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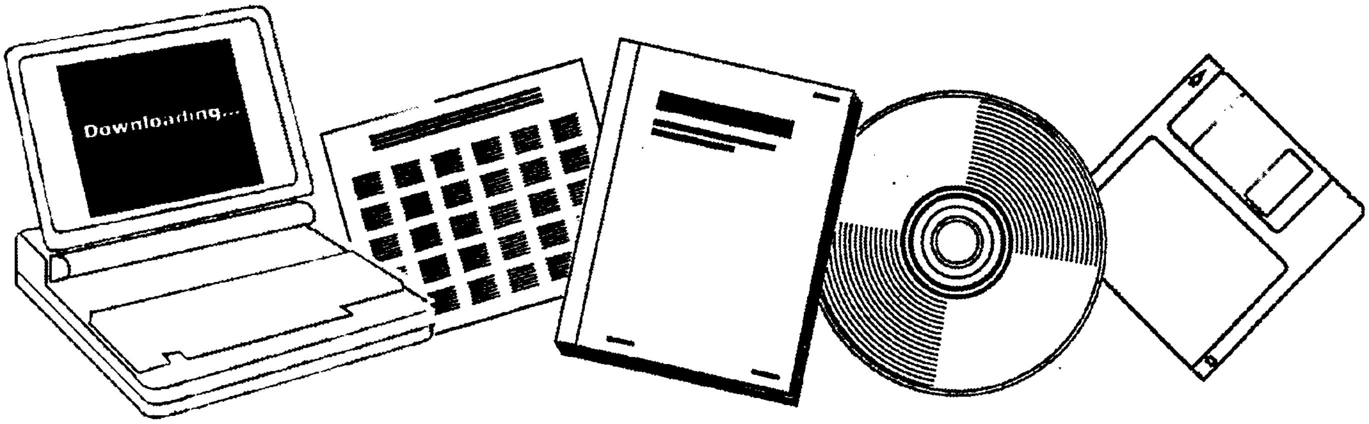
NOVEL FISCHER-TROPSCH SLURRY CATALYSTS AND PROCESS CONCEPTS FOR SELECTIVE TRANSPORTATION FUEL PRODUCTION: QUARTERLY TECHNICAL PROGRESS REPORT, 1 JANUARY-31 MARCH 1986

AIR PRODUCTS AND CHEMICALS, INC.
ALLENTOWN, PA

JAN 1987



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

QUARTERLY TECHNICAL PROGRESS REPORT

1 January - 31 March 1986

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EXECUTIVE SUMMARY

In the sixth 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 three major tasks: Task 2 -- Development of Improved Supported Catalyst Compositions, Task 3 -- Slurry Reactor Kinetic Studies, and Task 4 -- Fuel Product Characterization.

To study the effect of Co-to-promoter ratio on the performance of the silica-supported catalysts, four Co/Zr/silica catalysts were prepared by varying the Zr loading, with the Co loading held at 4%. This gave a series of catalysts, including the basecase Co/Zr/silica catalyst, having Co/Zr ratios of 0.53, 0.83, 1.9, 6.6 and a composition having no promoter.

Gas phase testing of this series of catalysts was completed this quarter. The results indicated that for optimum bulk activity, the Co/Zr ratio should be closer to 1 than to the basecase value of 0.5. Specific activity, however, was best for the basecase catalyst. Total fuels selectivity (C_{5-23}) was also best for the basecase catalyst, especially if straight run liquid fuels (C_{5-18}) was desired. Overall, it then appears that the optimum Co/Zr ratio is near 0.5 for gas phase performance, although lower ratios were not investigated.

One other Co/Zr/silica catalyst was prepared this quarter. It had a surface area analogous to that of the basecase Co/Zr/alumina catalyst so that an activity comparison could be made between them without the influence of surface area effects.

The $Fe_3(CO)_{12}/Zr(OPr)_4$/silica catalyst was gas phase tested to determine the inherent water-gas shift activity, since iron carbonyl was being added to the cobalt catalysts in an attempt to improve water-gas shift activity. This catalyst showed very little Fischer-Tropsch activity over the entire 220°C to 280°C temperature range (<6% syngas conversion at 280°C). Loss of iron from the catalyst did not occur. The cause of the low activity may be due to formation of very small Fe particles which are known to exhibit low Fischer-Tropsch activity.

