FINAL

TECHNOLOGY DEVELOPMENT FOR COBALT F-T CATALYSTS

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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 SBC 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 SBC 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 the 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 wt % 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-T) 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 CO conversions and product selectivities of the methane reduction catalysts.

VI. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

A. TASK 1: CATALYST DEVELOPMENT

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 in this subtask.

b. Catalyst Formulation (Subtasks 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 reports) is tabulated along with their compositions in Table 1 on pages 25 to 28. The last column of Table 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 Table 1 on page 28) have been formulated and prepared during this period. The detailed formulations 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) are both silica-supported catalysts, which are similar to Co.048; one with a lower loading of K; the other, without Ru. Co.053 (with 20% Co, 0.5% Ru, no promoter, on alumina) has the same composition as Co.018. This new batch of Co.053 was prepared in larger quantity in order to investigate the effect of calcination on the properties of the Co F-T catalysts. Co.051 and Co.052, both 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. Finally, CAL.02 and CAL.03 (each with 20% Co, 0.5% Ru on alumina) are two more batches of catalysts 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 (SBCR). 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.03, 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 Calsicat. 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 B.

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) 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-T 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 TiO_2 -supported catalysts (Co.014, Co.039, and Co.040) confirms the previous results obtained with all the TiO_2 -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 Al_2O_3 - or SiO_2 -supported catalysts. They had also a high selectivity for methane.

The effect of Ru and K promotion on the Zr-promoted Co/ SiO_2 catalysts was further investigated with Co.048 and Co.054. While it was observed previously that Ru had a negligible effect on the activity of the SiO_2 -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/ Al_2O_3 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 SiO_2 -supported catalysts, the results show that Ru has hardly any effect on the catalytic properties of Co/ SiO_2 .

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 $1^\circ\text{C}/\text{min}$ to 120°C . Then H_2 was added to the He feed to obtain a 3% H_2 fraction and a total flow rate of 60 cc/min. The temperature was raised at $1^\circ\text{C}/\text{min}$ 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% O_2/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 switch 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.06, WGS.08, and CoW.01-CoW.03 as well as two commercial catalysts (a Cu/ZnO- and a Cu/CrO-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, 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 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-SBCR 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-SBCR was started on April 18th with a charge of 15.8 gm of Catalyst No. Co. 047. This is an alumina 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 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-SBCR 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-SBCR was started on May 9th with a charge of 15.9 gm of CAL.02. This is a catalyst prepared by Calsicat 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-SBCR 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-SBCR 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-SBCR 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-SBCR 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-SBCR 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 1.27 vs. 1.00 gm/gm catalyst/hr.

Run No. 13 (M4-SBCR) 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 CH₄ 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 TiO₂-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	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 CH_4 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 12. The charge weights are in the H_2 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 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. CAL.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 REPORTING PERIOD

Several tasks are planned for the next reporting period:

A. The fixed-bed reactor testing 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 system.

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

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

B. The systematic characterization 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 Co F-T catalysts having water-gas shift activity will be continued using different preparation techniques for the incorporation of Co into the most active Al_2O_3 -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.

Table 1. List of Co-based FT Catalysts Formulated

CAT. NO.	wt% Co	wt% M	wt% Prom.	Support	Base	Prepared
Co.001	20%	1% Re	1% La ₂ O ₃ 0.13% K	γ-alumina	U.S. Pat. 4,880,763	P
Co.002	20%	0.43% Ru	1% La ₂ O ₃	γ-alumina	U.S. Pat. 4,413,064	P
Co.003	20%	0.5% Ru	1% La ₂ O ₃	γ-alumina	U.S. Pat. 4,413,064	P
Co.004	20%	0.43% Ru	1% La ₂ O ₃	γ-alumina	Reproduce Co.002	P
Co.005	20%	0	0	γ-alumina	Base Catalyst	P
Co.005A	20%	0.4% Ru	0	γ-alumina	Ru added to calcined Co.005 by IW impreg.	P
Co.006	12%	0.75% Re	0	Titania	U.S. Pat. 4,794,009	P
Co.007	20%	0	0	Titania	Base Catalyst	P
Co.008	20%	0	0	Silica	UK Pat. Appl. GB 2 125 062 A (Kneaded with excess liquid)	P
Co.009	20%	0.5% Ru	0	γ-alumina	Ru-Promoted Catalyst (use Ru Chloride, single-step aqueous IW)	P
Co.010	20%	0	0	γ-alumina	Base Catalyst (non-calcined)	P
Co.010A	20%	0.4% Ru	0	γ-alumina	Ru added to dried Co.010 by IW impreg.	P
Co.011	20%	0	0	Silica	UK Pat. Appl. GB 2 125 062 A (Kneaded)	P
Co.012	20%	0	0	Silica	Base Catalyst (Inc. Wetness)	P
Co.013	20%	0	0	Titania	Base Catalyst like Co.007, but all aqueous	P
Co.014	12%	0.5% Ru	0	Titania	Ru-Promoted Catalyst (aqueous IW co- impregnation)	P
Co.015	20%	0.43% Ru	1% La ₂ O ₃	γ-Alumina	Similar to Co.002, but all aqueous	P
Co.016	20%	0.43% Ru	1% La ₂ O ₃	γ-Alumina	Similar to Co.015, but calcined after Co impregnation	P

Table 1. List of Co-based FT Catalysts Formulated (Contd.)

CAT. NO.	wt% Co	wt% M	wt% Prom.	Support	Basis	Prepared
Co.017	20%	0.5% Ru	1% La ₂ O ₃	γ-Alumina	Similar to Co.003, but all aqueous	P
Co.018	20%	0.5% Ru	0	γ-Alumina	Ru-Promoted Catalyst (single-step, aqueous IW)	P
Co.019	20%	0.5% Ru	0	Silica	Ru-Promoted Catalyst (single-step, aqueous IW)	P
Co.020	0	0.5% Ru	0	γ-Alumina	Ru Base Catalyst	P
Co.020A	20%	0.4% Ru	0	γ-Alumina	Co added to dried Co.020 by IW impreg.	P
Co.020B	20%	0.4% Ru	0	γ-Alumina	Co added to reduced Co.020 by IW impreg.	P
Co.020C	20%	0.4% Ru	0	γ-Alumina	Co added to calcined Co.020 by IW impreg.	P
Co.021	20%	0	0.7% Zr	Silica	U.K. Pat. Appl. GB 2 125 062 A (single-step)	P
Co.022	20%	0	0.7% Zr	Silica	U.K. Pat. Appl. GB 2 125 062 A (multiple-steps)	P
Co.023	20%	0	1.4% Zr	Silica	U.K. Pat. Appl. GB 2 125 062 A (multiple-steps)	P
Co.024	20%	0	8.5% Zr	Silica	Eur. Pat. Appl. 0 167 215 A2 (non-aqueous Zr pre-impregnation)	P
Co.025	20%	0	8.5% Zr	Silica	Similar to Co.024 but aqueous Zr pre-impregnation	P
Co.026	20%	0	0	Silica (Davison Grade 59)	Similar to Co.012 but different grade silica	P
Co.027	20%	0.5% Ru	0	Silica (Davison Grade 59)	Similar to Co.019 but different grade silica	P
Co.028	20%	0.5% Ru	0.5% K	γ-alumina	Ru- and K-Promoted Catalyst (single-step IW)	P
Co.029	30%	0.5% Ru	0.5% K	γ-alumina	Similar to Co.028 but 30% Co	P

Table 1. List of Co-based FT Catalysts Formulated (Contd.)

CAT. NO.	wt% Co	wt% M	wt% Prom.	Support	Basia	Prepar ed
Co.030	20%	0	0.1% Zr	γ -alumina	Zr-Promoted Catalyst (single-step aqueous IW)	P
Co.031	20%	0	1.4% Zr	γ -alumina	Zr-Promoted Catalyst (single-step aqueous IW)	P
Co.032	20%	0	8.5% Zr	γ -alumina	Zr-Promoted Catalyst (aqueous IW co- impregnation)	P
Co.033	20%	0	8.5% Zr	γ -alumina	multiple-steps, aqueous IW, Co pre- impregnation	P
Co.034	20%	0	8.5% Zr	γ -alumina	multiple-steps, aqueous IW, Zr pre- impregnation	P
Co.035	20%	0	8.5% Zr	Silica	Zr-Promoted Catalyst (single-step aqueous, kneaded)	P
Co.036	20%	0	8.5% Zr	Silica	multiple-steps, aq. Co pre-impreg. by kneading, aqueous IW Zr impreg.	P
Co.037	12%	0	0	Titania	Similar to Co.013, but TiO ₂ mainly anatase	P
Co.038	12%	0.5% Ru	0	Titania	Similar to Co.014, but TiO ₂ mainly anatase	P
Co.039	12%	0	0	Titania	Similar to Co.007, but only 12% Co	P
Co.040	12%	0	0	Titania	Similar to Co.013, but only 12% Co	P
Co.041	20%	0.5% Ru	8.5% Zr	Silica	Similar to Co.025, but Ru-promoted	P
Co.042	0	0	8.5% Zr	Silica	Blank Zr-promoted SiO ₂	P
Co.043	20%	0.5% Ru	8.5% Zr 0.5% K	Silica	Similar to Co.041, but K-promoted	P
Co.044	20%	0	15% Zr	Silica	Similar to Co.025, but 15% Zr	P
Co.045	20%	0	4% Zr	Silica	Similar to Co.025, but 4% Zr	P
Co.046	12%	0.75% Re	4% SiO ₂	Titania	Similar to Co.006, but SiO ₂ -promoted	-
Co.047	20%	0.5% Ru	0.3% K	γ -alumina	Similar to Co.028, but 0.3% K	P

Table 1. List of Co-based FT Catalysts Formulated (Contd.)

CAT. NO.	wt% Co	wt% M	wt% Prom.	Support	Base	Prepared
Co.048	20%	0.5% Ru	8.5% Zr 0.3% K	Silica	Similar to Co.043, but 0.3% K	P
Co.049	20%	0.5% Ru	0.1% K	γ -alumina	Similar to Co.047, but 0.1% K	P
Co.050	20%	0.5% Ru	8.5% Zr 0.1% K	Silica	Similar to Co.048, but 0.1% K	P
Co.031	0	0.5% Ru	0	Titania (R)		P
Co.032	0	0.5% Ru	0	Titania (A)		P
Co.033	20%	0.5% Ru	0	γ -alumina	Similar to Co.018 (New Batch)	P
Co.034	20%	0	8.5% Zr 0.3% K	Silica	Similar to Co.043, but without Ru	P
CAL.01 (97E-13E)	20%	0.5% Ru	0	γ -alumina	Similar to Co.018 (Calsicat Prep.)	P
CAL.02 (97E-16B)	20%	0.5% Ru	0	γ -alumina	Similar to CAL.01 (New Batch)	P
CAL.03 (97E-13F)	20%	0.5% Ru	0	γ -alumina	2-step impreg., Similar to CAL.02	P

TABLE 2. DESIRED PROCESS CONDITIONS, ACTIVITY AND SELECTIVITY

PROCESS CONDITIONS	
Feed H ₂ /CO ratio	0.5-2.0
Temperature, °C	230-280
Pressure, bar	10-30
Syngas flow rate, Nm ³ /hr/kg cat.	3-6
ACTIVITY and SELECTIVITY	
Total Hydrocarbon Production, g/Nm ³ syngas used (g/hr/g cat.)	200 (0.6-1.2)
C ₃ + Hydrocarbon Production, % of Total HC production	90

TABLE 3. SLURRY BUBBLE COLUMN STANDARD REACTION CONDITIONS

Period #	Temperature (°C)	Pressure (psi)	H ₂ /CO Ratio	Period Time (hr)
1	240	450	2	48
2	220	450	2	48
3	240	450	2	24
4	240	450	1	48
5	240	600	1	48
6	240	450	2	24

Syngas flow rate: 24Nm³/hr/kg cat.

