NOVEL FISCHER-TROPSCH SLURRY CATALYSTS AND PROCESS CONCEPTS FOR SELECTIVE TRANSPORTATION FUEL PRODUCTION: QUARTERLY TECHNICAL PROGRESS REPORT, 1 JULY 1985-30 SEPTEMBER 1985

AIR PRODUCTS AND CHEMICALS, INC.
ALLENTOWN, PA

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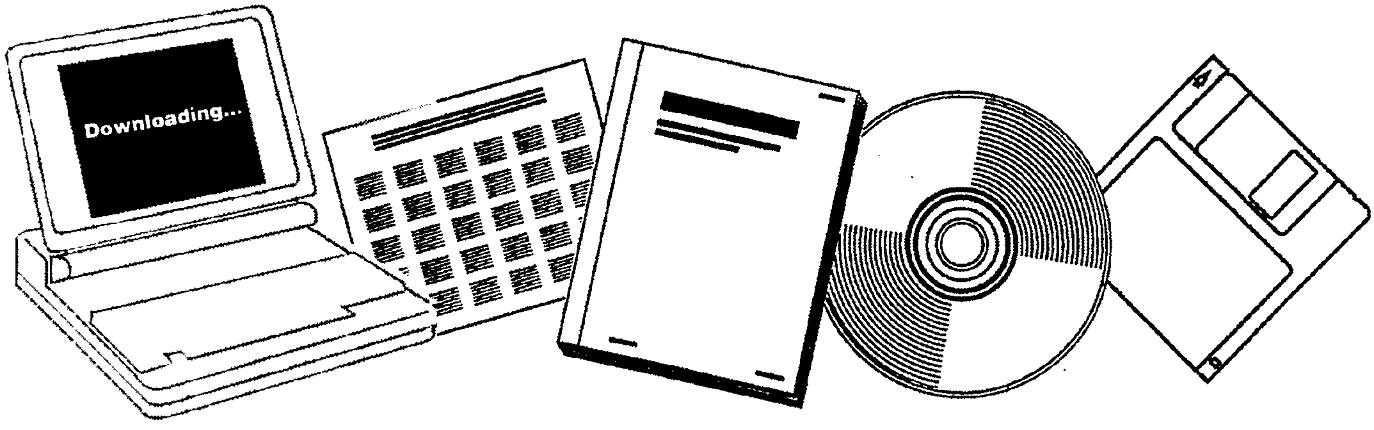

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NOVEL FISCHER-TROPSCH SLURRY CATALYSTS AND PROCESS CONCEPTS FOR SELECTIVE TRANSPORTATION FUEL PRODUCTION

QUARTERLY TECHNICAL PROGRESS REPORT

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DISCLAIMER

EXECUTIVE SUMMARY

In the fourth 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. Silica was examined as a support for the standard $Co_2(CO)_8/Zr(OPr)_4$ composition. A mixed Co/Fe catalyst on zirconated silica was prepared from $Co_2(CO)_8$ and $Fe_3(CO)_{12}$, rather than from the $[FeCo_3(CO)_{12}]^-$ anion. The use of Ti in place of Zr as the promoter was examined with the silica support. Further work on alternate supports was completed with the preparation of $Co_2(CO)_8$ and $Zr(OPr)_4$ on $MgO\ 3.6SiO_2$.

Gas-phase screening was completed on three catalysts during the quarter. The effect of increasing the cobalt loading from 4 to 11 wt% for the $Co/Zr/Al_2O_3$ composition was to improve the bulk activity but lower the specific activity and to slightly shift the hydrocarbon selectivity to higher molecular weight products. Using silica as the support for the standard Co/Zr composition resulted in the highest bulk and specific activities observed thus far in this contract. Selectivity to liquid fuels also improved. The use of silica as a support for the mixed Co/Fe catalyst also provided an improvement in the Fischer-Tropsch activity but did not enhance the water-gas shift activity.

The following three catalysts were screened in the slurry reactor this quarter:

o $Co(NO_3)_2/Zr(OPr)_4/Al_2O_3$ - To determine the effect of metal precursor, this catalyst was prepared from $Co(NO_3)_2$ in place of the usual $Co_2(CO)_8$. This catalyst did not perform as well as its carbonyl derived counterpart. A substantially lower bulk activity was observed at all temperatures, and in general, high yields of C24+ products were obtained.

