

I. EXECUTIVE SUMMARY

During the seventh quarter, significant progress in several areas have enabled us to make a number of important conclusions.

Preliminary catalyst preparation of 3 batches of a Ru-promoted 20% Co/Al₂O₃ has confirmed the similarity in catalysts prepared by EI and by Calsicat using the same procedure. This similarity was evident in both fixed bed and SBBC reactor studies.

All TiO₂-supported Co catalysts have been found to have poor F-T properties in both the fixed-bed and SBC reactors. These catalysts had been prepared following exactly the procedures given in the Exxon patents. One of the main problems in using TiO₂ as a support is the fact that it has low surface area for supporting a 20 wt % Co catalyst. Another problem is that it does not seem to be robust enough for use in a SBGC reactor.

Ru promotion of Co/SiO₂ does not have as dramatic effect on catalyst activity as seen for Co/Al₂O₃. However, it does play a major role in maintaining higher activity (factor of 2 in the SBCR) when K is added to Co/Sr/SiO₂.

Zr has been clearly shown by us to significantly enhance the F-T activity of Co/SiO₂. Such promotion is a basis for many of these Shell cobalt F-T patents. Latest results indicate that Zr also improves the activity of Co/Al₂O₃, although the methane selectivity is also slightly elevated.

Finally, for our design of a "benchmark" Co F-T catalyst, research has now shown using both fixed-bed and SBC reactors that 0.3 wwt % K is the optimum amount to use with Ru-promoted 20 wt % Co/Al₂O₃. This amount of K greatly improves higher hydrocarbon selectivity without causing an unacceptable loss of activity.

II. INTRODUCTION AND BACKGROUND

The goal of this project is the development of a commercially viable, cobalt-based Fischer-Tropsch (F-T) catalyst for use in a slurry bubble column reactor. Cobalt-based catalysts have long been known as being active for F-T synthesis. They typically possess greater activity than iron-based catalysts, historically the predominant catalyst being used commercially for the conversion of syngas based on coal, but possess two disadvantages that somewhat lessen its value: (1) cobalt tends to make more methane than iron does, and (2) cobalt is less versatile with low H_2/CO ratio syngas due to its lack of water-gas shift activity. Therefore, the major objectives of this work are (1) to develop a cobalt-based F-T catalyst with low (<5%) methane selectivity, (2) to develop a cobalt-based F-T catalyst with water-gas shift activity, and (3) to combine both these improvements into one catalyst. It will be demonstrated that these catalysts have the desired activity, selectivity, and life, and can be made reproducibly. Following this experimental work, a design and a cost estimate will be prepared for a plant to produce sufficient quantities of catalyst for scale-up studies.

III. PROJECT DESCRIPTION

The Cobalt Fischer-Tropsch Catalyst Project is divided into five tasks designed to systematically develop catalysts through thorough investigation of influences of various promoters, additives, and supports on minimizing methane selectivity and increasing water-gas-shift activity.

Cobalt has long been known to be an excellent catalyst for the F-T synthesis. Nevertheless, all currently operating F-T plants feeding coal produced syngas use iron catalysts, in spite of the fact that cobalt-based catalysts have higher activity. Two factors that lower cobalt's value as a F-T catalyst

are its poorer selectivity, that is, it produces more methane and its inability to be used with low H_2/CO ratio syngas because of its lack of water-gas shift activity. The broad objective of this proposal is to overcome these deficiencies.

In pursuing F-T catalyst development, there are several aspects that need to be considered. These are catalyst formulation, catalyst pretreatment, and catalyst performance. All of these aspects will be dealt with in this project.

In broad terms, the technical approach that will be used is outlined below:

- a. Conduct a thorough review of the literature on F-T synthesis, both the journal literature and the patent literature. In this review, identify approaches for improving methane selectivity of cobalt-based catalysts, identify additives that have WGS activity, identify catalyst formulation options, and define critical pretreatment parameters.
- b. Based on the above review, develop a list of catalyst formulations with potential for low methane selectivity and a list of catalyst formulations with potential for promoting the WGS reaction.
- c. Screen these catalysts in a small, fixed-bed reactor. If no catalyst meets the target specifications, go back to step b. Otherwise, run catalysts that meet discrimination criteria in a slurry bubble column reactor.
- d. Once catalysts with low methane selectivity and WGS activity have been identified, develop a catalyst combining both these functions and test as described above.
- e. Having found catalysts that meet the desired criteria for activity and selectivity, optimize the pretreatment conditions.
- f. Demonstrate catalyst reproducibility by having a commercial subcontractor prepare

multiple batches for testing.