TABLE 4. CATALYST SELECTION FOR LOW METHANE SELECTIVITY

Cat. #	Composition ^a	450 psi (H ₂ /CO=2)				600 psi (H ₂ /CO=1)		Attrition Resistance	Pass (P) or Fail (F) ^d
		220°C		240°C		240°C		Particle Size % Change ^c	
		Rate ^b	%C ₃₊	Rate ^b	%C ₃₊	Rate ^b	%C ₃₊		
Co.005	20Co/A	0.53	99.0	1.34	90.4	0.90	99.0	10.8	P
Co.018	20Co0.5Ru/A	0.59	97.2	1.56	88.1	0.84	96.7	-	F
Co.028	20Co0.5Ru0.5K/A	0.31	98.1	1.00	92.2	0.67	98.3	11.1	P
Co.047	20Co0.5Ru0.3K/A	-	-	1.29	90.7	0.80	96.5	-	P
Co.024	20Co8.5Zr/S	0.45	97.9	1.21	89.4	0.80	97.6	-	F
Co.041	20Co0.5Zr0.5Ru/S	0.41	98.5	1.16	86.8	0.91	97.0	17.0	F
Co.043	20Co8.5Zr0.5Ru0.5K/S	0.20	98.5	0.61	94.4	0.41	97.7	-	F
Co.048	20Co8.5Zr0.5Ru0.3K/S	0.28	97.1	0.90	88.4	0.83	96.3	-	P

^a numbers = nominal weight loadings of the various metals; A = Alumina; S = Silica

^b rate in g hydrocarbons per g catalyst per hour

^c % change after the entire reaction cycle

^d compared to target set by DOE under given process conditions

Table 5. List of Water-Gas Shift Catalysts and F-T Catalysts with WGS Function

CAT. NO.	wt% Co	wt% Ni	wt% Prom.	Support	Reactor	Prepared
WGS.01	0	5.0% Cu	0	γ -alumina	single-step, aqu. IW	P
WGS.02	0	5.0% Cu	10% Zn	γ -alumina	single-step, aqu. IW	P
WGS.03	0	5.0% Cu	4.0% Cr	γ -alumina	single-step, aqu. IW	P
WGS.04	0	0	4.0% Cr	γ -alumina	single-step, aqu. IW	P
WGS.05	0	0	4.0% Mn	γ -alumina	single-step, aqu. IW	P
WGS.06	0	5.0% Cu	4.0% Mn	γ -alumina	single-step, aqu. IW	P
WGS.07	0	4.0% Fe	0	γ -alumina	single-step, aqu. IW	P
WGS.08	0	4.0% Fe	4.0% Cr	γ -alumina	single-step, aqu. IW	P
CoW.01	20%	5.0% Cu	10% Zn	γ -alumina	multiple-steps, aqu. IW, Cu,Zn pre-impr.	P
CoW.02	20%	5.0% Cu	4.0% Cr	γ -alumina	multiple-steps, aqu. IW, Cu,Cr pre-impr.	P
CoW.03	10%	5.0% Cu	4.0% Cr	γ -alumina	similar to CoW.02 (10% Co only)	P
CoW.04	10%	10% Cu	8.0% Cr	γ -alumina	similar to CoW.03; 10% Cu and 8% Cr	P
CoW.05	20%	5.0% Cu	4.0% Cr	γ -alumina	similar to CoW.02 with support calcined at 750°C	P
CoW.06	20%	5.0% Cu	4.0% Cr	Silica	multiple-steps, aqu. IW, Cu,Cr pre-impr.	P

Table 6. Summary of Physical Properties

CATALYST	Composition	BET Surface Area (m ² /g)	Pore Volume (cc/g)	Average Pore Dia. (Å)	Average Part. Size (µm)
Vista-B Al ₂ O ₃	(0-400 mesh)	299	1.69	269	24
Vista-B Al ₂ O ₃	Calcined 500°C	240	0.49	82	
Vista-B Al ₂ O ₃	Calcined 600°C	206	0.49	95	
Vista-B Al ₂ O ₃	Calcined 600°C	174	0.47	109	
Davison SiO ₂	(0-400 mesh)	219	0.51	89	121
Degussa P25 TiO ₂	(as received)	47	0.40	335	6
Degussa P25 TiO ₂	Dried 60°C, Calc. 350°C/16hrs	46	0.48	419	51
Degussa P25 TiO ₂	Dried 60°C, Calc. 650°C/16hrs	12	0.17	573	212
Co.001	20Co/1Re/ 1La ₂ O ₃ /0.13K/A	191	0.31	66	42 40
Co.002	20Co/0.43Ru/ 1La ₂ O ₃ /A	149	0.33	89	74
Co.003	20Co/0.5Ru/ 1La ₂ O ₃ /A	122	0.26	87	77
Co.004	20Co/0.43Ru/ 1La ₂ O ₃ /A				
Co.005	20Co/A	173	0.34	81	65 86
Co.006	12Co/0.75Re/T	16	-	-	
Co.007	20Co/T	11	0.10	372	
Co.008	20Co/S	181	1.06	234	
Co.009	20Co/0.5/A				
Co.010	20Co/A				
Co.011	20Co/S	211	1.07	203	107
Co.012	20Co/S	211	-	-	105
Co.013	20Co/T				
Co.014	12Co/0.5Ru/T	15	0.12	328	
Co.015	20Co/0.43Ru/ 1La ₂ O ₃ /A	141	-	-	67

Table 6. Summary of Physical Properties (contd.)

CATALYST	Composition	BET Surface Area (m ² /g)	Pore Volume (cc/g)	Average Pore Dia. (Å)	Average Part. Size (µm)
Co.016	20CoB/0.43Ru/ 1La ₂ O ₃ /A	116	-	-	79
Co.017	20Co/0.5Ru/ 1La ₂ O ₃ /A	123	-	-	73
Co.018	20Co/0.5Ru/A	158	-	-	69
Co.019	20Co/0.5Ru/S				110
Co.021	20Co/0.7Zr/S	213	1.12	210	
Co.023	20Co/1.4Zr/S	213	-	-	
Co.024	20Co/8.5Zr/S	215	1.08	202	
Co.025	20Co/8.5Zr/S	208	0.97	187	
Co.026	20Co/S(59)	184	-	-	
Co.027	20Co/S(59)	189	-	-	
Co.028	20Co/0.5Ru/0.5K/A	161	0.33	82	
Co.029	30Co/0.5Ru/0.5K/A	140	-	-	
Co.032	20Co/8.5Zr/A	155	0.30	77	
Co.034	20Co/8.5Zr/A	150	0.31	83	
Co.035	20Co/8.5Zr/S	207	1.21	233	
Co.036	20Co/8.5Zr/S	209	-	-	
Co.037	12Co/T(A)	38	-	-	
Co.039	12Co/T(R)	13	-	-	
Co.041	20Co/0.5RU/8.5Zr/S	214	-	-	
CAL.01	20Co/0.5Ru/A	178	0.34	76	
CAL.02	20Co/0.5Ru/A	158	-	-	
CAL.03	20Co/0.5Ru/A	158	-	-	

Under "Composition" A = alumina; S = silica; T = titania

Table 7. H₂ Chemisorption and TPR Results

Catalyst	H ₂ Chemisorption ^a				H ₂ TPR	
	Total (μ mol H ₂ /g cat)	Irrevers. (μ mol H ₂ /g cat)	Average d_p^b (nm)	% Disp	%Co Red ^c (TPR calc. Cat.)	% Red ^d (stand. red.)
Co.001	174 $\pm$ 5	157 $\pm$ 5		10.2		
Co.002	155	130		9.1		
Co.003	165	140		9.6		
Co.004						
Co.005	48	42	20	2.8	89	58
Co.005a	129	110	11	7.6	92	84
Co.006	44	32	19	4	80	
Co.007	33	23	36	2.0	78	78
Co.008						
Co.009	133	109	13	7.8	98	
Co.010						
Co.010a	124	100	12.5	7.3	91	89
Co.011	82	70	15.6	4.8	75	75
Co.012	89	74	15	5.2	80	80
Co.013	21	17	79	1.2	97	
Co.014	38	30	21	3.7	79	
Co.015	146	124	11.7	8.6	94	94
Co.016	163	146	10.5	9.6	96	96
Co.017	202	183	8.5	11.9	97	97
Co.018	185	165	9.2	11	97	94

Table 7. H₂ Chemisorption^a and TPR Results (contd.)

Catalyst	H ₂ Chemisorption ^a				TPR	
	Total (μ mol H ₂ /g cat)	Irrev. (μ mol H ₂ /g cat)	Average d_p^b (nm)	% Disp.	%Co Red. ^c (TPR calc. Cat.)	% Red. ^d (stand. red.)
Co.018-Cl					95	
Co.019	112	92		6.6		
Co.020						
Co.020a	153	126	10	9.1	88	
Co.020b	134	113	11	7.9	86	
Co.020c	115	100	13	6.8	88	
Co.021	74	50		4.3		
Co.022	141	122		8.3	80	
Co.023	158	136		9.3	81	
Co.024	87	72		5.1	91	
Co.025	93	77		5.5	75	
Co.026						
Co.027						
Co.028	170	148		10		
Co.029	175	155		7		
Co.030						
Co.031	71	51	20	4.2	82	
Co.032	55	39	26	3.2	85	
Co.033	43	32	31	2.5	79	
Co.034	114	91	14	6.7	96	
Co.035	125	115	11	7.2	82	
Co.036	122	98		7.2		

Table 7. H₂ Chemisorption^a and TPR Results (contd.)

Catalyst	H ₂ Chemisorption ^a				TPR	
	Total (μ mol H ₂ /g cat)	Irrev. (μ mol H ₂ /g cat)	Average d_p^b (nm)	% Disp.	%Co Red ^c (TPR calc. Cat.)	% Red ^d (stand. red.)
Co.037	21	3	48	2	99	
Co.038	45	35	21	4.3	91	
Co.039	19	16	40	1.8	72	
Co.040	14	11		1.4		
Co.041	70	55		4		
Co.042						
Co.043	137	116		8		
Co.044						
Co.045						
Co.046						
Co.047						
Co.048						
CAL.01	-	-	58 ^e	4.4 ^e		
CAL.02	-	-	63 ^e	5.1 ^e		
CAL.03	-	-	57 ^e	4.2 ^e		

(a) static H₂ chemisorption at 100°C(b) Est. assuming $H_{tot}/Co_s = 1$, $5.46 \times 10^{-20} \text{ m}^2/Co_s$, and $d_p = 5/S_{Co}/\rho$
S_{Co} is based on amt. Co reducible during standard reduction

(c) % Co reducible from TPR of calcined catalysts up to 900°C

(d) % Co reduced after standard reduction procedure

(e) Based on CO chemisorption

(f) Catalyst Co.018-Cl is chlorinated.

