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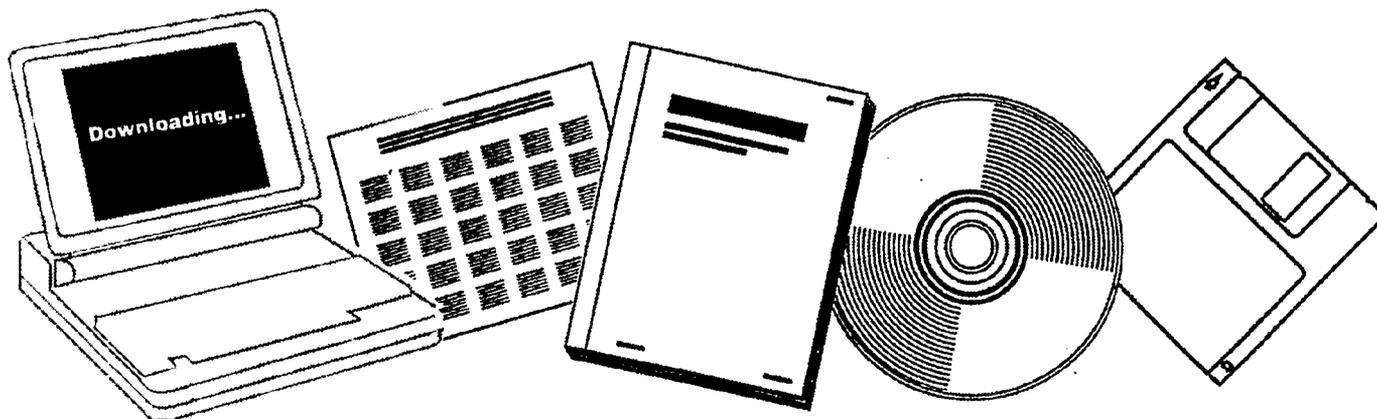
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**NOVEL FISCHER-TROPSCH SLURRY CATALYSTS AND
PROCESS CONCEPTS FOR SELECTIVE
TRANSPORTATION FUEL PRODUCTION. QUARTERLY
TECHNICAL PROGRESS REPORT, 1 OCTOBER-31
DECEMBER 1985**

**AIR PRODUCTS AND CHEMICALS, INC.
ALLENTOWN, PA**

JUL 1986



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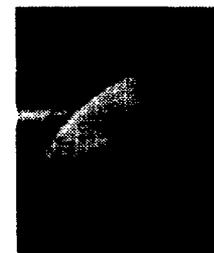
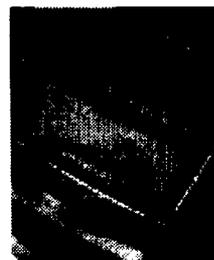
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AIR
PRODUCTS

NOVEL FISCHER-TROPSCH SLURRY CATALYSTS AND PROCESS CONCEPTS

FOR SELECTIVE TRANSPORTATION FUEL PRODUCTION

QUARTERLY TECHNICAL PROGRESS REPORT

FOR THE PERIOD 1 OCTOBER - 31 DECEMBER 1985

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PREPARED FOR UNITED STATES DEPARTMENT OF ENERGY

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EXECUTIVE SUMMARY

In the fifth quarter of the Air Products and Chemicals, Inc./United States Department of Energy Contract, "Novel Fischer-Tropsch Slurry Catalysts and Process Concepts for Selective Transportation Fuel Production", work continued on the two major tasks: Task 2 -- Development of Improved Supported Catalyst Compositions and Task 3 -- Slurry Reactor Kinetic Studies.

Four catalysts were prepared during this quarter. A Co/Zr/SiO₂ catalyst was prepared from a more conventional cobalt source (cobalt nitrate) to establish a comparative basis for the silica-supported, cobalt carbonyl based catalysts. A Zr-promoted Ru catalyst was prepared on silica, since the silica support provided enhanced performance for the cobalt catalyst. TiO₂ was examined in a dual purpose support/promoter role for the Co catalyst by preparing Co₂(CO)₈ on TiO₂. A Zr-promoted, Fe₃(CO)₁₂ on silica catalyst was prepared to establish the inherent water-gas shift activity of this type of Fe-based catalyst.

During this quarter five gas phase screening tests were performed. The effect of Ti as a promoter for the silica-supported cobalt carbonyl catalyst was investigated by a test of 4.4% Co/4.0% Ti on silica. The activity of the Ti-promoted catalyst was lower than the Zr-promoted catalyst with a significant shift in hydrocarbon selectivity to lighter products, particularly C₃₋₅ olefins. Combining the support properties of MgO and SiO₂ was examined by testing a Co₂(CO)₈/Zr(OPr)₄ on magnesium silicate catalyst. Activities were similar to the alumina-supported Co/Zr catalyst rather than to the silica catalyst. Hydrocarbon selectivity was also shifted to lighter products with high C₃₋₅ olefin selectivity and C₁₂⁺ selectivity that was never greater than 15%. The cobalt nitrate derived, zirconated silica catalyst mentioned above was tested. It was 20 to 50% less active than the carbonyl based catalyst and produced a greater amount of wax. The Ru₃(CO)₁₂/Zr(OPr)₄/SiO₂ catalyst discussed earlier was tested and showed the highest bulk and specific activities of any catalyst to date. Generally, the hydrocarbon selectivity of this catalyst was shifted toward higher molecular weight products. Finally, the TiO₂-supported cobalt catalyst was tested and showed moderate activity similar to that of the Ti-promoted, Co on silica catalyst and was 35 to 50% more active than the Ti-promoted, Co on alumina catalyst. The total liquid fuels selectivity (C₅₋₂₃) was in the 60-67% range.

During this quarter, slurry screening tests were performed on three catalysts and an extended test was initiated on a fourth catalyst. The results are summarized as follows:

- Co₂(CO)₈/Fe₃(CO)₁₂/Zr(OPr)₄/SiO₂ -- This catalyst was prepared in another attempt to incorporate water-gas shift activity into the cobalt catalyst. It was hoped that the silica support would also enhance the activity of the Fe. Compared to the mixed Co/Fe catalysts on alumina, this catalyst was substantially more active with similar hydrocarbon selectivity. It was not quite as active as the Co/Zr/SiO₂ catalyst and did not show enhanced water-gas shift activity.

- $\text{Co}_2(\text{CO})_8/\text{Zr}(\text{OPr})_4/\text{MgO}\cdot 3.6\text{SiO}_2$ -- Examination of alternate supports was continued with this screening test of a magnesium silicate-supported catalyst which was directed at combining the properties of MgO and SiO_2 . The activity and hydrocarbon selectivity were both low compared to previous catalysts activated with H_2 . Bulk and specific activities were never greater than 22 mols syngas/kg cat/hr and 0.14 mols Co/mol Co/min, respectively. Total fuels selectivity was generally between 50-62%.
- $\text{Co}_2(\text{CO})_8/\text{Ti}(\text{OPr})_4/\text{SiO}_2$ -- This catalyst was prepared and tested to examine the effect of the silica support with the Ti-promoter. Throughout this test the syngas conversion ranged from 11 to 41% compared to 21 to 62% for the Zr-promoted catalyst, indicating the lower activity obtained by using Ti. The total fuels selectivity was fair at between 60-70%.
- $\text{Co}_2(\text{CO})_8/\text{Zr}(\text{OPr})_4/\text{SiO}_2$ -- This catalyst was chosen for an extended slurry test because it had given the best performance of any catalyst to date in the slurry reactor. Besides determining catalyst life, other objectives of the test were to collect liquid products for fuel property characterization, to obtain data for kinetic studies and to collect wax product for DOE-funded wax-upgrading studies at UOP/Signal Co. For the initial 350 hours on-stream during this quarter, catalyst performance was stable with bulk activity between 47-53 mols syngas/kg cat/hr at 240°C .