- g. Demonstrate catalyst stability by running aging tests in a slurry bubble column reactor.
- h. Based on above results, prepare a design for a plant to produce demonstration scale batches of catalyst. Develop capital and operating costs of this plant.

The program to carry out the above outlined work will consist of five major tasks:

Task 1 -- Catalyst Development

Task 2 -- Catalyst Testing

Task 3 -- Catalyst Reproducibility Tests

Task 4 -- Catalyst Aging Tests

Task 5 -- Preliminary Design and Cost Estimate for a

Demonstration-Scale Catalyst Production Facility

All aspects of the catalyst's role in F-T processing will be addressed, including catalyst preparation, pre-treatment, and performance (activity, selectivity, and aging). In addition to gathering process data, the catalyst will be subjected to a number of analytical measurements at each stage to see how various treatments have affected the catalyst and its performance.

IV. OBJECTIVES

The objective of this project is to investigate the influence of various promoters, additives, and supports on minimizing the methane selectivity and increasing the water-gas shift (WGS) activity of cobalt (Co) Fischer-Tropsch (F-TT) catalysts. The ultimate goal of this investigation is to identify and demonstrate a catalyst preparation procedure that will be scaled up for the reproducible synthesis of commercial quantities of supported CO catalysts with desired activity, selectivity, and lifetime for use in F-T synthesis in three-phase slurry bubble column reactors.

V. SUMMARY OF WORK ACCOMPLISHED THIS QUARTER

Fourteen (14) new catalysts were formulated and prepared during this period under both subtasks 1.2 and 1.3. Two more catalysts were prepared by Calsicat.

The characterization of all the catalysts in order to determine their physical properties (BET surface area, pore volume, pore size diameter, particle size distribution), as well as the cobalt reducibility, extent of reduction, and dispersion) was continued.

Fixed-bed reactor testing of the catalysts was continued. Thirteen (13) new catalysts have been tested for their F-T synthesis performance. Some catalysts have been retested for reproducibility checks. Ten catalysts, three of which contain Co, were tested for water-gas shift activity.

An investigation of the effect that calcination (static versus flow, temperature) of a selected number of catalysts has upon their performance for F-T synthesis has been started during this period.

Two topical reports based on the data collected during this project, and which constitute our contribution to the ACS National Meeting in Washington, D.C., in August 1994, and to the Eleventh Annual International Pittsburgh Coal Conference in September, 1994, have been completed.

Under subtask 2.2 during this reporting period a total of 14 runs were made in the two slurry bubble column reactors with nine catalysts on alumina, three on titania, and two on silica support. Data was compiled to compare the COO conversions and product selectivities of the methane reduction catalysts.

VI. DETAILED DESCRIPTIONN OF TECHNICAL PROGRESS

A. TASK 1: CATALYST DEVVELOPMENT

a. Technology Assessment ((Subtask 1.1)

Except for regular updating of the literature with the most recent publications, there was no activity during this period to report t in this subtask.

b. Catalyst Formulation (Subbtasks 1.2, 1.3, 1.4)

An updated list of all the catalysts formulated so far within Subtask 1.2 (including those catalysts listed in previous quarterly n reports) is tabulated along with their compositions in Table 1 on pages 25 to 28. The last column of TTable 1 indicates whether the catalyst has already been prepared. Out of the 57 catalysts listed in Table 1, three (CAL.01-CAL.03) were prepared by Calsicat. Eight (8) new Co catalysts (highlighted in i Table 1 on page 28) have been formulated and prepared during this period. The detailed formulaticions of the new catalysts are given in Appendix A.