Table 8. Summary of Fixed Bed Reaction Results

Catalyst	Run	CO Conv (%)	Rate g CH ₂ /g cat/hr	wt% CH ₄	alpha	C3-C5 Ole/Par	CO ₂ (%) (CO)	g/g cat/hr	E act kcal/mol	Comment
Co.001	4	2.6	0.116	19.6	0.76	8.61	0.4	0.061		NSH**
Co.002	4	6.7	0.258	26.1	0.64	1.97	0.1	0.012		NS*, calcined
Co.003	1	5.5	0.185	30.8	0.57	4.22			28.9	old startup
Co.004	1	4.3	0.291	30.4	0.62	2.77	0.1	0.025	25.9	NSH
Co.005	2	3.3	0.087	21.4	0.66	3.40	0.1	0.005	25.1	NS
"	2a	2.5	0.066	25.9	0.59	4.92	0.1	0.004		CO:H ₂ :Ar = 1:2:2
"	2b	2.4	0.064	26.3	0.60	6.22	0.1	0.006		+ H ₂ O (eq. 7.5% CO conv.)
"	3	3.3	0.077	28.4	0.62	2.29	0.1	0.013		NSH
"	4	4.0	0.069	30.0	0.62	2.16	0.2	0.009		NSH
"	5	3.9	0.171	26.8	0.76	2.59	0.1	0.018		NSH, 10 atm
Co.005a	1	3.2	0.227	30.0	0.60	3.05	0.1	0.034		NSH
Co.006	1	2.7	0.052	45.0	0.49	1.90	0.1	0.006		NSH
Co.007	1	3.2	0.024	49.8	0.50	0.72	0.2	0.004		NSH
Co.009	1	4.9	0.346	31.1	0.57	1.69	0.1	0.020		NSH
"	2	4.9	0.338	31.1	0.58	1.64	0.1	0.026		NSH
Co.010a	1	3.5	0.246	29.5	0.62	2.58	0.2	0.040		NSH
"	2	4.1	0.262	30.0	0.61	2.31	0.1	0.022		NSH
Co.011	2	2.9	0.094	22.4	0.61	4.83	0.3	0.030		NSH
Co.012	1	3.8	0.083	26.3	0.64	4.40			22.5	slow CO startup (60 min)
"	2	4.4	0.085	29.1	0.64	1.93	0.3	0.018		NSH
"	3	2.1	0.081	28.6	0.66	3.57	0.4	0.049		NSH
Co.014	1	1.5	0.028	32.3	0.63	4.70	0.1	0.003		NSH
"	2	2.6	0.034	27.7	0.69	10.8	0.1	0.011	26.0	NSH
Co.015	1	6.8	0.211	26.7	0.60	3.30				slow CO startup (120 min)
Co.016	1	5.2	0.161	33.6	0.56	6.85				slow CO startup (30 min)
Co.017	2	4.6	0.139	22.0	0.69	3.72	0.1	0.012		NS
"	2a	3.7	0.111	25.9	0.64	4.19	0.1	0.011		CO:H ₂ :Ar = 1:2:2
"	2b	3.4	0.102	26.9	0.65	4.39	0.1	0.013		+ H ₂ O (eq. 7.5% CO conv.)
Co.018	2	3.4	0.170	27.2	0.69	2.24	0.1	0.013		NS
"	2a	2.7	0.133	33.2	0.64	2.52	0.1	0.011		CO:H ₂ :Ar = 1:2:2
"	2b	3.0	0.147	33.6	0.63	2.41	0.1	0.015		+ H ₂ O (eq. 7.5% CO conv.)
"	3	4.1	0.290	30.0	0.62	2.34	0.1	0.022		NSH
"	4	3.6	0.340	25.4	0.80	1.92	0.1	0.041		NSH, 10 atm
"	5	7.5	0.470	29.0	0.60	1.93	0.3	0.055		NSH, calcined in flow air
"	6	6.5	0.409	24.6	0.64	2.42				NSH, calcined in flow air, S2"
Co.018Cl	1	4.5	0.320	33.5	0.57	1.45	0.1	0.018		NSH
Co.019	1	4.4	0.088	15.2	0.74	7.61				NS
"	2	2.2	0.085	18.9	0.73	8.59	0.3	0.040		NSH

Table 8. Summary of Fixed Bed Reaction Results (cont'd)

Catalyst	Run	CO Conv (%)	Rate g CH ₂ / g cat/hr	wt% CH ₄	alpha	C3-C5 Ole/ Par	CO ₂ (%) g/g cat/hr	E act. kcal/ mol	Comment
Co.020a	1	4.6	0.343	33.5	0.57	1.70	0.1	0.024	NSH
"	2	4.4	0.315	31.2	0.59	1.96	0.1	0.028	NSH
Co.020b	1	4.4	0.311	31.7	0.58	1.81	0.2	0.051	NSH
Co.020c	1	4.0	0.287	30.4	0.60	2.38	0.1	0.017	NSH
Co.021	1	3.4	0.109	27.3	0.62	2.78	0.1	0.012	28.2 NSH
"	2	3.6	0.114	28.0	0.56	2.69	0.1	0.012	NSH
Co.022	1	3.8	0.121	26.7	0.55	2.91	0.1	0.015	30.1 NSH
Co.023	1	3.8	0.123	28.3	0.56	3.18	0.2	0.023	29.5 NSH
Co.024	1	5.1	0.165	32.8	0.62	2.08	0.5	0.055	NSH
"	2	5.7	0.182	28.7	0.62	2.25	0.3	0.035	NSH
Co.025	1	5.0	0.160	23.5	0.63	4.13	0.2	0.019	26.9 NSH
Co.026	1	4.4	0.129	26.9	0.62	2.65	0.2	0.022	NSH
"	1	22.9	0.170	22.6	0.67	0.64	1.5	0.037	NSH, high conv. study
Co.027	1	4.2	0.169	23.0	0.65	3.44	0.2	0.026	NSH
"	1	17.8	0.180	19.4	0.71	0.96	1.2	0.011	NSH, high conv. study
Co.028	1	3.8	0.146	18.2	0.76	7.63	0.2	0.031	28.4 NSH
"	2	4.3	0.167	14.7	0.80	13.2	0.2	0.030	NSH
"	3	4.5	0.206	15.5	0.79	13.4	0.2	0.037	NSH, re-calc. in flow air
Co.029	1	2.8	0.173	15.3	0.79	25.9	0.2	0.026	NSH
Co.031	1	1.9	0.060	26.1	0.64	4.65	0.3	0.031	NSH
Co.035	2	4.6	0.147	22.0	0.69	4.84	0.2	0.019	NSH
Co.036	2	3.9	0.125	28.9	0.67	4.20	0.1	0.013	NSH
Co.037	1	2.7	0.053	32.8	0.59	2.82			NSH
Co.038	1	4.5	0.051	25.1	0.68	4.63	0.3	0.013	24.2 NSH
Co.039	1	1.1	0.021	57.2	0.64	0.84	0.2	0.010	25.6 NSH, cracking in the line
"	2	3.9	0.049	42.4	0.48	0.95	0.2	0.009	NSH
Co.040	1	1.9	0.037	45.2	0.53	1.79	0.2	0.007	NSH
"	2	2.8	0.033	44.6	0.46	1.12	0.2	0.007	NSH
Co.041	1	3.5	0.136	40.7	0.69	1.47	0.6	0.079	NSH, cracking in the line
Co.043	1	4.6	0.104	15.3	0.78	12.1	0.6	0.048	NSH, 2.5 hr on-stream
"	2	3.7	0.078	16.3	0.78	7.75	0.5	0.035	35.1 NSH
Co.047	1	6.4	0.263	21.3	0.73	7.20	0.3	0.040	26.6 NSH
Co.048	1	3.5	0.162	16.3	0.77	17.1	0.2	0.027	28.0 NSH
Co.049	1	7.1	0.366	23.4	0.69	5.63	0.3	0.043	NSH
"	2	6.0	0.388	23.3	0.68	5.93	0.3	0.056	NSH, re-calcined in flow air
"	3	6.7	0.409	25.2	0.69	4.73	0.3	0.059	NSH, calcined in flow air
"		44.9	0.457	26.5	0.67	0.67	3.8	0.131	NSH, calcined in flow air, HCS

Table 8. Summary of Fixed Bed Reaction Results (cont'd)

Catalyst	Rtn	CO Conv (%)	Rate g CH ₂ / g cat/hr	wt% CH ₄	alpha	C3-C5 Ole/ Par	CO ₂ (%) g/g (CO)	E act kcal/ mol	Comment
Co.053	1	6.8	0.398	28.1	0.60	3.07	0.2	0.043	NSH
"	1	28.5	0.417	26.8	0.64	0.79	1.6	0.081	NSH, high conv. study
"	2	6.6	0.433	23.4	0.63	2.35	0.2	0.052	NSH, calcined in flow air
"	3	7.8	0.453	27.6	0.62	1.67	0.1	0.027	NSH
"	3	31.5	0.457	25.4	0.65	0.52	0.9	0.044	NSH, high conv. study
Co.054	1	1.2	0.041	17.8	0.79	16.3	0.2	0.014	NSH
CAL.01	1	4.8	0.181	24.4	0.66	5.86	0.3	0.036	NSH, temp. surge (startup)
"	2	7.4	0.491	28.7	0.61	2.06	0.4	0.083	NSH
"	3	2.5	0.164	25.6	0.63	4.97	0.2	0.052	NSH, HT, re-reduced
"	4	7.3	0.483	35.8	0.57	1.21	0.2	0.098	NSH, HT, re-calcined
CAL.02	1	6.1	0.379	27.3	0.63	3.04	0.2	0.040	NSH
CAL.03	1	7.3	0.459	29.0	0.60	2.59	0.2	0.048	NSH
CoW.01	1	1.2	0.016	30.2	0.58	3.78	0.2	0.006	NSH, reduced at 230 °C
"	1	0.5	0.007	42.1	0.51	0.95	0.1	0.003	NSH, re-reduced at 350 °C
"	2	0.2	0.006	40.9	0.51	11.3	0.1	0.006	NSH, reduced at 350 °C
CoW.02	1	0.3	0.009	25.6	0.60	4.94	0.1	0.008	NSH, reduced at 230 °C

* New startup, if not specified, calcined in UPARC

** New startup, heated inlet, if not specified, calcined in UPARC. In some cases, "re-calcined" means calcination of the calcined catalyst from UPARC for a longer period and "calcined" means calcination of the catalyst precursor.

" was done in the second system

~ Davison Grade 59 Silica, if not specified, S refers Davison Drade 952 Silica

corrected overheated line on 3/6/1994

Catalyst Co.018Cl is chlorinated

Table 9. Summary of WGS Fixed Bed Reaction Results

Catalyst	Run	CO Conv (%)	Rate gCO/ g cat/hr	R(CO) mmol/ g cat/hr	Eact. kcal/ mol	Comment
Commercial Cu/ZnO	1	2.8	0.39	14.00	10	
Commercial Cu/Chr	2	14.9	2.49	89.00		
WGS.01	2	2.7	0.476	17.00		
WGS.02	2	3.2	0.597	21.00		
WGS.03	1	4.7	0.79	28.00		
WGS.06	1	1.5	0.24	8.50		
WGS.08	1	0	0	0.00		no activity observed
CoW.01*	1	0	0	0.00		no activity observed
CoW.02*	1	1.8	0.32	10.00		
CoW.03*	1	2.5	0.39	14.00		

Reaction Conditions: 1.5 hours on stream, 171°C, Pco=0.096atm, H2O:CO=1.5, 1 atm
 * 220°C

Table 10

DATE: 07/07/94

COMPARISON OF CONVERSION AND SELECTIVITY OF
METHANE REDUCTION CATALYSTS AT STARTUP CONDITIONS

Period No.	Temp.	Pres.	H ₂ /CO Ratio
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1	240 C	450psi	2.0