- $Co_2(CO)_8/Zr(OPr)_4/Al_2O_3$ - The Co and Zr loadings of this catalyst were increased to 10.8 and 8.5 wt%, respectively (from 3.8 wt% Co and 6.8 wt%, Zr of the basecase). The bulk activities at 240 and 260°C were 10 - 15% lower than the basecase catalyst results; at 280°C, however, activity was 20 -25% greater. The fuels selectivity (C_5-C_{23}) was less than 60 wt% at all conditions tested compared with the maximum of 65 wt% of the basecase. A substantial increase in bulk activity was observed during the two days when the CO/H_2 ratio was reduced to 0.5. Exposure to high H_2 did not cause any appreciable irreversibility in activity and product selectivity. This is important if regular H_2 reactivation is necessary. Neither activity nor hydrocarbon selectivity were reproducible after over 380 and up to 570 hours of testing.

- $Co_2(CO)_8/Zr(OPr)_4/SiO_2$ - This silica supported catalyst showed the most promising results of all the catalysts tested to date. The silica support enhanced both activity and selectivity. A 50% increase in activity was observed at 240°C. When the temperature was raised to 280°C, the activity was improved by only 10%, relative to alumina support. Some of this change in relative activity may be due to the observed deactivation of the silica supported catalyst. Liquid fuels yields were in the 65 - 71 wt.% range.

A kinetic data analysis program was developed to aid in the analysis of catalyst data from the laboratory reactor tests operating at steady state. The required specifications include reaction stoichiometry and kinetics, the necessary reactor operating parameters, inlet conditions and gas phase product concentrations. Options include choice of fixing or fitting kinetic parameters and regressing rate coefficients in a normalized or standard fashion. Data from the catalyst slurry screening tests and more importantly the extended tests will be routinely analyzed for kinetic correlations.

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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 was particularly novel in that it was prepared by supporting metal carbonyl clusters on alumina which had been modified by promoters. 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 fourth 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 clusters 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:

- o Increasing catalyst activity
- o Improving product selectivity for liquid fuels and reducing the yield of methane
- o Developing catalyst systems active at high CO:H_2 ratios
- o 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) $Co_2(CO)_8/Zr(OPr)_4/SiO_2$ (Batch #8466-18)

Many different support materials were examined during the initial DOE/Air Products liquid-phase Fischer-Tropsch research contract, however, silica was not included. For several reasons it was decided that silica should be examined with the standard Zr-promoted, Co catalyst. One reason was that the early research done by the German investigators on cobalt catalysts showed that kieselguhr, which is mainly SiO_2, was the preferred support (1). Another reason, which pertains to the use of cobalt carbonyl as the metal source, was the low reactivity of silica toward metal carbonyls (2). The previously studied oxide supports such as alumina, titania and ceria react with metal carbonyls to oxidize the metal.

This catalyst was prepared using the standard procedure. The metal loadings were similar to those used on the other supports to facilitate comparisons in performance.

(ii) $Co_2(CO)_8/Fe_3(CO)_{12}/Zr(OPr)_4/SiO_2$ (Batch #8466-22)

The use of silica support for the $Co_2(CO)_8/Zr(OPr)_4$ based catalyst did result in improved activity. Since our previous work on the incorporation of Fe in the alumina-supported Co/Zr catalyst did not improve the water-gas shift activity, it was worthwhile to reexamine this approach using the silica support. Perhaps the activity of the Fe would not be suppressed with the silica support.

The preparation was slightly different from the $Co/Fe/Zr/Al_2O_3$ catalyst in that $Fe_3(CO)_{12}$ and $Co_2(CO)_8$ were used instead of the mixed metal cluster anion, $[FeCo_3(CO)_{12}]^-$. Since this was an ionic species it may have reacted more readily with the support. The metal loadings, however, were kept similar to the previous catalyst.

(iii) $Co_2(CO)_8/Zr(OPr)_4/MgO.3.6\ SiO_2$ (Batch #8466-25)

The investigation of alternate supports was continued with this examination of a commercially available magnesium silicate material known as Florisil$^{(R)}$. The objective was to combine the properties of MgO and SiO_2. Magnesia has been shown to result in stabilized cobalt subcarbonyl species that can be reversibly carbonylated and decarbonylated (3). Since cobalt carbonyl reacts to a lesser extend with magnesia than with alumina and the cobalt species still appear active towards CO adsorption, magnesia combined with unreactive silica might give some control over metal dispersion compared to silica alone.