Co.049 (with 20% Co, 0.5% Ru, 0.1% K) is an alumina-supported catalyst, similar to Co.047, except for a lower K loading. Co.050 (with 20% Co, 0.5% Ru, 8.5% Zr, 0.1% K) and Co.054 (with 20% Co, no Ru, 8.5% Zr, 0.3% K) a are both silica-supported catalysts, which are similar to Co.048; one with a lower loading of K; t the other, without Ru. Co.053 (with 20% Co, 0.5% Ru, no promoter, on alumina) has the same c composition as Co.018. This new batch of Co.053 was prepared in larger quantity in order to investstigate the effect of calcination on the properties of the Co F-T catalysts. Co.051 and Co.052, bothh with only 0.5% Ru on titania (one in the rutile form and the other in the anatase form), were prepared to complete the investigation of the adsorption properties of the titania-supported catalysts. F Finally, CAL.02 and CAL.03 (each with 20% Co, 0.5% Ru on alumina) are two more batches of catatalysts with the same formulation as that of Co.018 or CAL.01

which were prepared at Calsicat for formulation check. CAL.02 was prepared using the same impregnation technique as used for CAL.01. CAL.03 was prepared using a two-step impregnation of the Co-Ru solution with calcination of the catalyst precursor between the two impregnations. These new formulations are tabulated in Table 1 on page 28 and described in Appendix A.

An investigation of the effect on methane selectivity of various promoters, additives, and supports was carried out in Subtask 1.2 with the main objective being to determine the nature and amount of the promoters which play a significant role in achieving the desired activity and selectivity (see Table 2) on page 29.

Over 50 catalysts with various formulations were prepared, thoroughly characterized using different techniques, and screened in a fixed bed reactor. Out of the 50 catalysts, more than 20 catalysts which showed great potential in achieving the desired activity and selectivity were tested in a slurry bubble column reactor (SBCRR). The reaction procedure used for the SBCR testing is shown in Table 3 on page 30. A typical complete run lasted about 10 days.

Before and after each run the particle size distribution of representative samples of the catalysts were determined. Changes in particle size were then determined as a measure of the attrition resistance of the catalysts. Although not included in the requirements for an optimized low methane catalyst, the attrition strength plays a major role in the selection of a catalyst for SBCR application.

From the SBCR results several catalysts were found to meet or exceed the required criteria of activity and selectivity listed in Table 2. These catalysts are listed in Table 4 with their activities and selectivities under various process conditions. The last column indicates whether the catalyst passed or failed the selection criteria based only on the results shown, i.e. over the whole range of reaction conditions tested. However, in most cases an adjustment of the process conditions within

the range given in Table 2 would certainly improve their catalytic property to the desired range.

While some of the silica supported catalysts (e.g., Co.048) would meet the required activity and selectivity criteria, they tend to have lower resistance to attrition compared with the alumina supported catalysts. Thus, an alumina based catalyst (Co.047) which meets and even exceeds all the criteria has been selected for the reproducibility study. While plain Co on alumina (Co.005) does also meet the activity and selectivity criteria, the presence of Ru was shown to improve the reducibility of the Co. In addition, there are also claims in the literature that the presence of a noble metal in Co based FT catalysts may help in preventing fast deactivation by coking. Potassium is added in order to obtain the desired selectivity, since Ru promoted catalysts tend to result in higher methane selectivity under certain reaction conditions. While the K loading was optimized to obtain the desired activity and product distribution, only one loading of Ru was tested in all catalysts. Lower loadings of Ru would probably result in similar effects on reducibility and preventing coking.

The complete formulation of the selected catalyst (Co.047) is found in Appendix A, page 1.

Under Subtask 1.3 a series of Co catalysts (CoW.01-CoW.06) with a WGS function has been formulated and prepared by pre-impregnating the alumina with Cu-CrO or Cu-ZnO and calcining this support precursor before incorporating the cobalt. Except for CoW.01, Cu-Cr was selected as the water-gas shift function since WGS.003, a 5%Cu/4%Cr/Al₂O₃ showed the best activity for water gas shift. The loadings of Co, Cu, and Cr were varied from one formulation to the other in order to investigate the loading effect of the various constituents. The list of these catalysts is given in Table 5 with their composition, and the detailed formulations are included in Appendix A.

c. Catalyst Pretreatment (Subtask 1.5)

An investigation of the effects of the calcination procedure on the catalytic properties of a selected number of catalysts was started during this period. The effects of calcination in static atmosphere versus flow, and the effect of calcination temperature were addressed. Some preliminary results are included in subtask 2.1 where catalysts calcined under different conditions were tested.

d. Catalyst Characterization (Subtask 1.6)

(1) Physical Properties

Table 6 on page 34 gives an update on the physical property measurements carried out so far. Nitrogen physisorption at 77 K was used to obtain surface area, pore volume and pore diameter of the calcined catalysts. Average particle size of the catalysts was determined using a Microtrac particle size analyzer.