Run No	Cat. No	Cat. wt,g	Conv. %	Prod. Rate	Selectivities				Alpha GC	Alpha Liq	Catalyst Prom%	Composit. Metal%	Suppt
					%CH ₄	%C ₂	%C ₃ +	%CO ₂					
3	SBCR												
5	CO.003	15.1	31.7	1.53	16.7	2.4	79.8	1.16	0.71	--	1.0La	0.5Ru	Al
6	CO.011	15.3	14.3	0.67	7.6	1.6	89.4	1.42	0.78	0.83	0.0	0.0	Si
7	CO.012	15.8	13.9	0.63	6.1	1.5	90.6	1.74	0.80	0.89	0.0	0.0	Si
8	CO.015	15.0	28.3	1.37	12.7	2.0	84.1	1.24	0.76	0.80	1.0La	0.43Ru	Al
9	CO.011	15.0	18.5	0.89	8.8	1.7	88.8	0.77	0.78	0.83	0.0	0.0	Si
11	CO.017	15.0	27.2	1.32	11.2	1.8	85.9	1.14	0.77	0.80	1.0La	0.5Ru	Al
12	CO.018	15.6	33.8	1.56	9.7	2.0	86.6	1.68	0.75	0.85	0.0	0.5Ru	Al
13	CO.016	14.7	26.4	1.31	(1)	1.7	89.3	0.68	0.78	0.81	1.0La	0.43Ru	Al
14	CO.019	15.2	13.9	0.66	(2)	1.7	97.2	0.70	0.80	0.86	0.0	0.5Ru	Si
15	CO.005	14.7	27.1	1.34	7.9	1.6	89.7	0.82	0.79	0.82	0.0	0.0	Al
16	CO.002	15.4	30.1	1.42	12.5	2.5	83.9	1.09	0.75	0.80	1.0La	0.43Ru	Al
17	CO.025	15.6	26.6	1.24	10.7	2.1	86.4	0.82	0.76	0.82	8.5Zr	0.0	Si
18	CO.004	15.0	33.9	1.64	15.3	2.4	80.9	1.37	0.74	0.79	1.0La	0.43Ru	Al
19	CO.021	15.6	23.2	1.08	9.4	2.0	88.0	0.73	0.77	0.82	0.7Zr	0.0	Si
20	CO.041	15.8	25.3	1.16	11.0	2.1	86.0	0.88	0.76	0.84	8.5Zr	0.5Ru	Si
21	CO.014	15.1	8.5	0.40	8.3	3.5	85.8	2.43	0.74	0.83	0.0	0.5Ru	Ti
22	CO.040	14.5	1.8	0.09	0.0	4.0	94.1	1.89	0.71	0.82	0.0	0.0	Ti
23	CO.047	15.8	28.2	1.29	7.7	1.5	89.3	1.47	0.79	0.84	0.3K	0.5Ru	Al
24	CO.049	15.6	30.6	1.41	10.9	1.8	85.7	1.66	0.76	0.82	0.1K	0.5Ru	Al
25	CO.047	15.6	28.1	1.30	8.8	1.6	88.1	1.50	0.78	0.85	0.3K	0.5Ru	Al
26	CO.031	15.9	30.9	1.41	12.1	1.9	84.9	1.12	0.75	0.83	1.4Zr	0.0	Al
27	CO.029	15.9	28.3	1.27	8.3	1.6	87.9	2.21	0.77	0.84	0.5K	0.5Ru	Al
28	COW.01	15.0	1.1	0.05	0.0	12.	83.9	4.23	0.58	--	5.0Cu	10.0Zn	Al

Note: Catalyst Run 9 screened thru 170 x 400 mesh.

Catalysts For Runs 11 through 28 (except Runs 21 and 22) screened thru 150x 400 mesh.

Catalysts for Runs 21 and 22 screened thru 100 x 400 mesh.

Catalyst No. CO.029 contained 30 wt% cobalt.

.C.Problems

- (1) Weak TCD filaments in G.C. CH₄ peaks smaller than expected.
- (2) Internal valve in G.C. leaked. CH₄ peak undetected.

Table 11

DATE: 07/07/94

COMPARISON OF CONVERSION AND SELECTIVITY OF
METHANE REDUCTION CATALYSTS AT STARTUP CONDITIONS

Period No.	Temp.	Pres.	H ₂ /CO Ratio
-----	-----	-----	-----
1	240 C	450psi	2.0

Run No	Cat. No	Cat. wt,g	Conv. %	Prod. Rate	Selectivities				Alpha GC	Alpha Liq	Catalyst Promt	Composit. Metal	Suppt
					%CH ₄	%C ₂	%C ₃ +	%CO ₂					
4	SBCR												
3	Co.002	15.2	29.4	1.42	17.3	2.3	79.4	1.01	0.73	0.82	1.0La	0.43Ru	Al
4	Co.024	15.4	25.5	1.21	8.6	2.0	89.0	0.43	0.79	0.84	8.5Zr	0.0	Si
5	Co.035	15.4	24.8	1.18	8.5	2.1	89.0	0.47	0.78	0.84	8.5Zr	0.0	Si
6	Co.028	15.4	21.2	1.00	6.1	1.6	91.3	1.01	0.81	0.83	0.5K	0.5Ru	Al
7	Co.043	15.4	13.0	0.61	3.7	1.8	93.4	1.06	0.79	0.85	8.5Zr	0.5Ru	Si
											0.5K		
8	Co.006	15.0	2.7	0.13	0.1	0.2	98.0	1.75	0.67	0.85	0.0	0.75Re	Ti
9	Co.048	15.4	19.1	0.90	9.9	1.6	87.4	1.10	0.77	0.88	8.5Zr	0.5Ru	Si
											0.3K		
10	CAL.02	15.9	34.5	1.58	12.9	2.0	83.9	1.23	0.75	0.81	0.0	0.5Ru	Al
11	CAL.03	15.6	29.7	1.39	13.5	2.1	83.4	1.08	0.74	0.86	0.0	0.5Ru	Al
12	Co.053	15.9	34.2	1.56	12.6	2.0	84.2	1.23	0.75	0.83	0.0	0.5Ru	Al
13	Co.054	15.7	10.4	0.48	4.7	1.8	92.3	1.17	0.78	0.86	8.5Zr	0.0	Si
											0.3K		

te: Catalysts for all runs except Run 8 screened thru 150 x 400 mesh.

Catalyst for Run 8 screened thru 100 x 400 mesh.

.C.Problems

- (1) Weak TCD filaments in G.C. CH₄ peaks smaller than expected.
- (2) Internal valve in G.C. leaked. CH₄ peak undetected.

SBCR CATALYST EXTRACTIONS

Catalyst No. (Support)	Run No.	Charge		Charge		Recovered		Reduction in Particle Size, %
		(H ₂ Reduced) wt, gm	(Oxidized) wt, gm	Particle Size, mvd, microns	Particle Size at 10% microns	Particle Size, mvd, microns	Particle Size at 10% microns	
Co.001 (Al)	1	14.5	12.63	42.02	24.25	41.06	23.62	2.3
Co.001 (Al)	2	16.5	15.18	42.02	24.25	40.09	22.86	4.6
Co.005 (Al)	3	19.5	18.41	85.66	30.46	64.53	31.27	24.7
Co.002 (Al)	4	20.1	20.4	73.61	32.86	71.19	33.50	3.3
Co.003 (Al)	5	15.1	14.54	76.81	34.40	72.57	34.25	5.5
Co.011 (Si)	6	15.3	16.03	107.09 (1)	53.19	94.02	40.44	12.2
Co.012 (Si)	7	15.8	14.73	105.22 (1)	51.33	101.37	44.44	3.7
Co.015 (Al)	8	15.0	15.52	75.63 (1)	33.15	74.68	32.68	1.3
Co.011 (Si)	9	15.0	15.92	79.88 (2)	48.31	72.44	36.31	9.3
Co.016 (Al)	10	15.5	15.72	64.60 (2)	32.16	64.38	32.78	0.3
Co.017 (Al)	11	15.0	15.09	73.14 (3)	36.29	69.95	35.62	4.4
Co.018 (Al)	12	15.6	16.97	62.89 (3)	32.56	68.16	34.74	--
Co.016 (Al)	13	14.7	13.30	67.69 (3)	35.05	64.79	34.20	4.3
Co.019 (Si)	14	15.2	15.00	92.63 (3)	42.73	84.39	36.52	8.9
Co.005 (Al)	15	14.7	15.30	80.62 (3)	45.07	71.90	36.79	10.8
Co.002 (Al)	16	15.4	14.98	73.61 (3)	32.86	67.62	32.67	8.1
Co.002 (Al)	1 (M4)	15.0	11.00	73.61 (3)	32.86	66.26	35.75	10.0
Co.025 (Si)	17	15.6	14.60	87.19 (3)	47.35	78.31	36.27	10.2
Co.004 (Al)	18	15.0	15.25	78.12 (3)	44.15	66.86	33.83	14.4
Co.021 (Si)	19	15.6	16.06	86.18 (3)	46.54	77.95	35.59	9.55
Co.041 (Si)	20	15.8	17.02	87.48 (3)	49.26	68.74	26.72	17.0
Co.021 (Si)	3 (M4)	15.2	15.1	73.61 (3)	24.46	71.38	32.33	3.03
Co.024 (Al)	4 (M4)	15.4	(4)	--	--	--	--	--
Co.035 (Si)	5 (M4)	15.4	14.08	89.14 (3)	49.29	74.76	31.67	19.2
Co.028 (Al)	6 (M4)	15.4	15.7	80.83 (3)	44.81	71.83	36.34	11.1

- (1) Screened through 100x400 mesh screens. (2) Screened through 170x400 mesh screens.
 (3) Screened through 150x400 mesh screens. (4) Did not filter, too waxy

Note: The charge weights are in the hydrogen-reduced state and the recovered weights are in the oxidized state. The particle size is reported as the mean volume diameter (mvd) as measured by a Microtrac particle size analyzer.

Table 12
(Continued)

SBCR CATALYST EXTRACTIONS

Catalyst No. (Support)	Run No.	Charge		Charge		Recovered		Reduction in Particle Size, %
		(H ₂ Reduced) wt, gm	(Oxidized) wt, gm	Particle Size, mvd, microns	Particle Size at 10% microns	Particle Size, mvd, microns	Particle Size at 10% microns	
Co.014 (Ti)	21	15.1	15.1	111.70 (1)	32.65	106.66	33.49	4.51
Co.040 (Ti)	22	14.5	8.5	(5)	(5)	130.40	51.40	--
Co.047 (Al)	23	15.8	16.95	83.42 (3)	44.41	76.46	39.02	8.34
Co.049 (Al)	24	15.6	16.54	81.3 (3)	42.39	70.11	35.87	13.8
Co.047 (Al)	25	15.6	16.69	79.36 (3)	41.72	69.09	36.16	12.94
Co.031 (Al)	26	15.9	15.37	75.48 (3)	38.34	68.42	35.39	9.35
Co.029 (Al)	27	15.9	18.28	76.39 (3)	39.56	68.72	36.04	10.04
Co.043 (Si)	7 (M4)	15.4	15.1	(5)	(5)	85.51	40.20	--
Co.006 (Ti)	8 (M4)	15.0	9.09	121.38 (1)	52.80	99.31	38.62	18.2
Co.048 (Si)	9 (M4)	15.4	15.85	82.40 (3)	40.94	70.69	25.53	14.2
CAL.02 (Al)	10 (M4)	15.9	16.42	74.40 (3)	37.79	65.89	34.14	11.44
Co.053 (Al)	12 (M4)	15.9	16.95	82.02 (3)	43.10	69.53	35.76	15.23
Co.054 (Si)	13 (M4)	15.7	17.09	101.17 (3)	57.54	82.37	37.89	18.58

-
- (1) Screened through 100x400 mesh screens.
 (3) Screened through 150x400 mesh screens.
 (5) Insufficient feed sample.

Table 13

CATALYST ATTRITION STUDIESExperimental Procedure

Charge: 20 gm solids
500 ml n-C₇

Apparatus: One liter glass vessel with two internal baffles. Two 2-inch diameter turbine mixers with 6 blades (1/2x3/8 inch paddles).

Procedure: Mixture is stirred for 48 hours and 1000 RPM at room temperature. Particle size distribution is measured by Microtrac.