The Florisil$^{(R)}$ surface area was high at 298 m^2/g with an average pore diameter of 270A. The catalysts was prepared using the standard procedure with similar metal loadings to the basecase $Co/Zr/Al_2O_3$ catalyst.

(iv) $Co_2(CO)_8/Ti(OPr)_4/SiO_2$ (Batch #8466-27)

Since titanium had previously been examined as a promoter for the alumina-supported, Co catalyst, it was examined again in the more active Co/silica system. The standard preparation procedure was utilized and metal loadings were kept similar to previous catalysts.

(b) Gas Phase Screening

All of the catalysts screened in the fixed bed reactor this quarter were activated using a pure H_2 procedure as described in Section 4.1b. Specific run conditions did vary somewhat and are documented accordingly. Gas phase performance data is summarized in Table 1.

(i) $Co_2(CO)_8/Zr(OPr)_4/Al_2O_3$ - Run #8413-25-9, Batch #8466-9

This catalyst which had a 10.8% Co loading, showed higher bulk activity but lower specific activity than the 4% $Co/Zr/Al_2O_3$ basecase composition tested last quarter. The increased Co loading resulted in bulk activities of 39 and 44 moles syngas/kg cat/hr at 240° and 260°C, respectively. This was a 50 and 30% increase, respectively, in bulk activity compared to the 4% Co catalyst at the same conditions and activated with hydrogen. Specific activity declined by 33 and 45%, respectively, compared to the 4% Co catalyst at the same two conditions. This decline in specific activity indicated a smaller percentage of active sites were available as the metal loading was increased. Hydrogen chemisorption experiments are in progress to determine metal dispersion of these catalysts.

Hydrocarbon product selectivity was similar for the two catalysts of different metal loadings. The current test of the 10.8% $Co/Zr/Al_2O_3$ catalyst gave a total fuels selectivity (C_5-C_{23}) of 66 wt% at 240° and 60 wt% at 260°C. This compared to 61 and 60 wt%, respectively, for the 4% Co catalyst. A subtle shift in hydrocarbon selectivity, however, could be seen between the two catalysts. The 4% Co catalyst showed a slight increase in light hydrocarbon selectivity for each temperature tested. Conversely, the 10.8% Co catalyst had an increased tendency toward heavier hydrocarbon production, which agrees with the general observation that as metal dispersion decreases for FT catalysts, heavy hydrocarbon selectivity increases.

(ii) $Co_2(CO)_8/Zr(OPr)_4/SiO_2$ - Run #8413-28-18, Batch #8466-18)

Performance was quite good for this catalyst; it provided the highest bulk and specific activities observed thus far in this contract. At 220° the bulk activity was 31 moles syngas/kg cat/hr and specific activity was 0.26 moles CO/mole Co/min, indicating that this catalyst was as active at 220° as previous catalysts tested at 240 and 260°. At 260°, bulk activity reached 74 moles syngas/kg cat/hr, with specific activity of 0.62 moles CO/mole Co/min and total syngas conversion of 65%. A performance comparison of this catalyst with the standard $Co/Zr/Al_2O_3$ catalyst is shown in Table 2. At each temperature there was a substantial increase in activity compared to the alumina-supported catalyst.

Hydrocarbon selectivity also improved, at least at 220 and 240°C, where the total fuels selectivity (C_5-C_{23}) was 67 and 72%, respectively. At 260°, however, there was little difference in this selectivity between the silica and alumina supported catalysts, as shown in Table 2.

(iii) $Co_2(CO)_8/Fe_3(CO)_{12}/Zr(OPr)_4/SiO_2$ - Run #8413-36-22, Batch #8466-22

This catalyst showed fairly high activity, nearly double the bulk activity of the standard $Co/Zr/Al_2O_3$ catalyst, but not quite as high as the $Co/Zr/SiO_2$ catalyst discussed above. Bulk activities of 51 and 68 moles syngas/kg cat/hr were obtained at 240° and 260°, respectively. At 240° the effect of space velocity on performance was examined. No trends were observed for hydrocarbon selectivity as a function of space velocity.

The key objective of improving water-gas shift activity by adding iron was not achieved and the silica support did not lead to any enhancement of iron's shift activity. The usage ratios were quite similar to the $Co/Zr/SiO_2$ catalyst. Perhaps the Fe-to-Co ratio in these bimetallic catalysts has been too low.