Catalyst characterization during this quarter centered around surface area determination and H_2 chemisorption on the $\text{Co}/\text{Zr}/\text{SiO}_2$ catalyst. The surface area was $316 \text{ m}^2/\text{g}$, which was 50% greater than the $\text{Co}/\text{Zr}/\text{Al}_2\text{O}_3$ catalyst and likely accounts for some of its enhanced activity. The $\text{Co}/\text{Zr}/\text{SiO}_2$ catalyst had an active metal surface area which was an order of magnitude larger than that of the alumina catalyst, indicative of improved dispersion. The chemisorption data was similar to literature values reported for Co on silica.

Data from the slurry test of the H_2 -activated $\text{Co}/\text{Zr}/\text{Al}_2\text{O}_3$ basecase catalyst was fitted to two kinetic expressions. At a high H_2/CO feed ratio and high space velocity, the data was best described by the following rate equation:

$$-R_{\text{CO}+\text{H}_2} = kP_{\text{H}_2}^n, \text{ where } n=1.1$$

The data at low H_2/CO feeds were best fit by the following expression, which incorporates H_2O inhibition:

$$-R_{\text{CO}+\text{H}_2} = \frac{kP_{\text{H}_2} P_{\text{CO}}}{P_{\text{CO}} + KP_{\text{H}_2\text{O}}}, \text{ where } k=0.349, K=0.425$$

The activation energy was relatively low for Fischer-Tropsch catalysts, being in the range of 33-44 kJ/mole.

The $\text{Co}/\text{Zr}/\text{SiO}_2$ data was best described by the second expression also, with $k=0.328-0.775$ and $K=0.466-0.302$ for the $240^\circ\text{C}-280^\circ\text{C}$ range. The activation energy was slightly higher at 51 kJ/mole.

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1.0 INTRODUCTION

The future use of coal as a transportation fuel will depend on the development of an economical and energy efficient liquefaction process. The two most advanced processes are the direct liquefaction route involving the dissolution of coal in a solvent aided by a mild hydrogenation and the indirect route in which coal is first gasified to synthesis gas followed by the Fischer-Tropsch reaction. The indirect liquefaction process is the only one currently practiced commercially and, in this respect, has a firm data base of practical experience.

The Fischer-Tropsch reaction, in which carbon monoxide is reduced by hydrogen and polymerized, produces hydrocarbons with a broad range of molecular weights, from methane to paraffin waxes. This creates the need for further downstream processing such as hydrocracking and light olefin oligomerization to maximize the yield of liquid fuel product. Since the discovery of the Fischer-Tropsch reaction, extensive research has been aimed at controlling the product selectivity in order to minimize downstream refining and still remains a prime target for innovation. Previous research has shown that selectivity is mainly controlled by catalyst composition and process conditions. Despite the vast effort in catalyst research, no catalyst has been developed that yields a narrow product distribution of only gasoline or diesel fuel. Because of this, product selectivity has been more successfully controlled by manipulating process conditions.

Since the Fischer-Tropsch reaction is exothermic, control of the reaction heat plays a major role in determining product selectivity. Suspending the catalyst in a liquid medium offers the best means of heat transfer and temperature control. Thus slurry phase operation has been shown to give improved liquid product selectivity mainly by lowering the light gas yield. The amount of data from slurry phase operation, however, is limited to only a few studies and significant differences have been reported in yields, catalyst life and ease of operation. One consistent observation is the lower gas yields and improved gasoline and diesel product selectivity. The improved temperature control has allowed this technology to be useful in converting carbon monoxide-rich synthesis gas from the latest coal gasifiers.

Slurry phase operation also appears to be more amenable to scale-up. Much research remains to be done to fully determine the potential of slurry phase Fischer-Tropsch processing and its further development is an important part in our country's program to establish viable technology for converting coal to conventional hydrocarbon fuels.

Under prior contract number DE-AC22-80PC30021 with the Department of Energy, Air Products and Chemicals, Inc. developed several new slurry-phase Fischer-Tropsch catalyst systems that provided enhanced selectivity to liquid fuel products. One group of these catalysts included Co or Ru carbonyls on a specially promoted/modified support. To further develop and improve these catalyst systems, Air Products, by the current contract to DOE, has begun a program to reproduce, evaluate and characterize these catalysts in detail. Examination of the catalyst kinetics in the slurry phase, along with fuel product characterization will be used to improve process design. Knowledge gained from these studies will provide a basis for the development of novel improved catalysts and process concepts for the selective production of liquid transportation fuels from synthesis gas. Work accomplished in the fifth quarter is described in this report.

2.0 OBJECTIVE

The major goal of this project is to thoroughly investigate the preparation, characterization and performance of metal carbonyl cluster-based catalysts for use in slurry phase Fischer-Tropsch technology. As this understanding of catalyst behavior increases, improved catalysts will be designed and process concepts developed toward increasing catalyst activity, lifetime and selective production of liquid fuel product. The objectives will be addressed by the following four tasks:

Task 1 -- Develop a project work plan which presents the detailed activities to be performed in achieving the objectives of this project. This task has been completed in the first quarter.

Task 2 -- Develop improved supported cobalt and ruthenium carbonyl cluster-based catalysts by utilizing the promising leads discovered during prior work at Air Products under DOE contract number DE-AC22-80PC30021, which has shown that metal carbonyls supported on modified aluminas exhibit high activity, stability, and good selectivity to liquid fuels in the slurry phase Fischer-Tropsch process. New catalyst compositions designed to give enhanced selectivity to liquid fuels will also be developed.

In this task, catalysts will be evaluated and tested for their potential to convert synthesis gas into liquid hydrocarbon fuels. Catalysts will be studied by a combination of tests in stirred and fixed-bed reactors and will be evaluated on the basis of activity, selectivity, stability and aging. In addition, catalysts will be characterized by surface and bulk analyses.

Improvements in these catalysts will focus predominantly upon:

- Increasing catalyst activity
- Improving product selectivity for liquid fuels and reducing the yield of methane
- Developing catalyst systems active at high CO:H₂ ratios
- Incorporating water-gas shift activity, either directly in the catalyst or utilizing a mixture of catalysts in the slurry

Task 3 -- The baseline catalyst compositions derived from both cobalt and ruthenium carbonyl clusters will be used to establish baseline slurry Fischer-Tropsch rate constants and activation energies. Then the more active and selective slurry catalyst compositions, identified under Task 2, will also be used in deriving slurry FT kinetic parameters. An existing backmixed CSTR model will be used in fitting the kinetic parameters. The kinetic parameters obtained will then be input to a three-phase bubble column computer model in order to predict conversions and space time yields in commercial scale bubble column units under a range of operating conditions.

An attempt will be made to determine kinetic expressions that describe the rate of formation of individual products or product fractions. This will be used to predict space time yields of individual product components or fuel fractions in a commercial scale bubble column.