(2) Static Hydrogen Chemisorption

An updated summary of the properties of the Co catalysts as determined by H₂ chemisorption is given in Table 7 on page 35. Metal dispersions and particle sizes of CAL.01-CAL.03 were determined by CO chemisorption carried out at Calscat. No new catalyst has been characterized by static hydrogen chemisorption at the University of Pittsburgh because the system was down and being repaired during this period.

(3) Temperature Programmed Reduction (TPR)

TPR experiments were carried out in an automated Altamira Instruments AMI-1 system. The procedure for these measurements was described in the previous quarterly report. All the TPR results obtained so far are summarized in Table 7.

B. TASK 2: CATALYST TESTING

a. Subtask 2.1 - Fixed Bed Reaction Studies:

(1) F-T Synthesis

The reaction conditions and procedure were described in the previous quarterly report. Ten (10) new catalysts (Co.026, Co.027, Co.029, Co.047, Co.048, Co.049, Co.053, Co.054, CAL.02 and CAL.03) were tested for the first time during this reporting period. Catalysts Co.014, Co.039, and Co.040, all TiO₂-supported catalysts, were retested for confirmation of the data obtained previously when some problems were encountered with the analytical system. Co.018, Co.028, as well as CAL.01 were also retested using different pretreatment procedures.

The performances of all these catalysts (highlighted in Table 8) at steady state are compared in Table 8 with those reported in the previous quarterly report. All the pertinent data (CO conversion, rates, product distributions, chain growth probabilities, Anderson-Schulz-Flory distributions, time-on-stream activity and Arrhenius plots when available) obtained with each run for each catalyst is given in Appendix BB.

Co.018 was retested after calcination with air in a flow system. The data reported previously for this catalyst was obtained with the catalyst calcined in a "static" atmosphere in a muffle furnace at the University of Pittsburgh. However, the majority of the catalysts were calcined at PARC, also in a muffle furnace, but with forced air flowing on the top of the catalyst bed. The new results are comparable to those obtained with Co.053, CAL.01, CAL.02 and CAL.03 which have all the same composition. These results indicate that the calcination method used at the University of Pittsburgh may have affected negatively the catalytic properties of Co.018. Other catalysts which had been calcined using the same furnace will be retested after calcination in a flow-through system. Other

catalysts (Co.029, Co.049, Co.053 β) which had been calcined in static at PARC, but in a forced air flow furnace, had also been retested after calcination in a flow system. There seems to be no major difference between these two methods of calcination, at least in terms of their catalytic properties.

Catalyst CAL.01 was rereduced in-situ after a normal F-T run (run 2), and retested. This treatment was not sufficient for complete recovery of the catalyst activity. It was then recalcined and rereduced in-situ prior to a third F-TT test. Its activity was restored by this in-situ treatment, but the selectivity shifted to lower molecular weight hydrocarbons. The two new batches of this catalyst (CAL.02 and CAL.03) gave comparable results to those obtained with CAL.01.

The new data obtained with the three TiO₂-supported catalysts (Co.014, Co.039, and Co.040) confirms the previous results obtained with all the TiO₂-supported catalysts (Co.006, Co.014, Co.037-Co.040) which had a very poor performance in terms of their activity compared to that of Al₂O₃- or SiO₂-supported catalysts. They had also a high selectivity for methane.

The effect of Ru and K promotion on the Zr-promoted Co/SiO₂ catalysts was further investigated with Co.048 and Co.0054. While it was observed previously that Ru had a negligible effect on the activity of the SiO₂-supported catalysts, both with and without Zr promotion, the results obtained with these two catalysts indicate that Ru may have a significant effect when K is present. The rate dropped by a factor of 4 when Ru was not present.

Lower K loadings, compared to what had been used with Co.028, were investigated with Co.047 and Co.049, both Ru-promoted Co/Al₂O₃ catalysts, in order to achieve high chain growth probabilities without the negative effect on activity. The intermediate loading, 0.3% K, was found most satisfactory in order to optimize activity and selectivity for this type of catalysts. A similar effect was obtained with the silica-supported catalysts (Co.048 compared to Co.043).