Slurry screening tests were performed on two catalysts. One was a Zr - promoted ruthenium catalyst supported on silica. This catalyst gave good results in the gas phase tests but proved to be a poor performer in the slurry phase tests. The catalyst deactivated rapidly and was found to be covered with coke at the end of the run. The other screening test was on a Zr - promoted, cobalt catalyst supported on silica. This catalyst had less Zr than the previously tested catalyst of this type. The test showed that the specific activity was lower with the reduced Zr loading.

The extended slurry test which was begun last quarter continued this quarter. The same load of catalyst was run at 240°C for 1000 hours and then at 260°C for an additional 1200 hours. At each temperature, the catalyst underwent a gradual decline in activity.

All liquid organic and wax products were collected during the initial 1000 hours of operation of the $Co_2(CO)_8/Zr(OPr)_4/SiO_2$ catalyst in the extended slurry test #8862-1-31, in order to isolate and characterize the diesel fuel fraction. The diesel fuel produced during this period of operation had a fairly high flash point, essentially no water or sediment, low sulfur, and negligible ash and carbon residue. It showed very low corrosiveness and had an outstanding cetane index. As a result it met all specifications for the highest quality diesel fuel oil (ASTM No. 1-D) except for very small variations from viscosity, cloud point and 90% boiling point.

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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 sixth 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 $CO:H_2$ 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) $Co_2(CO)_8/Zr(OPr)_4/SiO_2$

To study the effect of Co-to-promoter ratio on the performance of the silica-supported catalysts, the following four Co/Zr/silica catalysts were prepared. The cobalt loading was kept at 4 wt%, while the zirconium loading was progressively lowered. This gave a series of catalysts, including the basecase catalyst, having Co-to-Zr ratios of 0.53, 0.83, 1.9, 6.6 and a final catalyst having no added promoter. All four catalysts were prepared using the standard impregnation procedure.

Catalyst #	Wt% Co	Wt% Zr	Co/Zr
8466-45	4.0	4.8	0.83
8466-46	4.4	2.3	1.9
8466-47	4.6	0.7	6.6
8466-49	4.2	0	∞

(ii) $Co_2(CO)_8/Zr(OPr)_4/SiO_2$ (Catalyst #8466-55)

An increase in activity was observed for the Co/Zr catalyst when silica was used as the support in place of alumina. Since the silica surface area was 50% larger than that of the alumina, it was of interest to determine if this larger surface area was responsible for the enchanced activity. Thus a Co/Zr/silica catalyst was prepered which had a very similar surface area as the alumina-supported catalyst. The metal loadings were anelogous as well. The low surface area silica was prepared from the standard high surface silica by calcination at 900°C.

(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 4.1(b). Specific run conditions did vary somewhat and are documented accordingly. Gas phase performance data is summarized in Table 1.

(i) $Fe_3(CO)_{12}/Zr(OPr)_4/SiO_2$ - Run #8413-88-40, Catalyst #8466-40

This catalyst, which was prepared last quarter, was tested in the fixed-bed reactor to examine the behavior of an Fe-only catalyst on zirconated silica. Of particular interest was the inherent water-gas shift (WGS) activity, since iron carbonyl was being added to the cobalt catalysts in an attempt to improve WGS activity. The test was performed in the usual manner with mass balances at 220°C, 240°C and 280°C. The fresh catalyst contained 2.4% Fe and 7.3% Zr.

This catalyst showed very little activity over the entire 220°C to 280°C temperature range. Even at 280°C the total syngas conversion was less than 6%. This surprisingly low activity was first thought to have been caused by loss of iron from the catalyst as volatile $Fe(CO)_5$. Analysis of the used catalyst, however, showed that it still contained 2.5% Fe, indicating that something else was responsible for the poor performance.

The low activity may be related to the particle size of the Fe on the catalyst. There are many literature reports concerning the structure sensitivity of carbon monoxide hydrogenation (1). It has been shown that the activity of Fe-based catalysts increases with increasing iron particle size (2). It is also known that very small particle sizes can be obtained by using $Fe_3(CO)_{12}$ to prepare supported catalysts (3, 4). Since our silica support had a high surface area (339 m^2/g) and the iron loading was fairly low, our catalyst may have had very small particles which limited the activity. For whatever reason, it is obvious why the addition of Fe, as iron carbonyl, to the cobalt carbonyl-based catalyst had no effect on the WGS activity.