Overall hydrocarbon selectivity was similar to that of the $Co/Zr/SiO_2$ catalyst. At 240 and 260° the total fuels selectivity (C_5-C_{23}) was good at 74 and 60%, respectively for space velocities of 1000 hr^{-1}. At 220° this C_5-C_{23} selectivity declined to 56% with a significant amount of C_2-C_4 product.

(c) Slurry Reactor Tests

Three catalysts were tested in the 1 liter slurry phase reactors this quarter. In each case a series of operating conditions were investigated to determine the optimum for activity and hydrocarbon selectivity. Due to the high activity and improved selectivity observed last quarter for the basecase catalyst (Run #8523-1-4) using the H_2 reduction method, this method was routinely used for all subsequent catalyst tests. The following three catalysts were tested this quarter:

- A cobalt catalyst derived from the nitrate instead of the carbonyl, with a metals loading similar to the basecase as shown: Co=4.25 wt%, Zr=7.10 wt%, and Co/Zr=0.60.
- $Co_2(CO)_8$ on zirconated alumina with an increase in Co loading to 10.8 wt% and zirconium to 8.5 wt% to determine the effects of metals loading on catalyst performance.
- $Co_2(CO)_8$ on zirconated silica with a metals loading similar to the basecase catalyst [illegible] alumina (Co=3.5 wt% and Zr=6.6 wt%, Co[illegible]=0.53).

Representative results from these tests are listed in Table 3 along with the results of all previous catalysts tested in this contract for comparison.

(i) $Co(NO_3)_2/Zr(OPr)_4/Al_2O_3$-7888-85-2

The major objective of this test was to determine if the cobalt catalyst prepared from the nitrate instead of the carbonyl would enhance the performance of this catalyst. The metals weight percent loadings were Co=4.25 and Zr=7.10 (Co/Zr=0.60). The details of the preparation and activation are given in Section 4.1.

The activity, conversion and selectivity data of the major sample points are summarized in Table 4. The individual mass balances of this screening test are listed in Tables 5-22 and 24-99 and illustrated in Figures 1-12.

The first four mass balances were conducted at 240°C, with the following variations in the CO/H_2 ratio and space velocity:

Sample	CO/H_2	SV,NL/g cat/hr
2	1.05	2.46
5	1.59	2.49
8	2.12	2.49
12	1.99	1.23

In each case, the bulk activity was poor compared with the carbonyl derived catalyst with similar metals loading (Run #8523-1-4). Sample 2 (Tables 5-6, Figure 1), for example, exhibited a 125% lower bulk activity at the same operating conditions. The selectivity of total liquid fuels, C_5-C_{23}, was 30% lower. For the next two mass balances the CO/H_2 ratio was raised to 1.59 and then to 2.12 (Samples 5 and 8, Tables 7-10, Figures 2-3). Wax yields above 30 wt% were observed with no improvement in catalyst activity. When the space velocity was reduced to 1.23 (Sample 12, Tables 11-12, Figure 4), the products continued to shift into the heavier molecular weight region with wax selectivity at 38.8 wt% of the total hydrocarbons.

The next five screening conditions were conducted at 260°C:

Sample	CO/H_2	SV,NL/g cat/hr
14	1.99	1.23
16	1.50	1.23
18	1.58	2.50
21	1.05	2.47
24	1.92	2.32

A 37% increase in bulk activity to 15.6 mol syngas/kg cat/hr was observed for sample 14 (Tables 13-14, Figure 5). The 28% decline in wax production, however, was not enough to improve liquid fuels selectivity. This trend continued with the reduction in the CO/H_2 ratio to 1.50 (sample 16, Tables 15-16, Figure 6), but the selectivity to wax remained high at over 20 wt%. During the next three test conditions at the higher space velocity (samples 18, 21 and 24, Tables 17-22, Figures 7-9), the total fuels selectivity was at the maximum for this catalyst at over 60 wt%. This was still low compared with the 72 wt% observed for the carbonyl derived catalyst as shown in Table 23. The usage ratio was also lower than that of the carbonyl catalyst indicating poorer water-gas shift activity.