Results:

	<u>Solids Charged</u>	<u>Particle Size</u> Charge mvd, microns	<u>Particle Size</u> Product mvd, microns	<u>Change</u> %
1.	Co.005	81.63	74.44	-8.8
2.	Silica 952 calc. @ 500 C	109.89	115.98	+5.4
3.	Titanium Dioxide P25 - as received	9.73	6.06	-37.7
4.	Co.002*	91.07	85.71	-5.9

*Catalyst stirred for 240 hours.

Co.002

catalyst

Figure 1

PARTICLE SIZE DISTRIBUTION OF CHARGED
AND RECOVERED CATALYST NO. Co.002
FROM ATTRITION UNIT

CAL. 03A

CAL. 03B

CAL. 03B

Figure 2

DUPLICATE ANALYSIS OF SAME SAMPLE
TO DETERMINE ANALYTICAL PRECISION

APPENDIX A

Co Catalyst Formulations

Catalyst Prep #	Co.049	Date Tech	Apr-08-94	Amount	200.0 g
Compound (%wt)	Co 20	Ru 0.5	K 0.1	Al2O3	

Support	y-Alumina VISTA B	Amount	158.80 g
Particle Size	400 - 0 mesh	Treatment	500°C / 10 hrs
Cobalt	Cobalt Nitrate	Amount	197.29 g
Metal	Ruthenium Nitrosyl nitrate	Amount	3.57 g
Promotor	Potassium Nitrate	Amount	0.52 g
Promotor		Amount	
Promotor		Amount	

PROCEDURE

Preparation	X	Incipient Wetness	Wet Impregnation
		Ion Exchange	Other

Notes Incipient wetness: aqueous solution - ca. 1.2 ml/g
Dry catalyst precursor in an oven at 115°C / 5 hrs, moderate stirring

Calcination	Temperature	300°C	Time	2 hrs
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Notes Remove 50g of dried catalyst (DO NOT CALCINE !!)
Rescreen after calcination to remove fines

Co.047: 20 wt% Co
 0.5 wt% Ru
 0.3 wt% K
 γ -alumina

Ru/K-promoted catalyst

Preparation Procedure:

Calcine the γ -alumina at 500°C for 10 hrs. Use Vista B alumina. Presieve to >38 microns (400-0 mesh).

Impregnate the support with an aqueous solution of Co nitrate [$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] and Ru nitrosyl nitrate and K nitrate using an appropriate quantity to get incipient wetness (ca. 1.2 ml/g) with the desired loading of Co, Ru, and K.

Dry the catalyst precursor in an oven for 5 hrs at 115°C with moderate stirring.

The dried catalyst is then calcined in air by raising its temperature at a heating rate of ca. 1°C/min to 300°C and holding for 2 hrs.

Reduction Procedure before Reaction:

Reduce the catalyst in a pure hydrogen flow of 3000 cc/g/hr by heating at 1°C/min to 350°C and holding for 10 hrs.

Co.049: 20 wt% Co
 0.5 wt% Ru
 0.1 wt% K
 γ -alumina

Ru/K-promoted catalyst similar to Co.028.

Preparation Procedure:

Calcine the γ -alumina at 500°C for 10 hrs. Use Vista B alumina. Presieve to >38 microns (400-0 mesh).

Impregnate the support with an aqueous solution of Co nitrate [$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] an Ru nitrosil nitrate and K nitrate using an appropriate quantity to get incipient wetness (ca. 1.2 ml/g) with the desired loading of Co, Ru, and K.

Dry the catalyst precursor in an oven for 5 hrs at 115°C with moderate stirring.

The dried catalyst is then calcined in air by raising its temperature at a heating rate of ca. 1°C/min to 300°C and holding for 2 hrs.

Reduction Procedure before Reaction:

Reduce the catalyst in a pure hydrogen flow of 3000 cc/g/hr by heating at 1°C/min to 350°C and holding for 10 hrs.

Catalyst Prep #	Co.050	Date Tech	Apr-08-94	Amount	200.0 g
Compound (%wt)	Co	Ru	K	Zr	SiO2
	20	0.5	0.1	8.5	

Support	Silica Davison Grade 952	Amount	141.80 g
Particle Size	400 - 0 mesh	Treatment	500°C / 10 hrs
Cobalt	Cobalt Nitrate	Amount	197.29 g
Metal	Ruthenium Nitrosyl nitrate	Amount	3.57 g
Promotor	Potassium Nitrate	Amount	0.52 g
Promotor	Zirconium Oxonitrate	Amount	50.92 g
Promotor		Amount	

PROCEDURE

Preparation	X	Incipient Wetness	Wet Impregnation
		Ion Exchange	Other
Notes	<p>Incipient wetness: aqueous solution of Zr</p> <p>Dry catalyst precursor in an oven 115°C / 5 hrs with stirring, calcine 300°C / 2 hrs</p> <p>Incipient wetness: aqueous solution of Co, Ru, K</p> <p>Dry catalyst precursor in an oven 115°C / 5 hrs with stirring, calcine 300°C / 2 hrs</p>		
Calcination	Temperature	300°C	Time 2 hrs
Notes	<p>Remove 50g of dried catalyst (DO NOT CALCINE !!)</p> <p>Rescreen after calcination to remove fines</p>		

Co.050: 20 wt% Co
 0.5 wt% Ru
 8.5 wt% Zr
 0.1 wt% K
 SiO₂

Ru/K/Zr-promoted catalyst similar to Co.043.

denotes deviations from the patent where indicated by or steps not stated in the patent
Bold type indicates steps listed in the patent.

Preparation Procedure:

- # Calcine the SiO₂ at 500°C for 10 hrs. Presieve to >38 microns (400-0 mesh).
- # Impregnate the support with an aqueous solution of Zr Oxonitrate [ZrO(NO₃)₂] using an appropriate quantity to get incipient wetness with the desired loading of Zr.
- # Dry the Zr-loaded SiO₂ in an oven for 5 hrs at 115°C with moderate stirring.
- # Calcine the dried support in air by raising its temperature at a heating rate of ca. 1°C/min to 300°C and holding for 2 hrs. [Note: the patent suggests calcination in air at 500°C.]
- # **Impregnate the Zr-loaded silica with an aqueous solution of Co nitrate [Co(NO₃)₂·6H₂O], Ru nitrosil nitrate (Ru(NO)(NO₃)₃), and K nitrate (KNO₃) using an appropriate quantity to get incipient wetness with the desired loadings of Co, Ru, and K.**
- # Dry the catalyst precursor in an oven for 5 hrs at 115°C with moderate stirring.
- # Calcine the dried catalyst in air by raising its temperature at a heating rate of ca. 1°C/min to 300°C and holding for 2 hrs.

Reduction Procedure before Reaction:

Reduce the catalyst in a pure hydrogen flow of 3000 cc/g/hr by heating at 1°C/min to 250°C and holding for 10 hrs.

Catalyst rep #	Co.051	Date Tech	Apr-20-94	Amount	10.0 g
Compound (%wt)	Ru 0.5				TiO ₂

Support	Titania Degussa P25	Amount	9.95 g
Particle Size	400 - 0 mesh	Treatment	wet / 650°C / 16 hr
Cobalt		Amount	
Metal	Ruthenium Nitrosylnitrate	Amount	0.18 g
Promotor		Amount	
Promotor		Amount	
Promotor		Amount	

PROCEDURE

Preparation	X	Incipient Wetness	Wet Impregnation	
		Ion Exchange	Other	
Notes	Incipient wetness: aqueous solution of Co and Ru, 60% of desired loading Dry catalyst precursor 115°C / 5 hrs, calcine 250°C / 3 hrs Incipient wetness: aqueous solution of Co and Ru, remaining 40% Dry catalyst precursor 115°C / 5 hrs, calcine 250°C / 3 hrs			
Calcination	Temperature	<u>250°C</u>	Time	<u>3 hrs</u>
Notes				

Co.051

**0.5 wt% Ru
TiO₂ [Rutile]**

Preparation Procedure:

Use TiO₂.

Wet TiO₂ to incipient wetness, then dry in an oven at 60°C with moderate stirring. Calcine the TiO₂ at 650°C for 16 hrs (this should result in a support having ca. 97% rutile).

Presieve to >38 microns (400-0 mesh).

Impregnate the support with an aqueous solution of Ru nitrosyl nitrate using an appropriate quantity to get incipient wetness with the desired loading of Ru.

Dry the catalyst precursor in an oven for 5 hrs at 115°C with moderate stirring.

Calcine the dried catalyst in air by raising its temperature at a heating rate of ca. 1°C/min to 250°C and holding for 3 hrs.

Rescreen to remove fines.

Reduction Procedure:

In the original patent it was just stated that the catalyst should be reduced at 250-450°C for 2-14 hours.

However, to be consistent with other catalysts, use the following procedure. Reduce the catalyst using pure hydrogen at a flow rate of 720 cc/g/hr. The impregnated catalyst is heated to 100°C at the rate of 1°C/min and then maintained for 1 hr. Next, the catalyst is heated to 200°C at the rate of 1°C/min and held for 2 hrs. The catalyst is then heated at 10°C/min until a temperature of 360°C is reached and is then held at that temperature for 16 hrs.

If the catalyst will be exposed to air, cool the catalyst below 200°C, purge with nitrogen, and cool further. Air is bled into the nitrogen stream at ca. 1 cc air in 50 cc nitrogen per min per 5 g of catalyst for 16 hours.

Catalyst Prep #	Co.052	Date Tech	Apr-20-94	Amount	10.0 g
Compound (%wt)	Ru			TiO2	
	0.5				

Support	Titania Degussa P25	Amount	9.95 g
Particle Size	400 - 0 mesh	Treatment	wet / 350°C / 16 hr
Cobalt		Amount *	
Metal	Ruthenium Nitrosylnitrate	Amount	0.18 g
Promotor		Amount	
Promotor		Amount	
Promotor		Amount	

PROCEDURE

Preparation	X	Incipient Wetness	Wet Impregnation
		Ion Exchange	Other
Notes	Incipient wetness: aqueous solution of Co and Ru, 60% of desired loading Dry catalyst precursor 115°C / 5 hrs, calcine 250°C / 3 hrs Incipient wetness: aqueous solution of Co and Ru, remaining 40% Dry catalyst precursor 115°C / 5 hrs, calcine 250°C / 3 hrs		

Calcination	Temperature	250°C	Time	3 hrs
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Notes

Prep. sheet - see Co. 051

Co.052

**0.5 wt% Ru
TiO₂ [Anatase]**

Preparation Procedure:

Use TiO₂.

Wet TiO₂ to incipient wetness, then dry in an oven at 60°C with moderate stirring. Calcine the TiO₂ at 350°C for 16 hrs (this should result in a support having ca. x% anatase and y% rutile (x > y)).

Presieve to >38 microns (400-0 mesh).

Impregnate the support with an aqueous solution of Ru nitrosyl nitrate using an appropriate quantity to get incipient wetness with the desired loading of Ru.

Dry the catalyst precursor in an oven for 5 hrs at 115°C with moderate stirring.

Calcine the dried catalyst in air by raising its temperature at a heating rate of ca. 1°C/min to 250°C and holding for 3 hrs.

Rescreen to remove fines.

Reduction Procedure:

In the original patent it was just stated that the catalyst should be reduced at 250-450°C for 2-14 hours.

However, to be consistent with other catalysts, use the following procedure. Reduce the catalyst using pure hydrogen at a flow rate of 720 cc/g/hr. The impregnated catalyst is heated to 100°C at the rate of 1°C/min and then maintained for 1 hr. Next, the catalyst is heated to 200°C at the rate of 1°C/min and held for 2 hrs. The catalyst is then heated at 10°C/min until a temperature of 360°C is reached and is then held at that temperature for 16 hrs.

If the catalyst will be exposed to air, cool the catalyst below 200°C, purge with nitrogen, and cool further. Air is bled into the nitrogen stream at ca. 1 cc air in 50 cc nitrogen per min per 5 g of catalyst for 16 hours.