(ii) $Co_2(CO)_8/Zr(OPr)_4/SiO_2$ -- Run #8413-93-45, Catalyst #8466-45

This was the first catalyst tested in the series of catalysts where the cobalt to promoter ratio was varied. This catalyst contained 4.0% Co and 4.8% Zr with a Co/Zr ratio of 0.83. This compares to 3.5% Co, 6.6% Zr and a Co/Zr ratio of 0.53 for the basecase catalyst composition. For comparison the results from the basecase catalyst test (#8413-28-18) are found at the bottom of Table 1. Lowering the amount of zirconium gave a slightly more active catalyst as reflected by the 11 - 12% increase in bulk activity over the basecase catalyst at 240°C and 260°C. Specific activity was somewhat lower than the basecase because carbon monoxide utilization was not as good.

Compared to the basecase total fuels selectivity (C_{5-23}) decreased and methane selectivity increased as the amount of promoter was lowered, especially at 220°C and 240°C. At 220°C and 260°C there was a general shift toward lighter products, while at 240°C, the product distribution became broad with the largest wax (C_{24}+) selectivity occurring at this temperature. This trend of increasing bulk activity and decreasing liquid fuels selectivity as the Co/Zr ratio increased was also observed for the gas phase tests of the $Co/Zr/Al_2O_3$ catalyst.

(iii) <u>$Co_2(CO)_8/Zr(OPr)_4/SiO_2$ -- Run #8413-99-46, Catalyst #8466-46</u>

This was the second in the series and contained 4.4% Co and 2.3% Zr with a Co/Zr ratio of 1.9. This time as the zirconium loading was decreased there was a drop in both bulk and specific activity at 220°C and 240°C. This amounted to a 16% decline in bulk activity at 240°C and over 50% decline at 220°C. At 260°C, however, there was a slight 7% increase in bulk activity with only a minor difference in specific activity.

There was no real trend established for the hydrocarbon selectivity. At 220°C, a shift toward light products predominated with CH_4 selectivity at a rather high value of 25 wt%. Increasing to 240°C caused a broadening of the hydrocarbon product slate similar to the previous catalyst. Liquid fuels selectivity was 69 wt% compared to 72 wt% for the basecase, however, the CH_4 selectivity was the same for both catalysts. At 260°C, both this catalyst and the basecase catalyst gave very similar hydrocarbon selectivities.

(iv) <u>$Co_2(CO)_8/Zr(OPr)_4/SiO_2$ -- Run #7743-2-47, Catalyst #8466-47</u>

The third catalyst in this series had a Co/Zr ratio of 6.6 with 4.6% Co and 0.7% Zr. At 220°C and 240°C the trend of declining activity with decreasing zirconium loading continued with bulk activities of 9 and 36 mols syngas/kg cat/hr, respectively. At 260°C, however, the bulk activity showed a dramatic increase to 98 mols syngas/kg cat/hr. This large increase may have been due more to local hotspots on the catalyst than to intrinsic catalyst activity since temperature control was very difficult at 260°C.

Hydrocarbon selectivity continued to shift toward lighter products as the zirconium loading was decreased. At 220°C and 260°C the methane selectivity was 22 and 36%, respectively, and the total liquid fuels selectivity was never greater than 50%. As with the previous catalysts in this series, the best selectivity was obtained at 240°C, where C_{5-23} was 63% and methane was 15%. This compares to 72 and 10% respectively, for the basecase catalyst at 240°C.

(v) $Co_2(CO)_8/Zr(OPr)_4/SiO_2$ -- Run #7743-8-49, Catalyst #8466-49

The final catalyst in this series was prepared without any promoter and contained 4.2% Co. This catalyst showed the lowest activity of all the catalysts tested in this series. At 260°C the bulk activity was only 33 mols syngas/kg cat/hr compared to 74 mols syngas/kg cat/hr for the basecase. At 240°C the bulk activity was 50% lower than the basecase. Specific activity showed an even greater decline and was only 0.20 mols CO/mol Co/min at 260°C.