Co.026 and Co.027, both supported on a different silica (Davison Grade 59) than the one used previously, were tested in order to investigate the effect of various supports. As with the other SiO₂-supported catalysts, the results show that Ru has hardly any effect on the catalytic properties of Co/SiO₂.

Co.018 (run 6) was tested in the second fixed-bed reactor system for reproducibility check between two different systems.

CoW.01 and CoW.02 were also tested under F-T synthesis conditions and the results are included in Table 8. Their activity for F-T synthesis was very low and no significant effect on the water-gas shift activity was observed during F-T synthesis.

(2) Water-Gas Shift Reaction

Prior to the reaction, the catalyst were first reduced ex-situ in a pretreatment system. The reduction procedure is as follows: the catalyst was kept under flowing helium while the temperature was ramped at 1°C/min to 120°C. Then H₂ was added to the He feed to obtain a 3% H₂ fraction and a total flow rate of 60 cc/min. The temperature was raised at 1°C/min to 200°C and maintained there for 2 hours, before being ramped again to 230°C in 30 minutes. These final conditions were maintained for 16 hours. The catalyst was then allowed to cool down to 150°C before passivation in a 2% O₂/He gas feed.

Before reaction 0.04 g of catalyst were loaded into the reaction system and the catalyst was rereduced in-situ using the same procedure as the one used for the initial reduction. Then, the inlet gas stream was switched over to the reaction gas mixture. Water was added by bubbling He through

an isothermal, jacketed water saturator connected to a heatable recirculating water bath. Ar was used as a standard for analytical purposes. The total flow rate was 157 cc/min at 1 atm. The H₂O/CO ratio was at 1.5 and the CO partial pressure was 0.096 atm. The reaction temperature was either 170 or 220°C. The exit stream was analyzed using a TCD.

WGS.01-WGS.03, WGS.006, WGS.08, and CoW.01-CoW.03 as well as two commercial catalysts (a Cu/ZnO- and a Cu/CrO-b-based) have been tested for their water-gas shift activity and the results are summarized in Table 9.

b. Subtask 2.2 - Slurry Bubble Column Testing ("SBCR")

(1) Run Chronology

During this reporting period a total of 14 runs were performed in the SBCR; runs 21 through 28 in M3 and 8 through 13 in M4. The following is a chronology of the experimental runs performed in the two slurry bubble column reactors - M3 and M4. A comparison of the CO conversions and product selectives of the methane reduction catalysts at the initial operation conditions (i.e. 240°C temperature, 450 psi pressure, and 2/1 H₂/CO ratio) are listed in Tables 10 and 11 on pages 42 and 43, respectively. All comparisons of CO conversions and CH₄ selectivities discussed in the following chronology were obtained at these startup conditions.

Run No. 21 was started in the M3-SBCR on March 28th with a charge of 15.1 gm of Catalyst No. Co. 014. This is the first titania supported catalyst (12% Co plus 0.5% Ru on titania) that was tested. The CO conversion was low, 8.5%, partly due to the lower cobalt content. The CH₄ selectivity was relatively high, 8.28%, particularly at the lower CO conversion level. About 1/3 of the catalyst was found on the bottom filter after the reactor was drained. This catalyst was larger in

particle size than most of the others, ϵ screened through 100 mesh screen vs. 150 mesh for most of the other catalysts to obtain sufficient catalyst to charge to the SBCR.

Run No. 8 in the M4-SBCR ϵ was started on April 4th with a charge of 15.0 gm of Catalyst No. Co. 006. This is a titania supported catalyst with 12% Co and 0.75% Re promoter. The CO conversion was very low, 1.7%; so, the unit was shut down on April 8th.

Run No. 22 in the M3-SBCRR was started on April 11th with a charge of 14.5 gm of Catalyst No. Co. 040. This is a titania supported catalyst with 12 wt% Co and no metals or promoters added. The CO conversion was only 1.8%; so, the unit was shut down on April 14th.