Finally, mechanistic concepts will be examined, such as olefin reincorporation into growing chains, by adding small amounts of olefins to the feed and determining the effect on product selectivities.

Task 4 -- In this task, hydrocarbon product fractions, accumulated from some of the longer slurry tests of the improved catalysts, will be collected under constant process conditions and subjected to a series of tests to evaluate their properties as specification fuel.

3.0 RESULTS AND DISCUSSION

3.1 Task 1 -- Project Work Plan

This task was completed and reported on in the first quarter report.

3.2 Task 2 -- Development of Improved Supported Catalyst Compositions

(a) Catalyst Preparation

(i) Co(NO₃)₂/Zr(OPr)₄/SiO₂ (Catalyst #8466-28)

This catalyst was prepared from a more conventional cobalt source to establish a comparative basis for the silica-supported, cobalt carbonyl based catalysts. This catalyst composition was also similar to that described in a patent by Shell Oil Company (1), except that our catalyst had a lower cobalt loading. This composition will thus provide for a comparison between low-oxidation state cobalt carbonyl and conventional cobalt salts as active metal precursors. Cobalt and zirconium loadings were kept at a level similar to our basecase cobalt carbonyl/Zr/SiO₂ catalyst (#8466-18) to facilitate performance comparisons.

(ii) Ru₃(CO)₁₂/Zr(OPr)₄/SiO₂ (Catalyst #8466-37)

Our previous gas phase test of the alumina-supported, Zr-promoted, Ru₃(CO)₁₂ catalyst showed some of the highest specific activities for any of the alumina-supported catalysts (see gas phase run #7977-32-478 in Oct-Dec 1984 Quarterly Report). It did perform poorly, however, in the slurry reactor. Since the silica support improved the cobalt catalyst performance, it was worthwhile to try it as a support for the ruthenium catalyst. It was prepared with a slightly higher Ru loading than the alumina supported catalyst. The Ru-to-Zr atom ratio was kept the same as the Co-to-Zr atom ratio in the basecase composition.

(iii) Co₂(CO)₈/TiO₂ (Catalyst #8466-38)

A titanium-promoted Co on alumina catalyst was previously studied in both the fixed-bed and slurry reactors and showed a trend toward producing larger quantities of C₃ and C₄ olefins. This unusual selectivity might be enhanced further by using TiO₂ as the support, as well as the promoter. Thus, this catalyst was also prepared as part of our effort in examining alternate supports.

(iv) Fe₃(CO)₁₂/Zr(OPr)₄/SiO₂ (Catalyst #8466-40)

One of our objectives has been to incorporate water-gas shift (WGS) activity into the cobalt-based catalysts. This has been attempted by adding Fe to the composition but with only limited success at relatively low Fe loadings. It appeared that an Fe-only catalyst with a standard metal loading should be prepared from the metal carbonyl to establish its inherent WGS activity. This was prepared this quarter using a silica support and the standard zirconium promoter.

(b) Gas Phase Screening

All of the catalysts screened in the fixed-bed reactor this quarter were activated using a pure H₂ procedure as described in Section 4.1 (b). Specific run conditions did vary somewhat and are documented accordingly. Gas phase performance data is summarized in Table 1.

(i) Co₂(CO)₈/Ti(OPr)₄/SiO₂ - Run #8413-51-27, Catalyst #8466-27

The effect of titanium as a promoter for the silica-supported cobalt carbonyl catalyst was investigated by this gas phase test of 4.4% Co/4.0% Ti on silica. The performance is compared in Table 2 with the zirconium-promoted catalyst that was examined last quarter. The activity of the titanium-promoted catalyst was significantly lower than the zirconium-promoted catalyst. At 220°C, the specific activity was only 0.072 moles CO/mole Co/min, which was 77% lower than with zirconium. The difference became less with increasing reaction temperature, but still, at 260°C the specific activity of the titanium-promoted catalyst was still 27% lower. Bulk activity was also low with the titanium promoter compared to the zirconium promoter. At 220°C the bulk activity was 13 moles syngas/kg cat/hr, a 58% decline from the zirconium-promoted catalyst, while at 260°C it was 20% less active than with zirconium.

A similar comparison of zirconium and titanium promoted cobalt catalysts supported on alumina did not show such a large difference in activity, although the titanium-promoted catalyst showed the lower activity in that comparison also. It should be noted that the titanium-promoted cobalt catalysts using either silica or alumina supports had similar activities when tested at similar conditions. Perhaps titanium interacts with cobalt more strongly than does zirconium and inhibits the cobalt activity. XPS and chemisorption studies may help to explain this difference.

There was also a substantial shift in hydrocarbon selectivity to lighter products with the titanium promoter, which was most prevalent at the lower temperatures. A significant amount of C₃, C₄ and C₅ olefins was produced, accounting for 39% selectivity at 220°C and 29% at 240°C. The best liquid fuel (C₅₋₂₃) selectivity was 71%, obtained at 260°C with the major portion being the lighter, gasoline-range fuel. A high olefin selectivity was also observed for the alumina-supported Co/Ti catalyst but it was only half of what the silica catalyst produced.

(ii) Co₂(CO)₈/Zr(OPr)₄/MgO·3.6SiO₂ - Run #8413-45-25, Catalyst #8466-25

An alternate support consisting of a commercially available magnesium silicate (Florisil, MgO·3.6SiO₂) was examined for the Co₂(CO)₈/Zr(OPr)₄-prepared catalyst system. The objective was to combine the properties of MgO and SiO₂ as discussed in the previous quarterly report.

The results for this 3.7% Co/7.2% Zr/MgO·SiO₂ catalyst in Table 1 show that the bulk and specific activities were similar to the basecase Co/Zr/Al₂O₃ catalyst. At 240°C the bulk activity was 24 moles syngas/kg cat/hr and specific activity was 0.23 moles CO/moles Co/min.

Hydrocarbon selectivity, however, was quite different from the basecase Co/Zr/Al₂O₃ catalyst but similar to the titanium-promoted Co/silica catalyst. Selectivity was shifted to light products with C₁₂+ selectivity never greater than 15%. The bulk of the hydrocarbon product was in the C₂ to C₁₁ range. The selectivity to C₃ - C₅ olefins was high for this catalyst also and was 38% at 220°C and 28% at 240°C.

(iii) Co(NO₃)₂/Zr(OPr)₄/SiO₂ - Run #8413-58-28, Catalyst #8466-28

As previously done with the alumina-supported, cobalt catalyst, a more conventional cobalt source was examined with the silica-supported catalyst. Cobalt nitrate was used and the resulting catalyst contained 4.6% Co and 7.5% zirconium.

Table 3 compares the gas phase results of this nitrate-derived catalyst with those of the carbonyl-based catalyst. As with the alumina-supported cobalt catalysts, this nitrate-derived, silica-supported catalyst was less active and produced a greater amount of high molecular weight hydrocarbons than the carbonyl catalyst. At 240°C, the nitrate catalyst had a bulk activity of 31 moles syngas/kg catalyst/hr compared to 55 moles syngas/kg cat/hr for the carbonyl catalyst. When the temperature was increased to 260°C, differences in activity were not as great. The bulk activity for the nitrate catalyst was 62 moles syngas/kg cat/hr at 260°C, with a specific activity of 0.43 moles CO/mole Co/min. This compares to 74 moles syngas/kg cat/hr and 0.62 moles CO/mole Co/min, respectively, for the carbonyl catalyst. It is worth noting that the silica-supported, nitrate-derived catalyst showed higher activity and similar selectivity when compared to the carbonyl-derived catalyst on alumina.