The hydrocarbon selectivity continued the trend toward lighter products with the best total fuels selectivity obtained at 240°C as usual. What was unusual was that at 240°C the C_{5-23} fraction contained an abnormally large amount of C_{19-23} material (21%) and the wax (C_{24}+) selectivity was high at 18%.

The effect of Co/Zr ratio on gas phase bulk and specific activity for this series of silica-supported catalysts is plotted in Figures 1 and 2. For optimum bulk activity it appears that the Co/Zr ratio should be closer to 1 than to the basecase value of 0.5. Specific activity, however, was best for the basecase catalyst. The usage ratio followed a trend toward higher values as the zirconium content increased. Total fuels selectivity was also best for the basecase catalyst, especially if straight run liquid fuels (C_{5-18}) was desired. Overall, it then appears that the optimum Co/Zr ratio is quite near 0.5, although lower ratios were not investigated.

(c) Slurry Reactor Tests

During this quarter, slurry screening tests were performed on two catalysts. Also, the extended test that was begun last quarter was continued. All of the tests were conducted in 1-liter reactors. In the screening tests, the operating parameters were varied to determine the conditions necessary for optimum catalyst performance. The primary objectives of the extended test were to examine performance stability at constant operating conditions and to obtain samples for fuel characterization studies. The two catalysts used in the screening tests were:

- A Zr - promoted, ruthenium catalyst supported on silica. As reported in the October - December 1985 Quarterly Report, this catalyst gave the highest bulk and specific activities of any catalyst tested to that time in the gas phase reactor (Run #8413-73-37). For this reason, the ruthenuim on silica catalyst was chosen as a candidate for the slurry reactor.

- A Zr - promoted, cobalt catalyst supported on silica with a Co/Zr ratio of 1.9. This compares to the slurry reactor test (#8670-11-18) where the Co/Zr ratio was 0.5. The gas phase tests showed a higher specific activity with more Zr and it was desired to see whether this was also true in the slurry reactors.

Selected results for the slurry tests are listed in Table 2, along with representative results of all previous slurry tests from this contract for comparison.

(i) $Ru_3(CO)_{12}/Zr(OPr)_4/SiO_2$ -- Test #8862-16-37, Catalyst #8466-37

Since the gas phase tests for this catalyst were so successful, it was decided to examine the catalyst in the slurry reactor. In summary, the catalyst performed poorly. It deactivated rapidly which was probably caused by coking of the catalyst that was observed at the completion of the run. The catalyst contained 4.1% Ru and 4.7% Zr. The activation procedure is described in Section 4.1 (c) and the activity, conversion and selectivity data of this catalyst are summarized in Table 3. The data for each mass balance sample are listed in Tables 4 - 23 and hydrocarbon distributions are illustrated in Figures 3 - 12.

The first set of runs was conducted at 240°C and 300 psig. A summary of the results is presented below:

Sample #	SV (L/g cat/hr)	CO/H_2 (mol ratio)	Conversion (% H_2+CO)	Bulk Activity (mol syngas/kg cat/hr)
3	2.0	0.5	47.8	42.7
6	1.0	0.5	36.8	16.4
9	1.0	1.0	20.8	9.3
12	2.0	1.0	5.8	5.2

The most notable feature of this catalyst was the rapid deactivation that occurred. This can be seen readily by examining the first two mass balance points which were taken after 44 and 116 hours of operation. Normally, the conversion as a percentage of reactants fed would be expected to be higher with a lower space velocity due to the increased residence time. However, in this case, conversion dropped by 23%. Similarly, bulk activity decreased significantly between Samples 9 and 12 which would not be the logical result when the only change was an increase in space velocity.

The next set of runs was conducted at 260°C and 300 psig.

Sample #	SV (L/g cat/hr)	CO/H_2 (mol ratio)	Conversion (% H_2+CO)	C_1 (Wt%)
15	2.0	1.0	9.3	19.4
18	1.0	1.0	6.8	25.4
21	1.0	0.5	19.5	45.6
24	2.0	0.55	10.4	51.3

Bulk activity did increase between Samples 12 and 15 when the temperature was raised from 240°C to 260°C with all other conditions being held constant. This would be expected. Comparing Sample 9 with 18 for which temperature was also the only change, shows a lower conversion at the higher temperature. The phenomena is also true when one makes a similar comparison between Sample pairs 6 - 21 and 3 - 24. This indicates that the deactivation is continuing.