The final three mass balances were conducted at 280°C:

Sample	CO/H_2	SV,NL/g cat/hr
32	1.57	2.50
35	1.49	1.23
38	1.04	2.47

It was expected that operation at 280°C would help shift the C_{24}+ products into the lighter molecular weight region (Samples 32-38, Tables 24-29, Figures 10-12). This trend was observed, but without centering of products in the liquid fuels range. The methane selectivity was high at above 14 wt% in each case.

From the above results it can be concluded that the catalyst prepared using the carbonyl precursor is more active and selective for liquid fuels. In addition, at most operating conditions, the usage ratio is closer to the feed ratio indicating better water-gas shift activity. Figures 13 and 14 summarize the effect of temperature, CO/H_2 ratio, and space velocity on bulk activity and hydrocarbon selectivity. The trends in bulk activity are linear with increasing temperature at all operating conditions with the highest activity at the lowest CO/H_2 ratio at each of the space velocities studied. The trends in the hydrocarbon selectivity appear to be dependent mainly on temperature and space velocity with a minor dependence on the CO/H_2 feed ratio. The total fuels selectivity, C_5-C_{23}, is maximum at 260°C and space velocity of 2.5 N/g cat/hr.

(ii) $Co_2(CO)_8/Zr(OPr)_4/Al_2O_3$ - 8523-41-9

The screening test of $Co_2(CO)_8$ on zirconated alumina with a metals weight percent loading of 10.8 Co and 8.5 Zr (preactivated) was completed. The major objective of this test was to determine the effect of increasing the Co loading on catalyst activity and selectivity. The description of the H_2 reduction procedure and details of the catalyst preparation are included in Section 4.1. The activity, conversion, and selectivity data of the major sample points of this screening test are summarized in Table 30. The individual mass balances are listed in Tables 31-66 and illustrated in Figures 15-25, 27 and 29-34.

The run was started at 240°C with the following five CO/H_2 ratios and space velocity changes:

Sample	CO/H_2	SV, NL/g cat/hr
3	1.00	2.10
5	1.50	2.10
9	2.00	2.08
12	2.01	1.04
16	1.00	1.05

The bulk activity was initially high at 30.7 mol syngas/kg cat/hr (Sample 3, Tables 31-32, Figure 15). The methane selectivity was promising at less than 10 wt%, but the liquid fuels selectivity was low at less than 60 wt%. When the CO/H_2 ratio was raised (Samples 5 and 9, Tables 33-36, Figures 16-17), a substantial decline in activity was observed with negligible changes in the hydrocarbon selectivity. The fuels selectivity continued to be poor at the lower space velocity of the next two test conditions (Samples 12 and 16, Tables 37-40, Figures 18-19).

The following seven process conditions were then tested at 260°C:

Sample	CO/H_2	SV,NL/g cat/hr
19	1.00	1.05
22	2.03	1.03
25	2.00	2.08
27	1.50	2.10
30	1.03	2.10
33	0.50	2.08
39	1.03	2.10

A 39% increase in bulk activity to 21.5 from 15.5 mol syngas/kg cat/hr of sample 16 was observed (Sample 19, Tables 41-42, Figure 20). The methane selectivity increased by 33% with no significant changes in the total fuels selectivity. A drastic 62% decrease in activity was apparent upon increasing the CO/H_2 ratio (Sample 22, Tables 43-44, Figure 21). This was due mainly to the poor water-gas shift activity since the change in hydrocarbon distribution was negligible. A similar trend of increasing activity and methane selectivity with decreasing CO/H_2 ratio at double the space velocity was observed in the next three test conditions (Samples 25, 27 and 30, Tables 45-48, Figures 22-24).

Because of the poor water-gas shift activity at all high CO/H_2 ratios, the catalyst performance using a balanced synthesis gas feed was next investigated (Sample 33, Tables 44-50, Figure 25). The activity increased by 63% with a usage ratio of 0.42 compared with the 0.50 feed ratio of CO/H_2. The methane selectivity, however, increased to 27.3 wt%.

Figure 26 illustrates the reduction in H_2, CO, and overall conversions with increasing CO/H_2 ratio due to poor water-gas shift activity. The trends are opposite to that of the precipitated Fe catalysts, where the conversions increase with CO/H_2 ratio and the CO conversion is consistently greater than H_2 conversion.

The operating conditions were then returned to those of sample 30 to check for reproducibility (Sample 36, Tables 51-52, Figure 27). Within the limits of error, the results were similar.