Liquid fuels (C₅₋₂₃) selectivity was reasonably good with the gasoline range predominating at 220°C and heavy diesel product at 240°C and 260°C. For all three temperatures the C₅₋₂₃ fraction was between 57 and 61%.

Initially at 240°C the wax selectivity (C₂₄₊) was low at <1% but during the run at 260°C the wax selectivity increased substantially. Following the 260°C mass balance, a sample was obtained at 240°C and showed 23% wax selectivity. This compares to 3% for the carbonyl catalyst. It is likely that a certain amount of time was needed for the heavy product to build up and drain from the reactor.

(iv) Ru₃(CO)₁₂/Zr(OPr)₄/SiO₂ - Run #8413-73-37, Catalyst #8466-37

Because ruthenium exhibited high activity with the alumina support, a 4.0% Ru/3.3% Zr on silica catalyst was examined and it gave the highest bulk and specific activities of any catalyst to date. At 240°C, this Ru/Zr/silica catalyst gave 49% syngas conversion with bulk activity of 71 moles syngas/kg cat/hr and specific activity of 0.83 moles CO/mole Ru/min. At 260°C, syngas conversion increased to 56% with bulk activity and specific activity increasing to 81 moles syngas/kg cat/hr and 1.05 moles CO/mole Ru/min, respectively.

When compared at the same temperature of 260°C, this 4.0% Ru/Zr/silica catalyst had triple the bulk activity and double the specific activity of the 2.91% Ru/Zr/alumina catalyst. An increase in catalyst surface area is at least partially responsible for the enhanced activity but catalysts prepared from different supports will have to be compared at similar surface areas to rule out this factor.

The water-gas shift activity of this Ru/Zr/silica catalyst was low as indicated by comparing the feed ratio, which was 1, to the observed usage ratios of 0.45, 0.39 and 0.46 at 220°, 240° and 260°C, respectively. This was similar to the shift activity observed on the alumina-supported Ru catalyst.

In general, the hydrocarbon selectivity of this Ru/Zr/silica catalyst was shifted toward higher molecular weight products. At 240°C, the C₁₉+ fraction was 54% of the hydrocarbon product and at 260°C it decreased to 39%. This enhanced selectivity to wax is not unusual since Ru catalysts are used for the polymethylene synthesis (2). In this process, CO is hydrogenated over Ru metal at low temperature (100°-140°C) and high pressure (1000 atm) to give 50-55 wt% solid wax having an average molecular weight of 15,000-20,000. Methane selectivity was low, especially for the gas phase reactor, and never was greater than 5.3%. The C₂₋₄ cut was also small and at most accounted for 6.4% of the hydrocarbons. Total liquid fuel (C₅₋₂₃) selectivity was between 59 and 64% with the major portion being in the diesel range.

(v) Co₂(CO)₈/TiO₂ - Run #8413-82-38, Catalyst #8466-38

Research by Bartholomew's group on supported Co catalysts for CO hydrogenation has shown that TiO₂ as a support yields catalysts having superior activity (3). As one of our objectives to examine alternate supports, we prepared a 3.5% Co on titania catalyst using Co₂(CO)₈. This catalyst would also test the effect of very high loadings of titanium as a promoter and in effect, examine the use of titanium as both a promoter/support combination.

This catalyst had moderate activity similar to that of the Ti-promoted Co/silica catalyst and was 35 to 50% more active than the Ti-promoted Co/alumina catalyst. At 240°C, this Co/titania catalyst gave 30% syngas conversion with 32 moles of syngas converted/kg cat/hr and 0.31 moles of CO converted/mole Co/min. At 260°C, there was a modest increase in syngas conversion to 39%, while bulk activity increased to 45 moles syngas/kg cat/hr. Specific activity increased 23% to 0.38 moles CO/mole Co/min. Overall, the activity was substantially lower than that of the Co/Zr/silica catalyst, which had given the best performance to date in the current contract, until the Ru/Zr/silica catalyst just tested.

The enhanced light olefin selectivity observed with the Ti-promoted, silica and alumina-supported Co catalysts was not obtained with this Co/TiO₂ catalyst. This resulted in an increase in the C₅₋₂₃ liquid fuel selectivity to the 60-67% range at 240°C and 260°C. Also, the distribution of liquid fuel products was more evenly spread-out between the gasoline, diesel and heavy diesel range. Wax (C₂₄₊) selectivity was substantial at >19% for all temperatures. This may be the result of low cobalt dispersion on the low surface area titania (50 m²/g).

(c) Slurry Reactor Tests

During this quarter, slurry screening tests were performed on three catalysts and an extended test was initiated on a fourth catalyst, all in the 1-liter reactors. In the screening tests, the operating parameters were varied to determine the conditions necessary for optimum catalyst performance. Since pure H₂ activation was previously shown to improve catalyst performance (see April-June 1985 Report), it was used for all subsequent catalyst tests, including this quarter's tests and will be used for all future tests. The following four catalysts were tested:

- A Zr-promoted, cobalt carbonyl catalyst supported on silica and containing some Fe in another attempt to incorporate water-gas shift activity. The use of silica, which is less reactive toward metal carbonyls, may allow the activity of Fe to be observed.
- A Zr-promoted, cobalt carbonyl catalyst supported on a magnesium silicate to examine an alternate support that combines the properties of magnesium oxide and silica.

- A silica-supported, cobalt carbonyl catalyst promoted with Ti to examine the use of an alternate promoter with the more active silica-supported system.
- The Co/Zr/silica catalyst was selected for study in an extended slurry test since its performance was the best to date of any catalyst examined during this contract. The objectives of the test were twofold: (1) to examine performance stability and (2) to study the reaction kinetics in more detail.

In gas phase testing, all four catalysts were as active or more active than the basecase Co/Zr/Al₂O₃ catalyst. Selected results from the slurry tests are listed in Table 5, along with representative results of all previous slurry tests from this contract for comparison.

(i) Co₂(CO)₈/Fe₃(CO)₁₂/Zr(OPr)₄/SiO₂ -- Test #8670-12-23, Catalyst #8466-22

The inclusion of Fe into the basecase Co/Zr/Al₂O₃ catalyst did not improve the water-gas shift activity as was hoped. Since the use of a silica support resulted in enhanced catalyst performance, perhaps the water-gas shift activity of Fe would also be enhanced. Thus this catalyst was prepared, containing 3.7% Co and 0.72% Fe on silica with the standard Zr (7.3%) promoter. The catalyst activation procedure is described in Section 4.1. The activity, conversion and selectivity data of this screening test are summarized in Table 6. The data for each mass balance sample are listed in Tables 7-34 and hydrocarbon distributions are illustrated in Figures 1-14.