Note also that a distinct shift toward lower molecular weight products is occurring. The methane selectivity figures shown above for 260°C operation compare with an average selectivity for methane of 8.0 wt% when operating at 240°C.

After 689 hours of operation, Sample 27 was taken at feed conditions identical to those for Sample 6. The deactivation and the shift to lighter products is evident below:

Sample #	6	27
Conversion (% H_2+CO)	36.8	11.1
Selectivity (Wt%)		
C_1	6.5	33.8
C_2 - C_4	3.8	12.8
C_5 - C_{11}	13.0	15.5
C_{12} - C_{18}	26.8	16.5
C_{19} - C_{23}	22.0	10.2
C_{24}+	28.0	11.3

For the last run (Sample 30) with this catalyst, the temperature was raised to 280°C. Pressure remained 300 psig with SV=1.0 L/g. cat/hr. and CO/H_2=0.5 mol. ratio. Overall conversion (H_2+CO) was 21.5%. Although this is higher than the preceding run (11.1%) at 240°C, it is still less than the conversion achieved at 240°C prior to deactivation.

When the silica supported ruthenium catalyst was removed from the reactor, a heavy coke formation was noticed. Active carbon species are important intermediates in the Fischer-Tropsch synthesis with Ru catalysts, however, transformation of these active species to graphitic carbon causes deactivation. This carbon deactivation mechanism for Ru catalysts has been well documented in the literature (5).

A ruthenium catalyst supported on alumina (Slurry run 7887-36-478) was also tested during this contract. The results are summarized in Table 35 of the January to March 1985 Quarterly Report. When the alumina supported and silica supported catalysts are compared, it can be seen that the latter is initially more active. However, the silica supported catalyst deactivated so rapidly, that it became the catalyst with lesser activity.

Finally, note that the comparative catalyst test data (Table 2) shows that this catalyst produced significantly more wax than any of the other catalysts tested up to this time.

(ii) $Co_2(CO)_8/Zr(OPr)_4/SiO_2$ -- Test #8862-41-46, Catalyst #8466-46

The catalyst for Slurry run 8670-11-18 contained 4.9% Co and 9.3% Zr. The catalyst for the current slurry run contained 4.8% Co and 2.7% Zr. It was desired to see if the gas phase trend of lower specific activity with lower Zr loadings was true in the slurry reactors. In summary, the results show that the answer is yes and that the selectivity for liquid fuels is similar for both catalysts. The activation procedure is described in Section 4.1 (c) and the activity, conversion and selectivity data of this screening test are summarized in Table 24. The data for each mass balance sample are listed in Tables 25 - 46 and hydrocarbon distributions are illustrated in Figures 13 - 23.

The initial operating temperature (Samples 3 - 12) for this catalyst was 240°C. The pressure was held constant for all runs at 300 psig. The first four mass balances were taken at the following conditions:

Sample #	CO/H_2 (mol ratio)	SV (L/g cat/hr)
3	0.5	2.0
6	0.5	1.0
9	1.0	1.0
12	1.0	2.0

The highest selectivity to liquid fuels (C_5 - C_{23}), 68.9%, occurred during Sample 9. Unfortunately, this was also the set of conditions that produced the lowest bulk activity, 15.8 mol. syngas/kg. cat/hr. Sample 9 also produced the highest wax and lowest methane selectivities, 11.2% and 9.8% respectively.

Sample 12 from the current slurry run was collected while operating at the same conditions as Sample 9 in the higher Zr test. The specific activity (mol CO/mol Co/min) for the lower Zr catalyst was 57% of the specific activity for the prior slurry run. This confirms the trend shown in the gas phase tests. The selectivity to liquid fuels was only 5.7% lower for the current catalyst.