Catalyst Prep #	Co.053	Date Tech	May-02-94	Amount	500.0 g
Compound (%wt)		Cu	Ru	Al ₂ O ₃	
		20	0.5		

Support	y-Alumina VISTA B	Amount	397.50 g
Particle Size	400 - 0 mesh	Treatment	500°C / 10 hrs
Cobalt	Cobalt Nitrate	Amount	493.22 g
Metal	Ruthenium Nitrosylnitrate	Amount	8.93 g
Promotor		Amount	
Promotor		Amount	
Promotor		Amount	

PROCEDURE

Preparation	X	Incipient Wetness	Wet Impregnation
		Ion Exchange	Other
Notes	Incipient wetness: aqueous solution - ca. 1.2 ml/g		
	Dry catalyst precursor in an oven at 115°C / 5 hrs, moderate stirring		

Calcination Temperature 300°C Time 2 hrs

Notes Remove 300g of dried catalyst (DO NOT CALCINE !!)

Co.053:

20 wt% Co
0.5 wt% Ru
 γ -alumina

Ru-promoted catalyst similar otherwise to Co.018.

Preparation Procedure:

Calcine the γ -alumina at 500°C for 10 hrs. Use Vista B alumina. Presieve to >38 microns (400-0 mesh).

Impregnate the support with an aqueous solution of Co nitrate [$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] and Ru nitrosil nitrate using an appropriate quantity to get incipient wetness (ca. 1.2 ml/g) with the desired loading of Co and Ru.

Dry the catalyst precursor in an oven for 5 hrs at 115°C with moderate stirring.

The dried catalyst is then calcined in air by raising its temperature at a heating rate of ca. 1°C/min to 300°C and holding for 2 hrs.

Reduction Procedure before Reaction:

Reduce the catalyst in a pure hydrogen flow of 3000 cc/g/hr by heating at 1°C/min to 350°C and holding for 10 hrs.

Catalyst Prep #	Co.054	Date Tech	May-13-94	Amount	200.0 g
Compound (%wt)		Co	K	Zr	SiO ₂
		20	0.3	8.5	

Support	Silica Davison Grade 952	Amount	142.40 g
Particle Size	400 - 0 mesh	Treatment	500°C / 10 hrs
Cobalt	Cobalt Nitrate	Amount	197.29 g
Metal		Amount	
Promotor	Potassium Nitrate	Amount	1.55 g
Promotor	Zirconium Oxonitrate	Amount	50.92 g
Promotor		Amount	

PROCEDURE

Preparation	X	Incipient Wetness Ion Exchange	Wet Impregnation Other
Notes	<p>Incipient wetness: aqueous solution of Zr Dry catalyst precursor in an oven 115°C / 5 hrs with stirring, calcine 300°C / 2 hrs Incipient wetness: aqueous solution of Co, Ru, K Dry catalyst precursor in an oven 115°C / 5 hrs with stirring, calcine 300°C / 2 hrs</p>		
Calcination	Temperature	300°C	Time 2 hrs
Notes	Remove 50g of dried catalyst (DO NOT CALCINE !!)		

Co.054: 20 wt% Co
 8.5 wt% Zr
 0.3 wt% K
 SiO₂

K/Zr-promoted catalyst similar to Co.043, but without Ru.

Preparation Procedure:

- # Calcine the SiO₂ at 500°C for 10 hrs. Presieve to >38 microns (400-0 mesh).
- # Impregnate the support with an aqueous solution of Zr Oxonitrate [ZrO(NO₃)₂] using an appropriate quantity to get incipient wetness with the desired loading of Zr.
- # Dry the Zr-loaded SiO₂ in an oven for 5 hrs at 115°C with moderate stirring.
- # Calcine the dried support in air by raising its temperature at a heating rate of ca. 1°C/min to 300°C and holding for 2 hrs.
- # Impregnate the Zr-loaded silica with an aqueous solution of Co nitrate [Co(NO₃)₂·6H₂O], and K nitrate (KNO₃) using an appropriate quantity to get incipient wetness with the desired loadings of Co and K.
- # Dry the catalyst precursor in an oven for 5 hrs at 115°C with moderate stirring.
- # Calcine the dried catalyst in air by raising its temperature at a heating rate of ca. 1°C/min to 300°C and holding for 2 hrs.

Reduction Procedure before Reaction:

Reduce the catalyst in a pure hydrogen flow of 3000 cc/g/hr by heating at 1°C/min to 250°C and holding for 10 hrs.

Catalyst Prep #	CoW.01	Date Tech	Apr-05-94	Amount	200.0 g
Compound (%wt)		Co	Cu	Zn	Al ₂ O ₃
		20	5	10	

Support	y-Alumina VISTA B	Amount	130.00 g
Particle Size	400 - 0 mesh	Treatment	500°C / 10 hrs
Metal I	Cobalt Nitrate	Amount	197.29 g
Metal II	Copper (II) Nitrate	Amount	38.01 g
Metal III	Zinc Nitrate	Amount	90.97 g
Promotor		Amount	
Promotor		Amount	

PROCEDURE

Preparation	X	Incipient Wetness	Wet Impregnation
		Ion Exchange	Other

Notes Incipient wetness: aqueous solution Cu + Zn, ca. 1.2 ml/g
 Dry catalyst precursor in an oven 110°C / 16 hrs/Calcine 500 C 10 hrs.
 Incipient wetness: aqueous solution Co.
 Dry catalyst precursor in an oven 115°C / 5 hrs.

Calcination Temperature 300°C Time 10 hrs

Notes

CoW.01

20 wt% Co

5 wt% Cu

10 wt% Zn

γ -alumina

Cobalt impregnation on calcined Cu-Cr/ γ -alumina

Preparation Procedure

Calcine γ -alumina at 500°C for 10 hrs. Use Vista B alumina. Presieve to > 38 microns (400-0 mesh).

Impregnate the support with an aqueous solution of $\text{Cu}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$, and $\text{Zn}(\text{NO}_3)_2$ using appropriate quantity to get incipient wetness (ca. 1.2 ml/g) with the desired loading of Co.

Dry the catalyst precursor in an oven for 16 hours at 110°C.

The dried catalyst is then calcined in air by raising its temperature at a heating rate of ca. 1°C/min to 500°C and holding for 10 hours.

Impregnate the Cu-ZnO/ Al_2O_3 with an aqueous solution of Co nitrate [$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] using an appropriate quantity to get incipient wetness with the desired loading of Co.

Dry the catalyst precursor in an oven for 5 hrs at 115°C with moderate stirring.

Calcine the dried catalyst in air by raising its temperature at a heating rate of ca. 1°C/min to 300°C and holding for 10 hrs.

Reduction Procedure before Reaction:

Heat the catalyst in inert gas to 120°C at a rate of 1°C/min then start adding hydrogen to give a concentration of 0.5% at the bed inlet. Raise the catalyst bed temperature to 165°C at a rate of ca. 30°C/hr. When the temperature of the bed has reached 160°C increase the hydrogen concentration in the carrier gas to 1.0%. As the reduction proceeds and the temperature rise begins to diminish, the inlet temperature may be raised to 200°C. The inlet hydrogen concentration can then be increased to about 3-5%, provided that the maximum temperature limit of 230°C is not exceeded. When the reduction appears to be complete the inlet temperature should be raised to 230°C and the inlet hydrogen concentration raised to ca. 20%.

Catalyst Prep #	CoW.02	Date Tech	May-02-94	Amount	200.0 g
Compound (%wt)		Cu	Cr	Co	Al ₂ O ₃
		5	4	20	

Support	y-Alumina VISTA B	Amount	142.00 g
Particle Size	400 - 0 mesh	Treatment	500°C / 10 hrs
Metal I	Copper (II) Nitrate	Amount	38.01 g
Metal II	Chromium (III) Nitrate	Amount	61.54 g
Metal III	Cobalt Nitrate	Amount	197.29 g
Promotor		Amount	
Promotor		Amount	

PROCEDURE

Preparation	X	Incipient Wetness	Wet Impregnation
		Ion Exchange	Other

Notes Incipient wetness: aqueous solution Cu + Zn, ca. 1.2 ml/g
 Dry catalyst precursor in an oven 110°C / 16 hrs/Calcine 500 C 24 hrs.
 Incipient wetness: aqueous solution Co.
 Dry catalyst precursor in an oven 115°C / 5 hrs.

Calcination Temperature 300°C Time 10 hrs

Notes Remove 50 g of dried catalyst (DO NOT CALCINE)

CoW.02

20 wt% Co
5 wt% Cu
4 wt% Cr
 γ -alumina

Cobalt impregnation on calcined Cu-Cr/ γ -alumina

Preparation Procedure

Calcine γ -alumina at 500°C for 10 hrs. Use Vista B alumina. Presieve to > 38 microns (400-0 mesh).

Impregnate the support with an aqueous solution of $\text{Cu}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$, and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ using appropriate quantity to get incipient wetness (ca. 1.2 ml/g) with the desired loading of Cu and Cr.

Dry the catalyst precursor in an oven for 16 hours at 110°C.

The dried catalyst is then calcined in air by raising its temperature at a heating rate of ca. 1°C/min to 500°C and holding for 24 hours.

Impregnate the Cu-Cr/ Al_2O_3 with an aqueous solution of Co nitrate [$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] using an appropriate quantity to get incipient wetness with the desired loading of Co.

Dry the catalyst precursor in an oven for 5 hrs at 115°C with moderate stirring.

Calcine the dried catalyst in air by raising its temperature at a heating rate of ca. 1°C/min to 300°C and holding for 10 hrs.

Reduction Procedure before Reaction:

Heat the catalyst in inert gas to 120°C at a rate of 1°C/min then start adding hydrogen to give a concentration of 0.5% at the bed inlet. Raise the catalyst bed temperature to 165°C at a rate of ca. 30°C/hr. When the temperature of the bed has reached 160°C increase the hydrogen concentration in the carrier gas to 1.0%. As the reduction proceeds and the temperature rise begins to diminish, the inlet temperature may be raised to 200°C. The inlet hydrogen concentration can then be increased to about 3-5%, provided that the maximum temperature limit of 230°C is not exceeded. When the reduction appears to be complete the inlet temperature should be raised to 230°C and the inlet hydrogen concentration raised to ca. 20%.

Catalyst rep #	CoW.03	Date Tech	May-13-94	Amount	200.0 g
Compound (%wt)		Co	Cu	Cr	Al ₂ O ₃
		10	5	4	

Support	γ -Alumina VISTA B	Amount	162.00 g
Particle Size	400 - 0 mesh	Treatment	500°C / 10 hrs
Metal I	Cobalt Nitrate	Amount	98.64 g
Metal II	Copper (II) Nitrate	Amount	38.01 g
Metal III	Chromium (III) Nitrate	Amount	61.54 g
Promotor		Amount	
Promotor		Amount	

PROCEDURE

Preparation	X	Incipient Wetness	Wet Impregnation
		Ion Exchange	Other
Notes	<p>Incipient wetness: aqueous solution Cu + Cr, ca. 1.2 ml/g</p> <p>Dry catalyst precursor in an oven 110°C / 16 hrs/Calcine 500 C 24 hrs.</p> <p>Incipient wetness: aqueous solution Co.</p> <p>Dry catalyst precursor in an oven 115°C / 5 hrs.</p>		
Calcination	Temperature	300°C	Time 10 hrs
Notes	Remove 50 g of dried catalyst (DO NOT CALCINE)		

CoW.03

10 wt% Co
5 wt% Cu
4 wt% Cr
 γ -alumina

Cobalt impregnation on calcined Cu-Cr/ γ -alumina similar to CoW.02, but with 10% Co

Preparation Procedure

Calcine γ -alumina at 500°C for 10 hrs. Use Vista B alumina. Presieve to > 38 microns (400-0 mesh).