The catalyst was brought on-stream at 240°C and the first 3 mass balances were done at this temperature. Initially the Co/H₂ feed ratio was high in CO at 1.6 and the space velocity (SV) was at 2.0 l/g cat.hr. For the first 3 samples, the CO/H₂ ratio and space velocity were varied as follows:

<u>Sample</u>	<u>CO/H₂</u>	<u>SV</u>
6	1.6	2.0 l/g cat.hr
14	1.7	1.0
17	1.0	1.0

Compared to the previously tested Co/Fe catalysts on alumina, this catalyst showed roughly twice the bulk activity and 50-100% greater specific activity at 240°C. Sample 6 showed good bulk activity at 34 mols syngas/kg cat/hr, which decreased by half as the space velocity was lowered by 50%. Total fuels selectivity (C₅₋₂₃) was quite good for Sample 6 at 73%, due to low methane selectivity (<5%) but with a fairly high wax make (13%). Surprisingly upon lowering the space velocity from 2.0 to 1.0, the light gas make increased to 14% C₁ and 24% C₂₋₄ (Sample 14). Then, while keeping the space velocity at 1.0, the H₂ concentration was increased (Sample 17) and the hydrocarbon selectivity returned to heavier products. Both of these selectivity trends are opposite what would be expected. Compared to the previous Co/Fe/Al₂O₃ catalysts at 240°C the selectivity was similar or slightly better for the current catalyst.

The temperature was then increased to 260°C for the next series of samples which are outlined as follows:

<u>Sample</u>	<u>CO/H₂</u>	<u>SV</u>
20	1.0	1.0 L/g cat/hr
23	1.5	1.0
26	2.0	2.0
32	1.5	2.0
35	1.0	2.0
38	1.1	2.0

Increasing the temperature from 240°C to 260°C resulted in a slight improvement in total fuels selectivity to 67% by lowering the light gas and wax selectivity. The activity increased only very slightly, however, as the temperature was raised. Perhaps catalyst deactivation was beginning to accelerate. CO-rich feeds were examined in the next two samples and, as expected, the C₁₋₄ selectivity decreased to give the best C₅₋₂₃ selectivity of this test at 74-76% (Samples 23 and 26). The highest straight-run diesel (C₁₂₋₁₈) selectivity was also obtained at these conditions at >30%. Surprisingly the wax selectivity did not increase. Bulk activity, however, was at its lowest level with these CO-rich feeds.

From this point the effect of increasing the H₂ concentration was examined in the next two mass balance periods (Samples 32 and 35, Tables 19-22, Figures 7 and 8). The result was a doubling of bulk activity from 14 to 30 moles syngas/kg cat/hr upon decreasing the CO/H₂ ratio from 2.0 to 1.0. Specific activity also increased by 70%. The hydrocarbon selectivity shifted as expected to lighter products with methane at 13% and wax (C₂₄+) at <5%. The straight run gasoline fraction became predominant at 40%. The final mass balance point in this set at 260°C (Sample 38, Tables 23 and 24, Figure 9) had only a slightly higher CO concentration than the previous sample (CO/H₂=1.1 vs. 1.0) but a doubling in pressure. Activity continued to rebound from the CO-rich conditions and the catalyst performed nicely at higher pressure. Total fuels selectivity was slightly improved from the previous sample as the selectivity shifted back slightly toward heavier product. This shift was greater than expected for such a slight increase in CO concentration and was probably more influenced by the pressure increase.

The temperature was further increased to 280°C for the following three samples:

<u>Sample</u>	<u>CO/H₂</u>	<u>SV</u>
41	1.1	2.0 L/g cat/hr
44	1.5	2.0
47	2.0	2.0

The highest bulk and specific activities for this catalyst were achieved with this temperature increase but the poorest total fuels selectivity (50%) resulted as well, with methane selectivity at 23% (Sample 41, Tables 25-26, Figure 10). The CO/H₂ ratio was increased to 1.5 and then 2.0 for the next two samples. The previous observation that the catalyst prefers CO-lean feeds was reconfirmed by these two mass balance points. Bulk and specific activities declined and C₅₋₂₃ selectivity increased with the increase in CO concentration (Samples 44 and 47, Tables 27-30, Figures 11-12). This third sample at 280°C showed a bulk activity of 24 moles syngas/kg cat/hr compared to 21 moles syngas/kg cat/hr for the Co/Fe/Al₂O₃ catalyst at the same conditions. Total fuels selectivity was also similar for both catalysts. Apparently the silica-supported catalyst had deactivated.

The degree of deactivation was determined by the next sample point in which conditions from earlier in the test (see Sample 35) were repeated as follows:

<u>Sample</u>	<u>Temp.</u>	<u>CO/H₂</u>	<u>SV</u>	<u>Same as Sample</u>
50	260°C	1.0	2.0 l/g cat/hr	35

Bulk activity declined 14% from the middle part of the test, while specific activity dropped 9%. Total fuels selectivity also declined from 62 to 54% (Sample 50, Tables 31-32, Figure 13). The exposure to 280°C was a likely reason for the accelerated deactivation and selectivity change.

Finally, with no change in CO/H₂ ratio and space velocity, the temperature was lowered to 240°C. Activity was quite low at 18 mols syngas/kg cat/hr with no change in selectivity from the previous 260°C sample. It was now showing similar activity to the Co/Fe/Al₂O₃ catalyst with even poorer C₅₋₂₃ selectivity, indicating that the Zr promoter was having little effect on catalyst performance once deactivation had become too extreme. The main objective of incorporating water-gas shift activity into the cobalt catalyst was not achieved as indicated by the low usage ratios compared to their corresponding feed ratios. The usage ratios were in the same range as those for the Co/Fe/Al₂O₃ catalyst. The water-gas shift activity of the Fe was still inhibited, perhaps by not including enough Fe in the composition. To address this an Fe-only catalyst on silica will be examined in the future.

(ii) Co₂(CO)₈/Zr(OPr)₄/MgO·3.6SiO₂ -- Test #8670-60-25, Catalyst #8466-25

Examination of alternate supports was continued with this screening test of a magnesium silicate-supported catalyst. As discussed in the previous quarterly (July-September 1985), it was hoped that magnesium silicate would combine the favorable properties of MgO and SiO₂. The catalyst contained 3.7% Co and 7.2% Zr which were similar loadings to the basecase alumina and silica catalysts. The activation procedure is described in Section 4.1 and the activity, conversion and selectivity data of this screening test are summarized in Table 35. The data for each mass balance sample are listed in Tables 36-61 and hydrocarbon distributions are illustrated in Figures 15-27.

The first series of conditions were at 240° and a space velocity of 2.0 l/g cat.hr. The CO/H₂ ratio was varied from 1.0 to 2.0 as shown:

<u>Sample</u>	<u>CO/H₂</u>	<u>SV</u>
3	1.0	2.0 l/g cat.hr
6	1.5	2.0
9	2.0	2.0

The initial sample showed relatively low activity at 22 mols syngas/kg cat.hr which became worse as the CO/H₂ ratio was increased (Samples 3-9, Tables 36-41, Figures 15-17). The hydrocarbon selectivity changed unexpectedly toward lighter products as the CO concentration was increased in this series of samples. The straight run gasoline fraction (C₅₋₁₁) increased from 29 to 41%. At the same conditions as Sample 3, the Co/Zr/silica catalyst had 67% greater bulk activity and a total fuels selectivity of 70%.

While maintaining the temperature at 240° and decreasing the space velocity to 1.0 l/g cat.hr, the CO/H₂ ratio was varied as follows:

<u>Sample</u>	<u>CO/H₂</u>	<u>SV</u>
12	2.0	1.0 l/g cat.hr
15	1.0	1.0
18	1.5	1.0

Bulk activity continued to be poor for these 3 mass balance periods and the total fuels selectivity declined to 60% or less (Samples 12-18, Tables 42-47, Figures 18-20). The slight decline in fuels selectivity could be attributed to an increase in wax selectivity at the lower space velocity and thus longer residence time.