Run No. 23 in the M3-SBCRR was started on April 18th with a charge of 15.8 gm of Catalyst No. Co. 047. This is an alumina ϵ supported catalyst with 20% Co, 0.5% Ru, and only 0.3% K promoter. The catalyst activity was quite good, 28.8% Co conversion and 7.2% CH₄ selectivity, in the initial run conditions. This catalyst has met all the criteria for the best methane reduction catalyst that meets all the contract requirements, i.e., (1) 0.6 gm hydrocarbons/gm catalyst/hour, (2) 10% or less C₁+C₂ selectivity, (3) 90% or higher C₃+ selectivity, and (4) a satisfactory alpha value.

Run No. 9 in the M4-SBCR ϵ was started on April 25th with a charge of 15.4 gm of Catalyst No. Co. 048. This catalyst is similar to Co. 043 (Run 7-M4) but contains only 0.3% K. The CO conversion was higher than in Run 7 - M4, 19.1% vs. 13.0%, but the CH₄ selectivity was much higher 9.9% vs. 3.7%. Catalyst Co. 043 meets all of the product selectivity requirements but exhibits lower CO conversion than Co. 047.

Run No. 24 in the M3-SBCRR was started on May 2nd with a charge of 15.6 gm of Catalyst

No. Co.049. This catalyst is similar to Co.047 (Run 23 in M3) but contains only 0.1%K. The CO conversion of 30.52% and the CH₄ selectivity was 10.9%. Both were higher than obtained with Catalyst Co.047, and CH₄ selectivity was much higher than expected. Apparently, more than 0.1% K is needed to reduce the CH₄ selectivity.

Run No. 10 in the M4-SBCRR was started on May 9th with a charge of 15.9 gm of CAL.02. This is a catalyst prepared by Calcicat similar to Co.018. The CO conversions were similar, 34.5% vs. 33.8%, and the THC production rates were the same, 1.58 vs. 1.56 gm/gm catalyst/hr. The CH₄ selectivity, however, was considerably higher for CAL.02, 12.9% vs 9.7%

Run No. 25 in the M3-SBCRR was started on May 16th with a charge of 15.6 gm of Catalyst No. Co.047. This is a second batch of the catalyst that was charged for Run No. 23 in the M3-SBCR. This experiment was performed to check experimental reproducibility. The gas conversions, total hydrocarbon productions, and product selectivities were found to be identical for both batches of this catalyst.

Run No. 11 in the M4-SBCRR was started on May 23rd with a charge of 15.6 gm of Catalyst No. CAL.03. This catalyst is similar to CAL.02, but was formulated using a two-step impregnation of the metals. The CO conversion was slightly lower, 29.7% vs. 34.5%, and the THC production rate was also lower, 1.39 vs 1.58 gm/gm catalyst/hr. The CH₄ selectivities were similar, 13.5% vs. 12.9%. This run was terminated during Period 2 after some catalyst inadvertently burped out of the top of the reactor into the overheads product. This will be repeated if deemed necessary.

Run No. 26 in the M3-SBCRR was started on May 30th with a charge of 15.9 gm of Catalyst No. Co.031. This is an alumina supported catalyst with 20% Co and 1.4% Zr promoter added (single-step aqueous IW). The CO conversion was higher, 30.9% vs. 27.1%, and the CH₄ selectivity was also higher, 12.1% vs. 7.9%, than that obtained using an unpromoted catalyst (Cat. No. Co.005 in Run 15.M3). Adding zirconium as a promoter on alumina supported catalysts apparently causes an increase in CO conversion and CH₄ selectivity. Similar increases were noted on silica supported catalysts.

Run No. 12 in the M4-SBCRR was started on June 6th with a charge of 15.9 gm of Catalyst No. Co.053. This was a new batch of catalyst similar to Catalyst No. Co.018. The CO conversion was the same as obtained with Co.018, 34.2% vs. 33.8%, however, the CH₄ selectivity was higher, 12.6% vs. 9.7%. The production rate and other product selectivities are similar.

Run No. 27 in the M3-SBCRR was started on June 13th with a charge of 15.9 gm of Catalyst No. Co.029. This catalyst contains 0.5% K and 0.5% Ru (similar to Co.028), but contains 30 wt% cobalt instead of the 20% added to all the other catalysts. As a result, the CO conversion increased from 21.2% to 28.3% with a corresponding increase in CH₄ selectivity, 8.3% vs. 6.1%, and total hydrocarbon production rate of 1.277 vs. 1.00 gm/gm catalyst/hr.