Impregnate the support with an aqueous solution of $\text{Cu}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$, and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ using appropriate quantity to get incipient wetness (ca. 1.2 ml/g) with the desired loading of Cu and Cr.

Dry the catalyst precursor in an oven for 16 hours at 110°C.

The dried catalyst is then calcined in air by raising its temperature at a heating rate of ca. 1°C/min to 500°C and holding for 24 hours.

Impregnate the Cu-Cr/ Al_2O_3 with an aqueous solution of Co nitrate [$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] using an appropriate quantity to get incipient wetness with the desired loading of Co.

Dry the catalyst precursor in an oven for 5 hrs at 115°C with moderate stirring.

Calcine the dried catalyst in air by raising its temperature at a heating rate of ca. 1°C/min to 300°C and holding for 10 hrs.

Reduction Procedure before Reaction:

Heat the catalyst in inert gas to 120°C at a rate of 1°C/min then start adding hydrogen to give a concentration of 0.5% at the bed inlet. Raise the catalyst bed temperature to 165°C at a rate of ca. 30°C/hr. When the temperature of the bed has reached 160°C increase the hydrogen concentration in the carrier gas to 1.0%. As the reduction proceeds and the temperature rise begins to diminish, the inlet temperature may be raised to 200°C. The inlet hydrogen concentration can then be increased to about 3-5%, provided that the maximum temperature limit of 230°C is not exceeded. When the reduction appears to be complete the inlet temperature should be raised to 230°C and the inlet hydrogen concentration raised to ca. 20%.

Catalyst Prep #	CoW.04	Date Tech	May-13-94	Amount	200.0 g
Compound (%wt)	Co	Cu	Cr	Al ₂ O ₃	
	10	10	8		

Support	γ -Alumina VISTA B	Amount	144.00 g
Particle Size	400 - 0 mesh	Treatment	500°C / 10 hrs
Metal I	Cobalt Nitrate	Amount	98.64 g
Metal II	Copper (II) Nitrate	Amount	76.02 g
Metal III	Chromium (III) Nitrate	Amount	123.08 g
Promotor		Amount	
Promotor		Amount	

PROCEDURE

Preparation	X	Incipient Wetness	Wet Impregnation
		Ion Exchange	Other
Notes	Incipient wetness: aqueous solution Cu + Cr, ca. 1.2 ml/g Dry catalyst precursor in an oven 110°C / 16 hrs/Calcine 500 C 24 hrs. Incipient wetness: aqueous solution Co. Dry catalyst precursor in an oven 115°C / 5 hrs.		

Calcination	Temperature	300°C	Time	10 hrs
Notes	Remove 50 g of dried catalyst (DO NOT CALCINE)			

CoW.04

10 wt% Co
10 wt% Cu
8 wt% Cr
 γ -alumina

Cobalt impregnation on calcined Cu-Cr/ γ -alumina similar to CoW.03, but with 10% Cu and 8% Cr.

Preparation Procedure

Calcine γ -alumina at 500°C for 10 hrs. Use Vista B alumina. Presieve to > 38 microns (400-0 mesh).

Impregnate the support with an aqueous solution of $\text{Cu}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$, and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ using appropriate quantity to get incipient wetness (ca. 1.2 ml/g) with the desired loading of Cu and Cr.

Dry the catalyst precursor in an oven for 16 hours at 110°C.

The dried catalyst is then calcined in air by raising its temperature at a heating rate of ca. 1°C/min to 500°C and holding for 24 hours.

Impregnate the Cu-Cr/ Al_2O_3 with an aqueous solution of Co nitrate [$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] using an appropriate quantity to get incipient wetness with the desired loading of Co.

Dry the catalyst precursor in an oven for 5 hrs at 115°C with moderate stirring.

Calcine the dried catalyst in air by raising its temperature at a heating rate of ca. 1°C/min to 300°C and holding for 10 hrs.

Reduction Procedure before Reaction:

Heat the catalyst in inert gas to 120°C at a rate of 1°C/min then start adding hydrogen to give a concentration of 0.5% at the bed inlet. Raise the catalyst bed temperature to 165°C at a rate of ca. 30°C/hr. When the temperature of the bed has reached 160°C increase the hydrogen concentration in the carrier gas to 1.0%. As the reduction proceeds and the temperature rise begins to diminish, the inlet temperature may be raised to 200°C. The inlet hydrogen concentration can then be increased to about 3-5%, provided that the maximum temperature limit of 230°C is not exceeded. When the reduction appears to be complete the inlet temperature should be raised to 230°C and the inlet hydrogen concentration raised to ca. 20%.

Catalyst Prep #	CoW.05	Date Tech	Jun-20-94	Amount	100.0 g
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Compound (%wt)	Co	Cu	Cr	Al ₂ O ₃
	20	5	4	

Support	γ -Alumina VISTA B	Amount	71.00 g
Particle Size	400 - 0 mesh	Treatment	500°C / 10 hrs
Metal I	Cobalt Nitrate	Amount	98.64 g
Metal II	Copper (II) Nitrate	Amount	19.01 g
Metal III	Chromium (III) Nitrate	Amount	30.77 g
Promotor		Amount	
Promotor		Amount	

PROCEDURE

Preparation	X	Incipient Wetness	Wet Impregnation
		Ion Exchange	Other

Notes Incipient wetness: aqueous solution Cu + Cr, ca. 1.2 ml/g
 Dry catalyst precursor in an oven 110°C / 16 hrs/Calcine 750 °C 24 hrs.
 Incipient wetness: aqueous solution Co.
 Dry catalyst precursor in an oven 115°C / 5 hrs.

Calcination	Temperature	300°C	Time	10 hrs
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Notes Remove 30 g of dried catalyst (DO NOT CALCINE)

CoW.05

20 wt% Co

5 wt% Cu

4 wt% Cr

γ -alumina

Cobalt impregnation on calcined Cu-Cr/ γ -alumina. Similar to CoW.02, but Cu-Cr/ Al_2O_3 calcined at 750°C.

Preparation Procedure

Calcine γ -alumina at 500°C for 10 hrs. Use Vista B alumina. Presieve to > 38 microns (400-0 mesh).

Impregnate the support with an aqueous solution of $\text{Cu}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$, and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ using appropriate quantity to get incipient wetness (ca. 1.2 ml/g) with the desired loading of Cu and Cr.

Dry the catalyst precursor in an oven for 16 hours at 110°C.

The dried catalyst is then calcined in air by raising its temperature at a heating rate of ca. 1°C/min to 750°C and holding for 24 hours.

Impregnate the Cu-Cr/ Al_2O_3 with an aqueous solution of Co nitrate [$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] using an appropriate quantity to get incipient wetness with the desired loading of Co.

Dry the catalyst precursor in an oven for 5 hrs at 115°C with moderate stirring.

Calcine the dried catalyst in air by raising its temperature at a heating rate of ca. 1°C/min to 300°C and holding for 10 hrs.

Reduction Procedure before Reaction:

Heat the catalyst in inert gas to 120°C at a rate of 1°C/min then start adding hydrogen to give a concentration of 0.5% at the bed inlet. Raise the catalyst bed temperature to 165°C at a rate of ca. 30°C/hr. When the temperature of the bed has reached 160°C increase the hydrogen concentration in the carrier gas to 1.0%. As the reduction proceeds and the temperature rise begins to diminish, the inlet temperature may be raised to 200°C. The inlet hydrogen concentration can then be increased to about 3-5%, provided that the maximum temperature limit of 230°C is not exceeded. When the reduction appears to be complete the inlet temperature should be raised to 230°C and the inlet hydrogen concentration raised to ca. 20%.

Catalyst Prep #	CoW.06	Date Tech	Jun-20-94	Amount	100.0 g
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Compound (%wt)	Co	Cu	Cr	SiO2
	20	5	4	

Support	SiO2	Amount	71.00 g
Particle Size	400 - 0 mesh	Treatment	500°C / 10 hrs

Metal I	Cobalt Nitrate	Amount	98.64 g
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Metal II	Copper (II) Nitrate	Amount	19.01 g
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Metal III	Chromium (III) Nitrate	Amount	30.77 g
Promotor		Amount	
Promotor		Amount	

PROCEDURE

Preparation	X	Incipient Wetness	Wet Impregnation
		Ion Exchange	Other
Notes	<p>Incipient wetness: aqueous solution Cu + Cr</p> <p>Dry catalyst precursor in an oven 110°C / 16 hrs/Calcine 500 °C 24 hrs.</p> <p>Incipient wetness: aqueous solution Co.</p> <p>Dry catalyst precursor in an oven 115°C / 5 hrs.</p>		

Calcination	Temperature	300°C	Time	10 hrs
Notes	Remove 30 g of dried catalyst (DO NOT CALCINE)			

CoW.06

20 wt% Co
5 wt% Cu
4 wt% Cr
Silica

Cobalt impregnation on calcined Cu-Cr/Silica

Preparation Procedure

Calcine silica at 500°C for 10 hrs. Use Davison Grade 952 silica. Presieve to > 38 microns (400-0 mesh).

Impregnate the support with an aqueous solution of $\text{Cu}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$, and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ using appropriate quantity to get incipient wetness (ca. 1.2 ml/g) with the desired loading of Cu and Cr.

Dry the catalyst precursor in an oven for 16 hours at 110°C.

The dried catalyst is then calcined in air by raising its temperature at a heating rate of ca. 1°C/min to 500°C and holding for 24 hours.

Impregnate the Cu-Cr/SiO₂ with an aqueous solution of Co nitrate [$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] using an appropriate quantity to get incipient wetness with the desired loading of Co.

Dry the catalyst precursor in an oven for 5 hrs at 115°C with moderate stirring.

Calcine the dried catalyst in air by raising its temperature at a heating rate of ca. 1°C/min to 300°C and holding for 10 hrs.

Reduction Procedure before Reaction:

Heat the catalyst in inert gas to 120°C at a rate of 1°C/min then start adding hydrogen to give a concentration of 0.5% at the bed inlet. Raise the catalyst bed temperature to 165°C at a rate of ca. 30°C/hr. When the temperature of the bed has reached 160°C increase the hydrogen concentration in the carrier gas to 1.0%. As the reduction proceeds and the temperature rise begins to diminish, the inlet temperature may be raised to 200°C. The inlet hydrogen concentration can then be increased to about 3-5%, provided that the maximum temperature limit of 230°C is not exceeded. When the reduction appears to be complete the inlet temperature should be raised to 230°C and the inlet hydrogen concentration raised to ca. 20%.