An increase in temperature to 260°C and space velocity followed for the next three mass balance periods as shown:

<u>Sample</u>	<u>CO/H₂</u>	<u>SV</u>
24	1.5	2.0 l/g cat.hr
27	2.0	2.0
30	2.0	2.0

An improvement in bulk activity was observed which amounted to a 32% increase above the activity at 240°C (Sample 24, Tables 48-49, Figure 21). Methane selectivity jumped to 19%, however, while C₅₋₂₃ selectivity declined to 51% from 62% at 240°C. Increasing the CO/H₂ ratio to 2.0 resulted in a bulk activity near 15 mols syngas/kg cat/hr for Samples 27 and 30 (Tables 50-53, Figures 22-23). Some deactivation had occurred since the activity at 240°C earlier in the run was also 15 mols syngas/kg cat/hr (see Sample 9). The hydrocarbon selectivity continued to be shifted toward methane and light gases. Three more samples at 260°C were obtained at a lower space velocity as follows:

<u>Sample</u>	<u>CO/H₂</u>	<u>SV</u>
35	2.0	1.0 L/g cat/hr
38	1.5	1.0
40	1.0	1.0

The trend observed with other cobalt catalysts was also evident in this series of samples in that as the H₂ concentration increased so did the catalyst performance, both in terms of activity and fuels selectivity. Bulk activity increased from 13 to 17 mols syngas/kg cat/hr and specific activity from 0.099 to 0.14 mols CO/mol Co/min on proceeding from Sample 35 through 40 (Tables 54-59, Figures 24-26). Total fuels selectivity did not follow a simple trend but was best for Sample 40, where the CO/H₂ ratio was lowest. Again, comparing the 260°C data of Samples 35-40 with the 240°C data of Samples 12-18, there was only a slight improvement in activity and a decline in fuels selectivity.

The final mass balance period was at the same conditions as the initial sample from this test: 240°C, CO/H₂=1.0 and space velocity=2.0 L/g cat/hr. Both bulk and specific activity had declined by 50% from the initial results. Total fuels selectivity had improved slightly from 62 to 65% with the major increase occurring in the C₅₋₁₁ range.

Overall this catalyst was significantly less active than both the silica and alumina-supported Co/Zr catalysts and yielded poorer fuels selectivity.

(iii) Co₂(CO)₈/Ti(OPr)₄/SiO₂ -- Test # 8670-57-27, Catalyst #8466-27

The use of Ti as a promoter was examined previously for the alumina-supported, cobalt catalyst, which showed improved liquid fuels selectivity but lower activity compared to the Zr-promoted basecase catalyst. The objective of this screening test was to improve the Ti-promoted catalyst activity while maintaining the selectivity enhancement by using a silica support instead of alumina. The atom ratio of Co to Ti was kept the same as the Co to Zr ratio in the basecase. The Co loading was also kept similar to the basecase and thus a 4.4% Co/4.0% Ti on silica catalyst was prepared. The gas phase test showed reasonable activity, not as good as the Zr-promoted catalyst but good enough to warrant this slurry screening test.

The catalyst was activated in the usual manner with pure H₂ as described in Section 4.1. The summary data from the test are presented in Table 62 and individual mass balance sample data and hydrocarbon distributions are found in Tables 63-94 and Figures 28-43, respectively.

The catalyst was initially studied at 240°C with the usual approach of varying the CO/H₂ feed ratio and the space velocity as outlined:

<u>Sample</u>	<u>CO/H₂</u>	<u>SV</u>
3	1.0	2.0 L/g cat/hr
6	1.9	2.0
9	1.5	2.0
12	2.0	1.0
15	1.0	1.0
18	1.5	1.1

In general, the activity of this catalyst was not good at 240°C. Bulk activity remained below 18 mols syngas/kg cat/hr and specific activity below 0.09 mols CO/mol Co/min for all samples at 240°C. The best activity was obtained with a low CO/H₂ ratio and high space velocity (Sample 3, Tables 63-64, Figure 28) but this was only 50% of the activity obtained with the Zr-promoted catalyst at the same conditions. As with the other cobalt catalysts, increasing the CO/H₂ ratio was detrimental to activity, however total fuels selectivity improved (Samples 6 and 9, Tables 65-68, Figures 29-30).

Decreasing the space velocity to 1.0 L/g cat/hr caused a further drop in activity to the lowest levels observed for this catalyst during the entire test (Samples 12-18, Tables 69-74, Figures 31-33). There was a slight improvement in total fuels selectivity to the 63-67% range which was quite similar to the Zr-promoted catalyst. The Ti-promoted catalyst tended to make less heavy product and consequently more methane and light gases. Compared to the Co/Ti/Al₂O₃ catalyst at 240°C, this catalyst showed the same range of activities and total fuels selectivity.

The next seven mass balances were performed at 260°C with the following variations in CO/H₂ ratio and space velocity:

<u>Sample</u>	<u>CO/H₂</u>	<u>SV</u>
24	1.0	2.0 L/g cat/hr
27	1.5	2.0
30	2.0	2.0
33	2.0	1.0
38	1.5	1.0
40	1.0	1.0
42	1.0	3.0

Of all 260°C samples, bulk activity increased to its highest level (30 mols syngas/kg cat/hr) with Sample 24, where again the space velocity was high and CO/H₂ ratio low. This was greater than any activity achieved with the Co/Ti/Al₂O₃ catalyst but still 34% lower than the Zr-promoted, silica catalyst. As the CO/H₂ ratio was increased to 2.0, the bulk activity declined to 20 mols syngas/kg cat/hr (Samples 27 and 30, Tables 77-80, Figures 35-36), while the C₅₋₂₃ selectivity increased from 62 to 68%.

Upon decreasing the space velocity to 1.0 L/g cat/hr, the bulk activity did not vary much with CO/H₂ ratio, falling in the 14-17 mols syngas/kg cat/hr range (Samples 33-40, Tables 81-86, Figures 37-39). This is only 10% below the activity of the Zr-promoted catalyst at the same conditions as Sample 40. Total fuels selectivity had improved to its best level, breaking 70% for Sample 33, putting it in the same range as the Zr-promoted catalyst.

A final mass balance at 260°C was performed at a high space velocity of 3.0 L/g cat/hr (Sample 42, Tables 87-88, Figure 40). The bulk activity was less than the initial 260°C sample, which was at a lower space velocity, indicating that catalyst deactivation had occurred. During the entire time at 260°C the methane selectivity varied over a narrow range of 11 to 15%.

Two mass balance periods were then examined at 280°C as follows:

<u>Sample</u>	<u>CO/H₂</u>	<u>SV</u>
44	1.0	2.0 L/g cat/hr
47	1.0	3.0

For Sample 44 (Tables 89-90, Figure 41) the bulk activity had increased to 37 mols syngas/kg cat/hr compared to 53 mols syngas/kg cat/hr for the Zr-promoted catalyst at analogous conditions. Selectivities were similar for the two catalysts, with CH₄ >20% and total fuels <60%. Increasing the space velocity for Sample 47 (Tables 91-92, Figure 42) boosted the activity slightly without any significant changes in selectivity. The Ti-promoted, alumina catalyst had deactivated to a much greater extent by this point since the bulk activity was never greater than 17 mols syngas/kg cat/hr at 280°C, albeit the CO/H₂ ratio was ≥1.5 during that period.