Run No. 13 (M4-SBCRR) was started on June 20th with a charge of 15.7 gm of Catalyst No. Co.054. This catalyst contains 8.5% Zr and 0.3% K on silica support. It is similar to Catalyst No. Co.048 but contains no ruthenium. The CO conversion was considerably lower without the

ruthenium, 10.4% vs 19.1%, but the CH_4 selectivity was also lower, 4.7% vs. 9.9%. Addition of potassium without any ruthenium reduced the catalyst activity significantly.

Run No. 28 (M3-SBCR) was started on June 27th with a charge of 15.0 gm of Catalyst No. CoW.01. This catalyst was the first formulated to have water gas shift activity. It contained 20% Co, 5.0% Cu, and 10% Zr on alumina. The CO conversion was only 1.06%, so the run was terminated after two days operation.

Data for Runs 5 to 28 in M3-SBCR and Run 3 to 13 in M4-SBCR are compiled on Tables I through X found in Appendix C and also in Tables 10 and 11 on pages 42 and 43.

A complete summary of all runs made in the M3-SBCR is given in Table I in Appendix C. Four tables of data were prepared in order to compare catalyst activities for Runs 5 to 28 in M3-SBCR at the same run conditions (see Tables, II, III, IV, and V, Appendix C).

A complete summary of all runs made in the M4-SBCR are given in Table VI, Appendix C. Four tables are used to present the comparison of catalyst activities for Runs 3 to 13 in M4-SBCR at the same run conditions (see Tables VII, VIII, IX, and X in Appendix C).

(2) Discussion of Results :

Three TiO_2 -supported catalysts (Co.014, Co.006, and Co.040) were tested in the SBCR. In

all cases TiO_2 -based catalysts fell far short of the contract target and were inferior to both SiO_2 and Al_2O_3 based material. TiO_2 appears to be an unsatisfactory catalyst support.

Several catalysts were tested to evaluate the effect of potassium addition on the catalysts. Potassium addition has the effect of reducing CH_4 selectivity while also reducing overall activity. This effect can be seen clearly by comparing Runs M3-12, 24, 25 and M4-6 for catalysts that all contained 20% Co, 0.5% Ru, and levels of K between 0 and 0.5%. The following table summarizes those runs. Also, shown for comparison is Run M3-27, which contained a higher level of Co.

Effect of Varying Potassium Addition

<u>Run No.</u>	<u>Wt %Co</u>	<u>Wt %K</u>	<u>CO Conversion, %</u>	<u>CH₄ Selectivity, %</u>
M3-12	20	0.0	33.8	9.7
M3-24	20	0.1	30.6	10.9
M3-25	20	0.3	28.1	8.8
M4-6	20	0.5	21.2	6.1
M3-27	30	0.5	28.3	8.3

A steady decline in both CO conversions and CH₄ selectivities are noted with increasing K level. Some of the lost activity can be recovered with a higher Co loading. Thus, it appears that the 0.3% K addition is near the optimum on alumina supports for reducing the CH₄ reduction without significantly lowering the CO conversion.

Several catalysts were tested to evaluate the addition of zirconium and potassium on silica supported catalysts. Addition of 0.5% Ru to silica supported catalysts showed little effect on catalyst activity (see Runs 9-M3 and 14-M3 on Table 10, page 42), while addition of 0.7% Zr to a silica supported material nearly doubled the catalyst activity (see Run 19-M3). Increasing the Zr to 8.5% resulted in an additional 10% in catalyst activity. Adding 0.5% Ru with 8.5% Zr did not seem to affect the catalyst activity (see Runs 17-M3 and 20-M3 on Table 10). The addition of K to a Zr- and Ru- promoted catalyst had a negative effect on catalyst activity, significantly lowering the CO conversion (see Runs 7-M4 and 9-M4). It has been noted that Ru has a significant effect on the activity of Co on alumina in the fixed bed reactor. While Ru can form volatile carbon species in the

presence of CO under F-T conditions in the presence of hydrogen and for pressure less than 30 atmospheres, this does not seem to occur. A detailed study of the effect of Ru-promoter on alumina will be carried out at a latter date.