The next four runs were conducted at 260°C:

Sample #	CO/H_2 (mol ratio)	SV (L/g cat/hr)
15	0.96	2.0
18	1.0	1.0
21	0.49	1.0
24	0.49	2.0

As expected, the increased temperature resulted in an increase in activity. Selectivity to liquid fuels remained above 60% until the CO/H_2 ratio was reduced to 0.49. For Samples 21 and 24, the selectivity to liquid fuels reduced to 54.8% and 44.8% respectively. There was a corresponding increase in the selectivity to methane.

At 260°C, Sample 15 of the current run corresponds to Sample 39 of the higher Zr test. The trend to lower specific activity with lower Zr continued, although the reduction was only 25%. Liquid fuels selectivity was actually 5.2% higher with the current catalyst.

After 720 hours of operation with this catalyst, Sample 27 was run at the same conditions as Sample 6 to check for deactivation. The bulk activity had declined from 20.6 to 13.4 (mol syngas/kg cat/hr), a 35% reduction. Selectivity to liquid fuels had also declined from 63.7% to 49.4%.

For the last two runs (Samples 30, 33), the temperature was increased to 280°C. The conditions tested were:

Sample #	CO/H_2 (mol ratio)	SV (L/g cat/hr)
30	0.49	2.0
33	1.0	2.0

Sample 30 was run at the same conditions as Sample 3 except for the increase in temperature from 240°C to 280°C. The increase in temperature apparently compensated for the deactivation since bulk activity was 41.2 mol syngas/kg. cat/hr. compared to 40.8 for Sample 3. Selectivity to liquid fuels was much lower at 32.0% vs. 61.7%. Selectivity to liquid fuels improved to 52.7% when the CO content of the feed was raised for Sample 33. However, specific activity also declined from 0.244 to 0.168 mol CO/mol Co/min.

At 280°C, Sample 33 of the current run was conducted at the same conditions as Sample 42 of the higher Zr loading catalyst. Lower specific activity at lower Zr was also true here with values of 0.168 and 0.375 mol CO/mol Co/min. for the low and high loadings respectively. Liquid fuels selectivities were close again with the lower loading showing 9% lower values.

(iii) $Co_2(CO)_8/Zr(OPr)_4/SiO_2$ -- Extended Test #8862-1-31

The extended slurry phase test run was begun in December 1985 (see page 20 from the October - December 1985 Quarterly Report). The silica supported, Co/Zr catalyst was chosen for the extended slurry test because it had shown the best performance in the previous slurry screening studies. A summary of the performance data obtained during this quarter is found in Table 47 along with the results from the last quarter. Tables 48 - 95 list the mass balance process conditions and hydrocarbon product distributions for each sample point taken this quarter. The weight distributions for the same samples are shown graphically in Figures 24 - 47.

For the first 1012 hours of the slurry test, the reactor was run with the following conditions: temperature=240°C, pressure=300 psig, CO/H_2=0.5 mol ratio, and space velocity=1.8 L/g cat/hr. During the course of the run, the bulk activity declined from 52.7 to 46.9 mol syngas/kg cat/hr. This gradual loss of activity is shown graphically in Figure 48. Figure 49 depicts the conversions of H_2, CO, and H_2+CO. The selectivity to the various hydrocarbon fractions is shown to be stable in Figure 50.

During this period, a power outage occurred after operating for approximately 420 hours. The automatic safety features built into the reactor system cause the feed gas and heater to shutoff, a nitrogen purge to be introduced into the reactor, and water to flow through the reactor cooling coils. During the next scheduled shift, the reactor heater was restarted and syngas was re-introduced into the reactor. Normal operation was restored about 22 hours after the power failure. It is apparent that the catalyst suffered no significant harm due to this process upset. All of the characteristics such as activity and selectivity had returned to the trend line.

The average results for the operation at 240°C are summarized below:

Conversion (% H_2+CO)	61.3
Bulk Activity (Mol syngas/kg cat/hr)	49.2
Specific Activity (Mol CO/mol Co/min)	0.29
Selectivity (Wt%)	
C_1	19.5
C_5 - C_{11}	39.1
C_{12} - C_{18}	11.2
C_{19} - C_{23}	3.0
C_{24+}	1.8

The organic liquid and wax products were collected and saved for analysis as a suitable diesel fuel as described in Section 3.4.

Next, the catalyst temperature was raised to 260°C. The following operating conditions were then held constant from 1012 - 2188 hours of operation: pressure=300 psig, CO/H_2=1.0 mol. ratio, SV=2.0 L/g. cat/hr.