In the last quarterly report, it was noted that the specific activity decreases with increasing Co/Zr ratio using the synthesis gas method of activation. A comparison of the results of the present test with Co/Zr=1.27 and the basecase catalyst with Co/Zr=0.63 indicate no effect on specific activity as illustrated in Figure 28. Also, it appears that the cobalt loading has no effect on specific activity since the Co loading is 5 and 10 wt%, respectively.

The next three mass balances were conducted at 280°C before returning to the initial operating conditions:

Samples	CO/H_2	SV,NL/g cat/hr
39	1.00	2.10
42	1.50	2.10
47	0.50	2.08
53	1.00	1.05

At these conditions the bulk activity was high, 62.5 mol syngas/kg cat/hr at CO/H_2=0.50, but the hydrocarbon selectivity became progressively worse with methane selectivity as high as 39 wt% (Samples 39-53, Tables 55-62, Figures 29-32).

The temperature was returned to 260°C and then to 240°C to check for any catalyst deactivation (Samples 58 and 63, Tables 63-66, Figures 33-34). In each case, both activity and hydrocarbon selectivity were not reproduced. The losses in activity were accompanied by high methanation activity.

Figure 35 summarizes the bulk activity results obtained at the three temperature levels at the various CO/H_2 ratios and space velocities. It is clearly evident that these cobalt based catalysts prefer the hydrogen-rich feed-gas due to their poor water-gas shift capability. At these high H_2 conditions, however, the selectivity for liquid hydrocarbon products is poor.

(iii) $Co_2(CO)_8/Zr(OPr)_4/SiO_2$ - 8670-11-18

The screening test of $Co_2(CO)_8$ on zirconated silica with a metals weight percent loading of Co=3.5 and Zr=6.6 (preactivated) was completed. The major objective of this test was to determine if the silica support has any advantage in either activity or selectivity for fuels over the alumina supported catalyst.

The activation procedure and method of preparation are discussed in Section 4.1. The activity, conversion, and selectivity data of the major sample points of this screening test are summarized in Table 67. The individual mass balances are listed in Tables 68-103 and illustrated in Figures 36-52.

This screening test was initiated at 240°C with the following six CO/H_2 ratio and space velocity changes:

Sample	CO/H_2	SV, NL/g cat/hr
9	1.00	2.00
12	1.50	2.00
14	2.00	2.00
18	2.00	1.00
21	1.50	1.00
24	1.00	1.00

During the first three mass balances the selectivity for total liquid fuels product was in the 67.0 - 72.5 wt% range (Samples 9-14, Tables 68-73, Figures 36-38). As with the previous cobalt catalyst tests, the bulk activity decreased with increasing CO/H_2 feed ratio. Compared with the alumina supported catalyst, a 50% improvement in bulk activity was observed accompanied by a significant enhancement in liquid fuels selectivity. When the space velocity was reduced to 1.0 NL/g cat/hr in the next three test conditions (Samples 18, 21 and 24, Tables 73-78, Figures 39-41), the selectivity to liquid products decreased into the 61.5-67.2 wt% range since the increase in residence time enhanced the formation of heavier products.

The following five operating conditions were conducted at 260°C:

Sample	CO/H_2	SV,NL/g cat/hr
26	1.00	1.00
30	1.50	1.00
33	1.50	2.00
36	2.00	2.00
39	1.00	2.00

Compared with the results at 240°C, the medium increase in bulk activity at comparable space velocity and H_2/CO ratio was 22.7% (Samples 26-39, Tables 80-89, Figures 42-46). The total fuels selectivity varied between 61 and 80 wt% with shift of products into the lighter molecular weight region.

Table 104 compares the hydrocarbon selectivities of the alumina supported catalyst and the present silica supported catalyst. Overall, no appreciable increase in hydrocarbon selectivity is observed. The increase in activity may be due to the increased surface area provided by the silica support. A better understanding of support effects is necessary to make any final conclusions as to their role in catalyst performance.

The following five operating conditions were conducted at 280°C:

Sample	CO/H_2	SV,NL/g cat/hr
42	1.00	2.00
45	1.50	2.00
48	2.00	2.00
51	1.00	1.00
54	2.00	1.00

A more significant increase in bulk activity was observed in going from 260 to 280°C than when the temperature was raised from 240 to 260°C (Samples 42-54, Tables 90-99, Figures 47-51). The liquid fuels selectivity varied between 58 and 66 wt% with methane selectivity above 13 wt%.