A final sample was obtained at the initial run conditions of 240°C, CO/H₂=1.0 and space velocity=2.0 L/g cat/hr (Sample 50, Tables 93-94, Figure 43). A 37% decline in bulk activity occurred, however, specific activity had actually increased by 6% compared to the initial results (see Sample 3). This was unusual and resulted in an improved usage ratio. The total fuels selectivity also improved slightly due to a large drop in C₂₋₄ selectivity, although CH₄ selectivity was fairly high at 18%.

Throughout this screening test the syngas conversion ranged from 11 to 41% compared to 21-62% for the Zr-promoted catalyst, again indicating the lower activity obtained by using Ti. As discussed for the gas phase results, which showed the same behavior, the Ti may interact more strongly with the Co, inhibiting its activity.

The enhanced selectivity to C₃₋₅ olefins observed during the gas phase test of the Ti-promoted silica catalyst was not as pronounced in this slurry test. The C₃₋₅ olefin selectivity was still double that of the Zr-promoted catalyst, at least during the initial period at 240°C.

- (iv) Co₂(CO)₈/Zr(OPr)₄/SiO₂ -- Extended Test #8862-1-31,
Catalyst #8466-31

The silica-supported, Co/Zr catalyst was chosen for an extended slurry test because it had given the best performance of any catalyst studied to date in this contract, and, for that matter, in the previous contract. There were several other objectives for this test besides determining catalyst life. These included collecting liquid products for fuel property characterization, collecting wax for DOE-funded wax-upgrading studies at UOP/Signal Co., and to obtain the necessary data for kinetic studies.

The test was begun in December and achieved over 350 hours on-stream by the end of the quarter. The following conditions were chosen for the initial 1000 hour test period: 240°C, CO/H₂=0.5, space velocity=1.8 L/g cat/hr and 300 psig. The low CO/H₂ ratio was chosen due to the poor water-gas shift activity of these cobalt catalysts. Because of a slightly higher catalyst charge and the maximum flow rate limitation of the mass flow controller, a space velocity of 2.0 L/g cat/hr could not be used with a CO/H₂ ratio of 0.5.

A summary of the performance data obtained during this quarter is found in Table 95. Tables 96-105 list the mass balance process conditions and hydrocarbon product distributions for each sample point, while the hydrocarbon weight distributions are shown graphically in Figures 44-48.

During the first 200 hours on-stream the performance was good. Bulk activity and syngas conversion was steady at 53 mols syngas/kg cat/hr and 66%, respectively. Methane selectivity was fairly high at 21 wt%, while total liquid fuels selectivity was only 52 wt%. On day 12 (262 hours on-stream, Sample 14) unexpected low activity was observed but by day 16 (359 hours) the activity had begun to return to its original level. No changes were made and the test was continued at the initial conditions.

(d) Catalyst Characterization

Hydrogen chemisorption experiments and B.E.T. surface area analysis were carried out on the 3.5% Co (ex carbonyl)/Zr/SiO₂ catalyst (#8466-18) that had been prepared and tested in the previous quarter (see July-September 1985 Quarterly Report). This catalyst had a 50% greater surface area (316 m²/g) than the basecase Co/Zr/Al₂O₃ catalysts (209 m²/g). The increased surface area may be partially responsible for the increase in activity observed with the silica-supported catalyst. The silica prior to loading had a surface area of 339 m²/g. Thus a 7% loss of surface area occurred through catalyst preparation. In the future a Co/Zr catalyst will be prepared on this same silica after lowering its surface area to that of the alumina. This will allow a more direct comparison of the two supports in the absence of any surface area effect.

Hydrogen chemisorption on this silica catalyst was an activated process, with the largest H₂ uptake occurring at 100°C just as with the alumina catalysts. The data are presented in Table 4, along with previous data from the alumina catalysts and some literature data. The 3.5% Co/silica catalyst had an active metal surface area nearly equal to that of the 10.8% Co/alumina and an order of magnitude larger than that of the 4% Co/alumina catalyst. Apparently, because of the reactivity of alumina with cobalt carbonyl, at low cobalt loadings nearly all of the cobalt had reacted with the alumina leaving only small amounts of active cobalt for H₂ chemisorption. As the loading was increased the reactive alumina sites were used up thus allowing more cobalt to remain active. Silica, however, does not show this reactivity toward metal carbonyls and thus more cobalt remains active for chemisorption.

In comparing our data with what Bartholomew (3) reported for 3% Co on silica and alumina, we observed quite similar H₂ uptake values and percent dispersions. A 22% cobalt/0.5% ruthenium catalyst reported in the patent literature by Gulf showed high H₂ uptake. This catalyst was prepared from Co(NO₃)₂ and the dispersion amounted to 8%.

3.3 Task 3 -- Slurry Reactor Kinetic Studies

The first set of slurry operation data to be analyzed by the Kinetic Analysis Program (KAP) was from the basecase Co/Zr/Al₂O₃ composition, which had been activated using pure H₂ (Test #8523-1-4, see April-June 1985 Quarterly Report). Fitting the data to one of the five rate expressions outlined in the previous quarterly report was not straight-forward. The data at high H₂/CO feed ratios and high space velocities (2.0 L/g cat/hr) was best described by the familiar first order rate equation (eq. 1).

$$-R_{CO+H_2} = kP_{H_2}^n \quad (1)$$

most commonly found to fit Fischer-Tropsch data. In our case the exponent n was equal to 1.1 and there was no dependence on CO. The data at low H₂/CO feed ratios and high space velocities (2.0 L/g cat/hr) was best described by equation (2), where H₂O inhibition is incorporated:

$$-R_{CO+H_2} = \frac{kP_{H_2} P_{CO}}{P_{CO} + KP_{H_2} O} \quad (2)$$

The rate constant k was 0.349 and the constant K, which relates to surface reaction equilibria, was 0.425. The energy of activation, E_A, for this catalyst was determined to be in the range of 33-44 kJ/mole.

Data from the Co/Zr/SiO₂ catalyst, which has shown the best performance to date (Test #8670-11-18, July-September 1985 Quarterly Report), was analyzed to derive a kinetic expression. None of the kinetic expressions were fully able to describe all the data. The expression that came closest was the same one that best fit the high CO feed data of the Co/Zr/Al₂O₃ catalyst (equation 2).

Equation 2 can be arranged as:

$$P_{H_2} / (-R_{CO+H_2}) = (K/k)(P_{H_2} O / P_{CO}) + (1/k) \quad (3)$$

so that a plot of $P_{H_2} / (-R_{CO+H_2})$ vs. $P_{H_2} O / P_{CO}$ should be linear if this rate

expression is applicable. The data are plotted in Figure 49 for the 240°C, 260°C and 280°C samples. The limited set of data appear to fit the linear expression fairly well. From the intercept, the rate constant k is derived with the values ranging from 0.328 to 0.775 cc/g cat/sec. K is then determined from the slope and ranges from 0.466 to 0.302.