The results of this portion of the test were similar to those at 240°C. Specifically, there was a gradual decline in catalyst activity which is shown graphically in Figure 51. Conversion data from H_2, CO, and H_2+CO is shown in Figure 52. The selectivity to the hydrocarbon fractions is also shown in Figure 53. The selectivity data are somewhat scattered, but there appears to be a slight trend toward more methane and less wax which did not occur at 240°C. The liquid fuels C_5 - C_{23} was little changed. The average results for the extended test operation at 260°C are shown below:

Conversion (% H_2+CO)	52.6
Bulk Activity (Mol syngas/kg cat/hr)	46.9
Specific Activity (Mol CO/mol Co/min)	0.30
Selectivity (Wt%)	
C_1	12.5
C_5 - C_{11}	41.6
C_{12} - C_{18}	18.5
C_{19} - C_{23}	6.9
C_{24}+	4.7

All of the organic liquid and wax products were collected from this portion of the extended test as was done at 240°C.

At this point, it was decided to attempt to obtain data that could be used for kinetic studies from this reactor. The catalyst stability test continued concurrently. Initially, the temperature was kept at 260°C, but feed conditions such as space velocity and CO/H_2 feed ratio were varied. The major difference between this test and the slurry screening tests was that each new operating condition would be allowed time to stabilize between sampling times. Further, if a mass balance closure was not acceptable, another sample point could be taken before operating conditions were changed for the next test in the sequence.

The kinetic runs were begun late in this quarter and will continue next quarter. The results from this quarter's runs are included in the Tables and Figures for the extended slurry test for completeness. A full discussion of the tests will await the April - June 1986 Quarterly Report when they are finished.

3.3 Task 3 -- Slurry Reactor Kinetic Studies

As reported in Section 3.2 (c), near the end of this quarter the focus of the extended slurry run shifted from stability testing to developing data for use in kinetic studies. These experiments are not yet complete. A discussion of the results will be presented in the April - June Quarterly Report.

3.4 Task 4 -- Fuel Product Characterization

All liquid organic and wax products were collected during the initial 1000 hours of operation of the $Co_2(CO)_8/Zr(OPr)_4/SiO_2$ catalyst in the extended slurry test #8862-1-31. The reactor was at the same conditions of 240°C, CO/H_2=0.5, SV=1.8, L/g cat/hr and 300 psig during that entire period. These products were collected in order to isolate and characterize the diesel fuel fraction. The diesel range product contained in the wax was isolated by vacuum distillation in a Kugelrohr (trap-to-trap) apparatus and combined with the one gallon of liquid organic product. The wax contained 9 wt% diesel product. The combined sample was then fractionated by vacuum distillation with the diesel product boiling range defined as 190°C to 338°C at 760 mm Hg (ASTM standard). The pot temperature was maintained below 240°C to prevent decomposition. 1.06 kg of diesel range product was obtained.

The diesel fuel properties were determined by E. W. Saybolt and Company (Philadelphia, PA) using 11 standard ASTM tests. The results are shown in Table 96, along with the ASTM requirements for No. 1-D diesel fuel oil, which is the highest quality diesel fuel and intended for use requiring frequent speed and load changes. Our diesel product falls within all the specifications except for viscosity, cloud point and the 90% boiling point. High values for these three properties indicate that our diesel product contain a bit more heavier hydrocarbons. Our diesel fuel falls well within all the specifications for the No. 2-D grade diesel fuel oil. This diesel fuel has a fairly high flash point, essentially no water or sediment, low sulfur, and negligible ash and carbon residue. As a result of being this "clean", it is not corrosive. One outstanding property of our diesel fuel product is the high cetane value. For reference, the ASTM requirements for all 3 grades of diesel fuel oil are listed in Table 97, as well as the ASTM copper strip corrosion test classifications, which are listed in Table 98.

