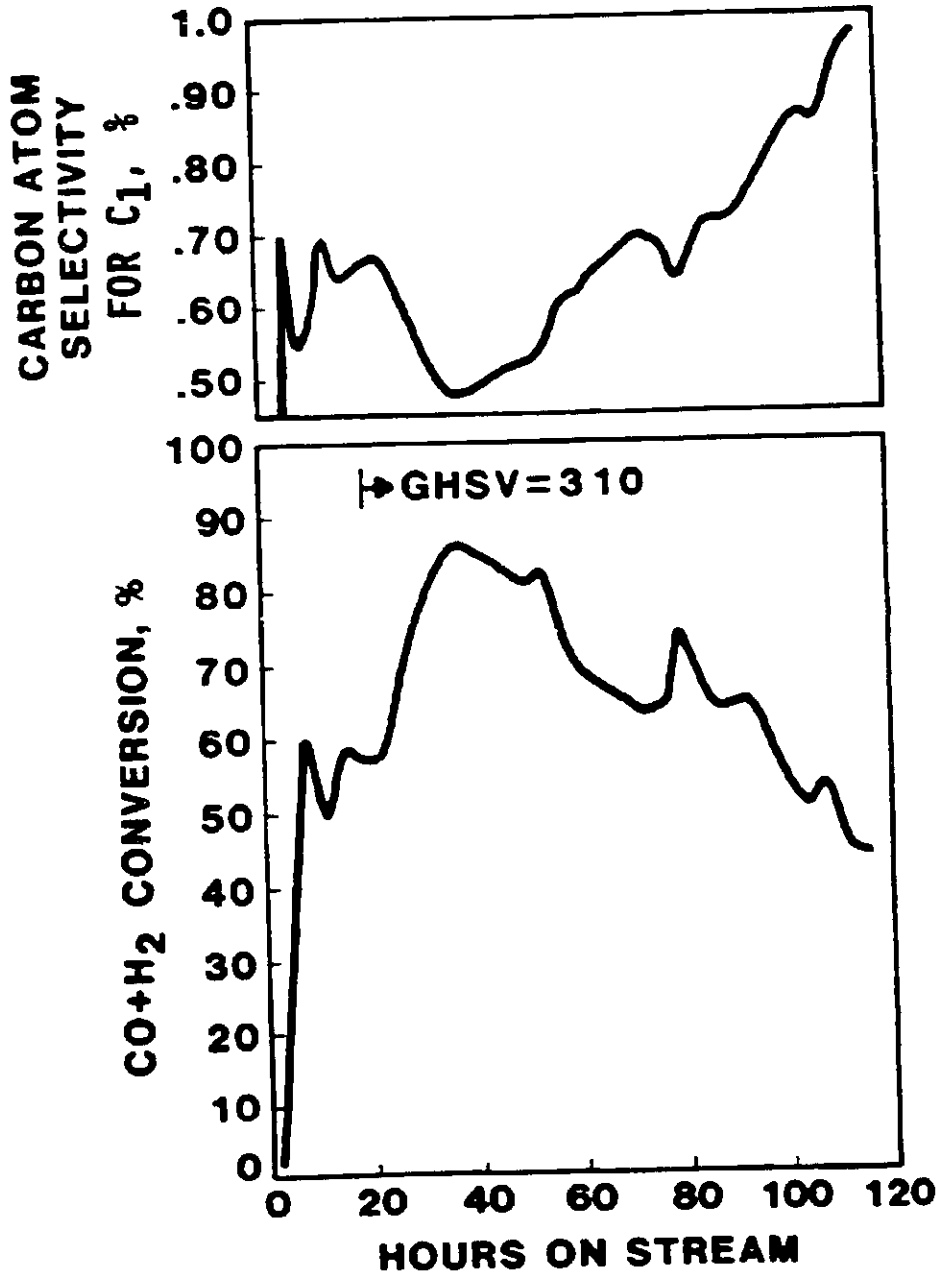


FIGURE 5

ANDERSON-SCHULZ-FLORY-TYPE DISTRIBUTION FOR Ru / Al₂O₃-TiO₂

210°C, 900 psig, 2H₂:1CO feed, 65% CO + H₂ Conversion