Finally, a check on reproducibility was conducted by returning the process conditions to that of Sample 39 (Sample 57, Tables 100-101, Figure 52), and Sample 9 (Sample 60, Tables 102-103, Figure 53).

The bulk activity was 33.4 compared with the original 44.8 mol syngas/kg cat/hr., for Samples 57 and 39 respectively. For Sample 60, the bulk activity had decreased to 18.4 compared to 36.5 for Sample 9. In each case, the hydrocarbon selectivity data showed an increase in the selectivity of light hydrocarbons.

Figure 54 shows the differences in bulk activity trends for the two supports. The silica supported catalyst is more active than the alumina catalyst above 240°C. Figure 55 illustrates in composite the effects of high CO feed gas and low space velocity on the bulk activity of this catalyst. At the lower space velocity it is obvious that temperature and CO/H_2 dependency is less pronounced.

Figure 56 shows the effect of temperature, at the same CO/H_2 ratios and space velocities, on hydrocarbon selectivity. The general trend was a worsening of selectivity with increasing temperature. The best selectivities were obtained at 240°C.

Upon returning to 260°C after testing at 280°C, the selectivity was not reproduced, but the trend toward methane reduction is apparent. In all of the screening tests, the hydrocarbon selectivities reported are trend data and should not be taken as absolute numbers. Since the process conditions are being changed on a daily basis, it is not possible to obtain absolute data.

The metal cluster catalysts tested to date have shown poor water-gas shift activity worsening with increasing CO as illustrated in Figure 57. The ruthenium based catalyst shows better activity, but the precipitated iron appears to be superior to it. Hydrogen-rich feed gas appears to be more compatible with these cobalt based catalysts. Future testing will, therefore, include balanced feed gas testing.

3.3 Task 3 -- Slurry Reactor Kinetic Studies

A kinetic data analysis program was developed to help determine the kinetic parameters of the catalysts tested in the laboratory reactors. The program correlated the rate of CO/H_2 consumption with the species concentrations at the catalyst surface, subject to the kinetic functionality chosen by the user. Henry's law is assumed to be valid for relating the liquid concentrations to the vapor partial pressures. The mass transfer from the bulk liquid to the solid surface is assumed to be rapid (this was verified during the first slurry test conducted for this contract), thus surface concentrations are taken as identical to the bulk liquid values. The Henry's law correlations are based on regressions of data taken from a paper by Peter and Weinert (4). The solvent densities are calculated based on correlations proposed by Deckwer(5).

A summary of the program requirements and results are presented in Figure 58. The specifications include reaction stoichiometry and kinetics, the necessary reactor operation parameters, inlet conditions and observation data. The options include the choice of fixing or fitting kinetic parameters and regressing rate coefficients in a normalized or standard fashion. The kinetic rate expressions which are available are summarized in Table 105.

4.0 EXPERIMENTAL

4.1 Task 2 -- Development of Improved Supported Catalyst Compositions

(a) Catalyst Preparation

(i) $Co_2(CO)_8/Zr(OPr)_4/SiO_2$ (Batch #8466-18)

The silica (87.2g, Davison 952) was calcined at 500°C for 3 hrs in static air and further dried at 100-110°C in vacuo (50 Hg) for 1 hr prior to use. The silica was impregnated in one portion with a 330-cc solution of 50.8g of $Zr(OC_3H_7)_4 \cdot XC_3H_7OH$ (10.6g Zr) in hexane. After mixing thoroughly by shaking the flask, the hexane was evaporated off in vacuo with slight warming in a 40-50°C bath. To load the cobalt, a 200-cc solution having 17.5g of cobalt carbonyl in 60/40 toluene/hexane solvent was used. The toluene/hexane solvent was removed in vacuo. After complete removal of the solvent, 132g of a greenish-tan catalyst was obtained and analyzed as having a composition of 3.5 wt% cobalt and 6.6 wt% zirconium (Co/Zr=0.53).