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) $Co_2(CO)_8/Zr(OPr)_4/SiO_2$ (Catalyst #8466-45)

The silica (110.7g, Davison 952) was pretreated using the standard method. A 370-cc hexane solution containing $Zr(OC_3H_7)_4 \cdot XC_3H_7OH$ (33.9g, 6.0g Zr) was impregnated onto the silica. After thorough mixing, the hexane was evaporated off in vacuo. A solution containing $Co_2(CO)_8$ (17.76g, 6.0g Co) in 180-cc toluene and 120-cc hexane was then added to the support and the solvent removed in vacuo. This gave 148.5g of brownish, black solid that contained 4.0% Co and 4.8% Zr (Co/Zr=0.83).

(ii) $Co_2(CO)_8/Zr(OPr)_4/SiO_2$ (Catalyst #8466-46)

This catalyst was prepared using the same procedure as the previous catalyst with the following materials:

SiO_2	121.5g
$Zr(OC_3H_7)_4 \cdot XC_3H_7OH$	16.95g, 3.0g Zr
$Co_2(CO)_8$	17.76g, 6.0g Co

148.3g of catalyst was obtained and analysis showed it to contain 4.4% Co and 2.3% Zr (Co/Zr=1.9).

(iii) $Co_2(CO)_8/Zr(OPr)_4/SiO_2$ (Catalyst #8466-47)

Using the same procedure as the two previous catalysts, this catalyst was prepared from the following materials:

SiO_2	129.6g
$Zr(OC_3H_7)_4 \cdot XC_3H_7OH$	4.24g, 0.75g Zr
$Co_2(CO)_8$	17.76g, 6.0g Co

150.1g of catalyst was obtained and had the following analysis: 4.6% Co and 0.7% Zr (Co/Zr=6.6).

(iv) $Co_2(CO)_8/Zr(OPr)_4/SiO_2$ (Catalyst #8466-49)

Using the same procedure as above, this catalyst was prepared from 132.2g of SiO_2 and 17.76g of $Co_2(CO)_8$ (6.0g Co) to give 147.3g of catalyst. The catalyst contained 4.2% Co with no promoter.

(v) $Co_2(CO)_8/Zr(OPr)_4/SiO_2$ (Catalyst #8466-55)

To lower the surface area of the Davison 952 silica it was calcined at 900°C in static air for 16 hours. The surface area of the calcined material was 196 m^2/g. This silica (83.6g) was impregnated with a 130-cc hexane solution containing 55.68g $Zr(OC_3H_7)_4 \cdot XC_3H_7OH$ (9.86g Zr). After removal of the solvent, the support was impregnated with a 130-cc toluene (90%)/hexane (10%) solution containing 15.99g $Co_2(CO)_8$ (5.4g Co). Upon removal of the solvent, 134.9g of greenish black catalyst was obtained, having the following elemental analysis: 4.1% Co and 6.8% Zr (Co/Zr=0.60). The surface area of the catalyst was 210 m^2/g.

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

(c) Slurry Reactor Tests

(i) $Ru_3(CO)_{12}/Zr(OPr)_4/SiO_2$ -- Test #8862-16-37

This catalyst was activated in the 150-cc fixed-bed, tubular reactor using pure H_2 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 N_2. The reactor was heated at 0 psig to 300°C at a rate of 1°/min with a H_2 flowrate of 1000 sccm. The temperature was maintained at 300°C for 8 hours. After cooling, the reactor was flushed with N_2, 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 N_2 purge.

For this slurry test, 83.1g of reduced catalyst in a 450-cc slurry volume was charged to the one-liter reactor giving a 19.2 wt% catalyst concentration. The metal loadings before and after activation were as follows:

	Fresh	Activated
Ru	4.0 wt%	4.1 wt%
Zr	3.3	4.7

(ii) $Co_2(CO)_8/Zr(OPr)_4/SiO_2$ -- Test #8862-41-46

This catalyst was activated and slurried in the same manner as above. The reactor charge was 450-cc of a 20.0 wt% slurry containing 83.7g of activated catalyst. Elemental analysis of the catalyst was as follows:

	Fresh	Activated
Co	4.4 wt%	4.8 wt%
Zr	2.3	2.7

(iii) $Co_2(CO)_8/Zr(OPr)_4/SiO_2$ -- Extended Test #8862-1-31

The activation and slurry charge for this test was described in the previous quarterly report.

(d) Catalyst Characterization

B.E.T. surface areas were obtained using a Micromeritics Digisorb 2500.

5.0 REFERENCES

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