Two batches of 20% Co with 0.5% Ru promoter on alumina-supported catalysts were obtained from Calsicat and tested in the SBCR (see Runs 10-M4 and 11-M4 on Table 11). Both catalysts showed high activity and were nearly identical within our analytical precision thereby showing the reproducibility of the preparation recipe. Calsicat is currently preparing new catalyst batches for reproductibility and aging studies.

A batch of catalyst was tested that contained 20% Co in addition to water gas shift promoters, 5% Cu and 10% Zn. This catalyst was very inactive with only 1% CO conversion (see Run 28-M3 in Table 10).

In conclusion, several alumina and silica supported catalysts have been found that meet all the criteria for the methane reduction contract requirements. Additional catalysts are being prepared to optimize the addition of the various promoters for reducing CH₄ formation.

(3) Catalyst Recovery Analyses

The catalysts charged for all runs, except for Run 21 in M3 and Run 7 in M4, have been recovered and the particle size distributions have been measured. The charge and recovered weights of all catalysts are given in Table 1.12. The charge weights are in the H₂ reduced state while the

recovered weights are in the oxidized state. Taking this into account, catalyst recoveries are quite good (greater than 90%). The mean volumetric diameters of both the charged and recovered catalysts with the calculated percent reductions in particle size are also given in Table 12. The particle size at the lower 10% passing-through point of the sample for both the charged and recovered catalysts are also given in Table 12.

A comparison of the mean volume diameters of the total feed and recovered sample shows that most of the alumina supported catalysts exhibited the least amount of particle size attrition (5 to 10%) during the reaction. The silica supported catalysts showed a 10 to 20% particle size reduction while a titania supported catalyst had the highest reduction, 18.2% (see Run 8 M4-SBCR in Table 12).

If you compare the particle size of each sample of the 10% pass-through point, the increase in the amount of fines found in the recovered catalysts, as indicated by the lower particle size at the 10% point, is nearly proportional to the reduction in particle size obtained by comparing the mean volume diameters of the charge vs. recovered catalysts (see Table 12). Since the particle size of the charge catalyst was determined on the catalyst after hydrogen reduction and air oxidation, we know that attrition occurred only during the SBCR reaction.

(4) Catalyst Attrition Tests

One test was made in the catalyst attrition apparatus; see Test 4 in Table 13 "Catalyst

Attrition Studies" on page 45 and 1 Figure 1 on page 47. Catalyst No. Co.002 was stirred for 240 hours. The particle size reduction was 5.9%, which is in the range that most alumina catalysts attrited in the SBCR. Further tests will be made at shorter mixing times in order to determine whether there are any solvent or experimental handling effects.

A sample of Catalyst No. CAAL.03 was riffled into two equal portions and the particle size of each half was measured by Microtrac. The particle size distribution curves for both samples were identical (see Figure 2 on page 48).). This confirms the high precision of our Microtrac analyzer.

VII. PLANS FOR THE NEXT RREPORTING PERIOD

Several tasks are planned foir the next reporting period:

A. The fixed-bed reactor teststing of new catalysts will be continued on both reactor systems. The catalysts that had been calcined at the University of Pittsburgh under static atmosphere be retested after calcination in a flow ssystem.

A selected number of catalyststs will be tested at high pressure (similar to the conditions used in the slurry bubble column reactor)r) for direct comparison with the SBCR data.

The fixed-bed reactor testing g of the series of Al_2O_3 -supported Co catalysts with a water-gas shift function will be continued.

B. The systematic characterirization of all the catalysts will be continued using the following techniques:

- Selective hydrogen chemisorption on the reduced catalysts at 100°C;
- X-ray diffraction before reduction, after reduction, and after slurry bubble column reaction;
- Temperature programmed reduction (TPR).

C. New catalyst formulations will be generated in order to pursue the effect of selectivity promoters. The formulation of new CCo F-T catalysts having water-gas shift activity will be continued using different preparation techniques for the incorporation of Co into the most active Al₂O₃-supported WGS catalysts.

D. A thorough investigation of the effect of pre-treatment conditions including calcination and reduction will be carried out.

VIII. ASSESSMENT OF PROSPECTS FOR FUTURE PROGRESS

The technical approach which had been proposed remains the same and all the tasks are proceeding within schedule.