(ii) $Co_2(CO)_8/Fe_3(CO)_{12}/Zr(OPr)_4/SiO_2$ (Batch #8466-22)

The silica (89.0g, Davison 952) was calcined and dried in the same manner as the previous catalyst. The silica was then impregnated with a 325-cc solution of $Zr(OC_3H_7)_4 \cdot XC_3H_7OH$ (63.5g, 10.5g Zr) in hexane. After thorough mixing the hexane was evaporated off in vacuo. $Fe_3(CO)_{12}$ (5.88g, 1.96g Fe) was then added to the zirconated silica as a solution in THF. Due to the limited solubility of $Fe_3(CO)_{12}$, three impregnation steps were necessary (225-cc for each) to completely load the iron carbonyl. $Co_2(CO)_8$ (17.4g, [illegible].0g Co) was finally added to the catalyst material by impregnation of a 225-cc solution in THF. Upon evaporation of the solvent in vacuo, 148g of a dark brown-green solid was obtained which analyzed as 3.7% Co, 0.72% Fe and 7.3% Zr (Fe/Co=0.19, Co/Zr=0.51).

(iii) $Co_2(CO)_8/Zr(OPr)_4/MgO\ 3.6SiO_2$ (Batch #8466-25)

The MgO $3.6SiO_2$ (87.2g, Florisil^R, Floridin Co.) was calcined at 650°C for 5 hrs in static air and dried further at 100°C for 1.5 hrs. in vacuo (50 Hg) prior to use. The Florisil^R was then impregnated with a 130-cc solution of $Zr(OC_3H_7)_4 \cdot XC_3H_7OH$ (64.4g, 10.65g Zr) in hexane. Upon removal of the solvent in vacuo, the material was similarly treated with a 100-cc solution of $Co_2(CO)_8$ (17.5g, 6.0g CO) in THF. Removal of the solvent in vacuo yielded 146.8g of a black solid, which contained 3.7% Co and 7.2% Zr (Co/Zr=0.51).

(iv) $Co_2(CO)_8/Ti(OPr)_4/SiO_2$ (Batch #8466-27)

The silica (99.6g, Davison 952) was treated in the usual manner as described for the previous catalyst preparations. A 325-cc solution of $Ti(OC_3H_7)_4 \cdot XC_3H_7OH$ (34.2g, 5.59g Ti) in hexane was added to the silica and the hexane was subsequently removed in vacuo. The $Co_2(CO)_8$ (17.5g, 5.91g Co) was dissolved in a 200-cc THF/50-cc hexane mixture and impregnated onto the support. Upon removal of the solvent in vacuo, 137.5g of greenish-tan solid was obtained, which analyzed as 4.4% Co and 4.0% Ti (Co/Ti=1.1).

(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 H_2 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 3000 hr^{-1} and O 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/H_2 at 1000 hr^{-1} and finally the total pressure was increased to 300 psig.

(c) Slurry Phase Tests

(i) $Co(NO_3)_2/Zr(OPr)_4/Al_2O_3$ -- 7888-85-2

This catalyst was activated in the gas phase reactor using the same H_2 activation procedure as used for the $Co_2(CO)_8/Zr(OPr)_4/Al_2O_3$ (8523-1-4) catalyst last quarter. The fresh catalyst was loaded into the 150-cc tubular reactor (approximately 110-cc catalyst bed volume). The reactor was heated at ambient pressure to 300°C at a rate of 1°C/min at the maximum allowable H_2 flowrate of 1000 sccm. The temperature was maintained at 300°C for 8 hours with full H_2 flow. After cooling under N2, the activated catalyst was slurried in deoxygenated Fisher paraffin oil and transferred to the reactor under a N_2 atmosphere. For this catalyst, the final loading was 480.0 mls of a 13.9 wt% slurry containing 59.7 gms of catalyst. The elemental analysis before reduction was:

	Wt%
Co	4.25
Zr	7.10

(ii) $Co_2(CO)_8/Zr(OPr)_4/Al_2O_3$ -- 8523-41-9

This catalyst was activated and slurried in the same manner as above. The final reactor loading was 450.0 mls of a 15.1 wt% slurry containing 64.25 gms of catalyst. The elemental analyses before and after activation were:

Fresh (Wt%)		Activated (Wt%)
Co	10.8	12.4
Zr	8.5	12.0

(iii) $Co_2(CO)_8/Zr(OPr)_4/SiO_2$ -- 8670-11-18

This catalyst was activated and slurried in the same manner as described above. The final reactor loading was 450.0 mls of a 19.2 wt% slurry containing 79.0 gms of catalyst. The elemental analyses before and after activation were:

Fresh (Wt%)		Activated (Wt%)
Co	3.53	4.9
Zr	6.57	9.3

5.0 REFERENCES

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