The Arrhenius plot of ln k vs. 1/T is shown in Figure 50. An activation energy of 51 kJ/mole was obtained from this plot. This is slightly higher than the range found for the alumina supported catalyst. The literature contains relatively few kinetic studies of the Fischer-Tropsch reaction using cobalt catalysts (4-7), compared to the numerous studies with iron catalysts. From this available literature, the range of activation energies for cobalt catalysts was 67-117 kJ/mole. None of these catalysts were prepared from metal carbonyls nor studied in a slurry phase reactor. Our activation energies for metal carbonyl derived catalysts are significantly lower.

4.0 EXPERIMENTAL

4.1 Task 2 -- Development of Improved Supported Catalyst Compositions

(a) Catalyst Preparation

Unless otherwise noted, all catalyst preparations were carried out under a N_2 atmosphere using standard Schlenk techniques and a Vacuum Atmospheres dry box.

(i) $Co(NO_3)_2/Zr(OPr)_4/SiO_2$ (Catalyst #8466-28)

The silica (117.7g, Davison 952) was pretreated in the same manner as reported in the previous quarterly report (July-September 1985). A 350-cc solution of $Zr(OC_3H_7)_4 \cdot XC_3H_7OH$ (64.7g, 11.45g Zr) in hexane was impregnated onto the silica. After thorough mixing the hexane was evaporated off in vacuo. At this point the material was exposed to the laboratory air by spreading it into a large crystallizing dish and allowing it to stand overnight. A 350-cc aqueous solution of $Co(NO_3)_2$ (31.73g, 6.42g Co) was added to the silica in 5 portions, with thorough mixing between portions. The material was dried in a vacuum oven at ambient temperature overnight, then at $50^\circ C$ for 7 hours. The light pink solid was then placed in a muffle furnace at $115^\circ C$ for 2 hours and finally calcined at $300^\circ C$ in static air for 5 hours. The resulting black solid (144.0g) had the following elemental analysis: 4.6% Co and 7.5% Zr (Co/Zr=0.61).

(ii) $Ru_3(CO)_{12}/Zr(OPr)_4/SiO_2$ (Catalyst #8466-37),

The silica (99.8g, Davison 952) was pretreated in the same manner as the previous catalyst. The silica was impregnated with a 300-cc hexane solution containing $Zr(OC_3H_7)_4 \cdot XC_3H_7OH$ (25.2g, 4.46g Zr) and the hexane was removed in vacuo. The $Ru_3(CO)_{12}$ (9.22g, 4.37g Ru) was added to the silica in four steps, with each impregnation using a 225-cc THF solution. Solvent was evaporated off in vacuo between each step. 124.2g of yellow solid was obtained and had the following elemental analysis: 4.0% Ru and 3.3% Zr (Ru/Zr=1.2).

(iii) $Co_2(CO)_8/TiO_2$ (Catalyst #8466-38)

The TiO_2 (132.6g, Degussa P-25) was pretreated in the same manner as the silica was in the previous catalysts. The TiO_2 was impregnated with a 600-cc hexane/toluene (1:2) solution containing $Co_2(CO)_8$ (17.4g, 6.0g Co) in one step. After thorough mixing the solvent was removed in vacuo to yield 141.0g of tan catalyst. The elemental analysis showed 3.5% Co.

(iv) Fe₃(CO)₁₂/Zr(OPr)₄/SiO₂ (Catalyst #8466-40)

The standard pretreatment was used for the silica (92.8g, Davison 952), which was then impregnated with a 300-cc hexane solution containing 61.58g (10.9g Zr) of Zr(OC₃H₇)₄·XC₃H₇OH. The solvent was removed in vacuo. The Fe₃(CO)₁₂ (19.5g, 6.0g Fe) was added to the silica in four steps with each step using a 250-cc THF solution. The resulting purple catalyst (148.8g) had the following metal loadings: 2.4% Fe and 7.3% Zr (Fe/Zr=0.33).

(b) Gas Phase Screening

A detailed description of the gas phase screening reactor and procedure can be found in the Project Work Plan. The catalyst charge was 10 cc for each test. Generally, only reactor temperature and CO to H₂ feed ratio were varied while pressure and space velocity were kept at 300 psig and 1000 h⁻¹ (v/v), respectively, for all the runs. Hydrogen activation was used for all the tests as follows: Hydrogen at 1000 to 3000 hr⁻¹ and 0-70 psig was passed over the catalyst as it was heated to 300°C at 3°/min and maintained there for 16 hours. The temperature was then reduced to the desired reaction temperature, CO was introduced to give 1:1 CO/H₂ at 1000 hr⁻¹ and finally the total pressure was increased to 300 psig.

(c) Slurry Phase Tests

(i) Co₂(CO)₈/Fe₃(CO)₁₂/Zr(OPr)₄/SiO₂ -- Test #8670-12-23

This catalyst was activated in the 150-cc fixed-bed, tubular reactor using pure H₂ as follows: The reactor tube was charged with catalyst in a dry box to give approximately a 110-cc bed volume and transferred to the reactor manifold sealed under N₂. The reactor was heated at 0 psig to 300°C at a rate of 1°/min with a H₂ flowrate of 1000 scfm. The temperature was maintained at 300°C for 8 hours. After cooling, the reactor was flushed with N₂, sealed and transferred to the dry box for catalyst removal. In the dry box the reduced/activated catalyst was slurried in deoxygenated Fisher paraffin oil and transferred to the slurry autoclave reactor under a N₂ purge.

For this slurry test, 76.9g of reduced catalyst in a 459-cc slurry volume was charged to the slurry reactor giving a 16.8 wt% catalyst concentration. The metal loadings before and after activation were:

	<u>Fresh</u>	<u>Activated</u>
Co	3.7 wt%	4.9 wt%
Fe	0.72	0.93
Zr	7.3	9.1

(ii) Co₂(CO)₈/Zr(OPr)₄/MgO·3.6SiO₂ -- Test #8670-60-25

This catalyst was activated and slurried in the same manner as described in the previous test. 450-cc of a 16.4 wt% slurry containing 70.1g of activated catalyst was charged to the reactor. Metal loadings before and after activation were:

	<u>Fresh</u>	<u>Activated</u>
Co	3.7 wt%	4.8 wt%
Zr	7.2	9.4

(iii) Co₂(CO)₈/Ti(OPr)₄/SiO₂ -- Test #8670-57-27

This catalyst was activated and slurried in the same manner as described above. The reactor charge was 450-cc of a 17.4 wt% slurry containing 76.3g of activated catalyst. Elemental analysis of the catalyst before and after activation was:

	<u>Fresh</u>	<u>Activated</u>
Co	4.4 wt%	5.2 wt%
Ti	4.0	4.8

(iv) Co₂(CO)₈/Zr(OPr)₄/SiO₂ -- Extended Test #8862-1-31

This catalyst was activated and slurried in the same manner as the previous 3 catalysts. The reactor was charged with 450-cc of a 21.1 wt% slurry containing 91.4g of activated catalyst. Elemental analysis of the catalyst before and after activation was:

	<u>Fresh</u>	<u>Activated</u>
Co	4.4 wt%	5.3 wt%
Zr	7.6	10.2

(d) Catalyst Characterization

H₂ chemisorption experiments were conducted on a Micromeritics Chemisorb 2800 using catalyst samples prereduced in the 10 cc reactor. After transfer of the samples to the chemisorption sample tubes, they were treated with H₂ at 300°C and 1 atmosphere prior to data acquisition. B.E.T. surface areas were obtained using a Micromeritics Digisorb 2500.

5.0 REFERENCES

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