APPENDIX B

Fixed Bed Reaction Data

FISCHER-TROPSCH SYNTHESIS

Co.014 - Run #2

Co wt%	NM wt %	Promotor wt%		Support
12	Ru 0.50			TiO2

SUMMARY REACTION DATA

Reaction Conditions:

P = 1.0 atm

T = 220 °C

H₂/CO = 2

weight of catalyst = 0.437 g

WHSV = 2.94 1/hr

time on stream = 20.0 hrs

CO₂ (g/g cat/hr) = 0.011CO₂ (% of CO) = 0.3

O/P = 10.87

E_a = 26.0 kcal/mol

CO conversion (%)	2.6
rate (g CH ₂ /g cat/hr)	0.03
alpha	0.69
C1 (wt%)	27.7
C2 - C4 (wt%)	24.9
C5 - C12 (wt%)	42.4
C13 + (wt%)	5.0

Performance of Co.014

Dates: 04/21/94 - 04/22/94 Run #2

flow rate = 45.0 cc/min, loading = 0.4 g, WHSV = 2.9 1/hr, H₂/CO ratio in feed = 2

time on stream, hr	0.5	2.5	5.0	8.0	18.0	20.0
reaction temperature, °C	220	220	220	220	220	220
pressure, atm	1.0	1.0	1.0	1.0	1.0	1.0
flow, cc/min	45.0	45.0	45.0	45.0	45.0	45.0

C1 - C15 product distribution, weight %

C1	21.34	23.62	23.97	25.35	27.18	28.15
C2	4.00	4.89	5.06	5.32	5.08	5.25
C3	10.12	9.57	9.57	9.91	10.12	10.25
C4	11.31	9.95	9.75	9.88	9.89	9.83
C5	11.70	10.24	10.14	9.96	9.92	9.78
C6	9.69	8.89	9.49	8.60	8.30	7.94
C7	8.52	8.27	8.12	7.82	7.59	7.48
C8	6.50	6.53	6.36	6.13	5.92	5.72
C9	4.78	5.05	4.92	4.80	4.54	4.45
C10	3.82	3.97	3.87	3.86	3.61	3.49
C11	2.57	2.87	2.85	2.77	2.49	2.48
C12	2.18	2.16	2.01	2.03	2.07	1.91
C13	1.45	1.68	1.69	1.50	1.34	1.45
C14	1.13	1.39	1.29	1.19	1.13	1.07
C15	0.89	0.93	0.91	0.86	0.81	0.74
alpha chain growth probability	0.69	0.70	0.70	0.70	0.69	0.69

C1 - C50 estimated total product distribution, weight %

C1	20.7	23.1	23.4	24.8	26.6	27.7
C2 - C4	24.7	23.8	23.8	24.6	24.5	24.9
C5 - C12	48.6	46.7	46.6	44.8	43.4	42.4
C13 - C50	6.0	6.4	6.2	5.9	5.5	5.0

CO conversion, %	4.7	3.6	3.5	3.3	2.6	2.6
rate, g CH ₂ /g cat/hr	0.06	0.05	0.05	0.04	0.03	0.03
CO ₂ formation, %	0.5	0.3	0.4	0.4	0.3	0.3

Performance of Co.014

Dates: 04/21/94 - 04/22/94 Run #2

flow rate = 45.0 cc/min, loading = 0.4 g, WHSV = 2.9 1/hr, H₂/CO ratio in feed = 2

time on stream, hr	24.0	26.0	28.0	30.0	32.0	36.0
reaction temperature, °C	220	210	240	230	220	220
pressure, atm	1.0	1.0	1.0	1.0	1.0	1.0
flow, cc/min	45.0	45.0	45.0	45.0	45.0	6.0

C1 - C15 product distribution, weight %

C1	28.05	23.10	46.23	35.52	26.85	33.59
C2	5.34	4.69	6.64	5.98	5.57	4.70
C3	10.32	8.47	13.56	12.24	10.16	10.04
C4	9.79	8.86	9.29	10.58	9.91	9.76
C5	9.62	9.25	7.71	9.39	9.96	9.36
C6	7.59	8.21	5.03	6.98	8.54	7.43
C7	7.40	7.83	4.25	6.23	7.53	6.59
C8	5.81	6.64	2.69	4.26	5.88	5.00
C9	4.50	5.60	1.72	2.93	4.48	3.84
C10	3.55	4.51	1.20	2.14	3.47	3.01
C11	2.58	3.54	0.66	1.36	2.53	2.17
C12	1.96	3.27	0.42	0.90	1.93	1.62
C13	1.52	2.36	0.29	0.73	1.34	1.15
C14	1.16	2.07	0.22	0.46	1.12	0.95
C15	0.81	1.60	0.11	0.31	0.72	0.78
alpha chain growth probability	0.70	0.75	0.58	0.65	0.70	0.71

C1 - C50 estimated total product distribution, weight %

C1	27.5	21.8	46.1	35.3	26.5	32.6
C2 - C4	24.9	20.8	29.4	28.6	25.3	23.8
C5 - C12	42.1	46.1	23.7	34.0	43.2	38.2
C13 - C50	5.5	11.4	0.8	2.1	4.9	5.3

CO conversion, %	2.6	1.6	7.5	4.2	2.6	21.5
rate, g CH ₂ /g cat/hr	0.03	0.02	0.10	0.05	0.03	0.04
CO ₂ formation, %	0.2	0.2	0.5	0.3	0.3	2.7

Co.014 Arrhenius Plot - Run #2

Schulz-Flory Plot for Co.014 - Run #2
Time on Stream (hrs)

hrs.

Time-on-Stream Plot for Co.014 - Run #2

Co.018 - Run #5

Co wt%	NM wt %	Promotor wt%		Support
20	Ru 0.50			Al ₂ O ₃

SUMMARY REACTION DATA

Reaction Conditions:

P = 1.0 atm

T = 220 °C

H₂/CO = 2

weight of catalyst = 0.179 g

WHSV = 14.36 1/hr

time on stream = 24.5 hrs

CO₂ (g/g cat/hr) = 0.055CO₂ (% of CO) = 0.3

O/P = 1.93

CO conversion (%)	7.5
rate (g CH ₂ /g cat/hr)	0.47
alpha	0.60
C1 (wt%)	29.0
C2 - C4 (wt%)	31.8
C5 - C12 (wt%)	37.8
C13 + (wt%)	1.4

Performance of Co.018

Dates: 04/11/94 - 04/12/94 Run #5

flow rate = 90.0 cc/min, loading = 0.2 g, WHSV = 14.4 1/hr, H₂/CO ratio in feed = 2

time on stream, hr	0.5	2.5	5.5	8.0	23.0	24.5
reaction temperature, °C	220	220	220	220	220	220
pressure, atm	1.0	1.0	1.0	1.0	1	1
flow, cc/min	90.0	90.0	90.0	90.0	90.0	90.0

C1 - C15 product distribution, weight %

C1	28.61	28.09	28.51	29.01	28.47	29.09
C2	5.47	5.33	5.35	4.80	6.43	5.34
C3	13.51	13.44	13.50	13.52	13.68	13.42
C4	13.50	13.45	13.43	13.40	13.36	13.15
C5	11.62	11.78	11.65	11.57	11.39	11.48
C6	8.25	8.58	8.27	8.03	7.85	8.44
C7	6.62	6.79	6.76	6.78	6.66	6.74
C8	4.40	4.56	4.54	4.61	4.43	4.55
C9	2.86	2.93	2.98	3.01	2.93	2.90
C10	2.06	1.91	1.88	1.92	1.82	1.91
C11	1.26	1.23	1.28	1.23	1.24	1.28
C12	0.82	0.85	0.87	0.99	0.87	0.79
C13	0.44	0.48	0.43	0.57	0.39	0.42
C14	0.33	0.33	0.32	0.33	0.27	0.29
C15	0.25	0.25	0.24	0.24	0.21	0.21
alpha chain growth probability	0.61	0.61	0.60	0.60	0.60	0.60

C1 - C50 estimated total product distribution, weight %

C1	28.4	27.9	28.3	28.9	28.3	29.0
C2 - C4	32.2	32.0	32.1	31.6	33.3	31.8
C5 - C12	37.8	38.5	38.0	37.9	36.9	37.8
C13 - C50	1.7	1.7	1.6	1.6	1.4	1.4

CO conversion, %	8.4	8.0	7.8	7.3	7.7	7.5
rate, g CH ₂ /g cat/hr	0.53	0.50	0.49	0.46	0.48	0.47
CO ₂ formation, %	0.4	0.4	0.3	0.4	0.3	0.3

Performance of Co.018

Dates: 04/11/94 - 04/12/94 Run #5

flow rate = 90.0 cc/min, loading = 0.2 g, WHSV = 14.4 l/hr, H₂/CO ratio in feed = 2

time on stream, hr	29.0
reaction temperature, °C	220
pressure, atm	1
flow, cc/min	90.0

C1 - C15 product distribution, weight %

C1	29.26
C2	5.43
C3	13.49
C4	13.11
C5	11.58
C6	7.97
C7	6.82
C8	4.55
C9	2.93
C10	1.90
C11	1.21
C12	0.87
C13	0.42
C14	0.28
C15	0.19
alpha chain growth probability	0.59

C1 - C50 estimated total product distribution, weight %

C1	29.2
C2 - C4	32.0
C5 - C12	37.5
C13 - C50	1.3

CO conversion, %	7.3
rate, g CH ₂ /g cat/hr	0.46
CO ₂ formation, %	0.3

Schulz-Flory Plot for Co.018 - Run #5
Time on Stream (hrs)

Time-on-Stream Plot for Co.018 - Run #5

Co.026 - Run #1

Co wt%	NM wt %	Promotor wt%		Support
20				SiO2

SUMMARY REACTION DATA*

Reaction Conditions:

P = 1.0 atm

T = 220 °C

H₂/CO = 2

weight of catalyst = 0.381 g

WHSV = 1.69 1/hr

time on stream = 24.0 hrs

CO₂ (g/g cat/hr) = 0.037CO₂ (% of CO) = 1.5

O/P = 0.64

CO conversion (%)	22.9
rate (g CH ₂ /g cat/hr)	0.17
alpha	0.67
C1 (wt%)	22.6
C2 - C4 (wt%)	24.1
C5 - C12 (wt%)	49.1
C13 + (wt%)	4.1

* high conversion study

Co.026 - Run #1

Co wt%	NM wt %	Promotor wt%		Support
20				SiO ₂

SUMMARY REACTION DATA

Reaction Conditions:

P = 1.0 atm

T = 220 °C

H₂/CO = 2

weight of catalyst = 0.381 g

WHSV = 6.76 1/hr

time on stream = 21.0 hrs

CO₂ (g/g cat/hr) = 0.022CO₂ (% of CO) = 0.2

O/P = 2.65

CO conversion (%)	4.4
rate (g CH ₂ /g cat/hr)	0.13
alpha	0.62
C1 (wt%)	26.9
C2 - C4 (wt%)	29.0
C5 - C12 (wt%)	42.3
C13 + (wt%)	1.8

Performance of Co.026

Dates: 05/30/94 - 05/31/94 Run #1

flow rate = 90.0 cc/min, loading = 0.4 g, WHSV = 6.8 l/hr, H₂/CO ratio in feed = 2

time on stream, hr	0.5	6.0	9.0	12.0	15.0	18.0
reaction temperature, °C	220	220	220	220	220	220
pressure, atm	1.0	1.0	1.0	1.0	1.0	1.0
flow, cc/min	90.0	90.0	90.0	90.0	90.0	90.0

C1 - C15 product distribution, weight %

C1	24.87	27.05	27.38	27.52	27.55	27.27
C2	4.89	5.00	5.01	5.01	5.01	4.94
C3	12.06	12.11	12.14	12.15	12.14	12.15
C4	12.48	12.32	12.37	12.35	12.32	12.26
C5	12.23	11.96	11.97	11.96	11.96	11.96
C6	10.19	9.29	9.27	9.25	9.21	9.34
C7	7.18	7.27	7.26	7.21	7.26	7.28
C8	5.07	5.06	4.99	5.00	4.98	5.06
C9	3.60	3.51	3.49	3.40	3.42	3.50
C10	2.63	2.56	2.43	2.40	2.43	2.48
C11	1.84	1.58	1.45	1.50	1.53	1.49
C12	1.23	1.00	0.92	0.92	0.87	0.99
C13	0.80	0.62	0.60	0.61	0.66	0.61
C14	0.55	0.42	0.42	0.43	0.40	0.40
C15	0.39	0.27	0.27	0.28	0.25	0.28
alpha chain growth probability	0.64	0.61	0.61	0.62	0.61	0.62

C1 - C50 estimated total product distribution, weight %

C1	24.7	27.0	27.3	27.4	27.5	27.1
C2 - C4	29.2	29.4	29.4	29.4	29.4	29.2
C5 - C12	43.5	41.9	41.6	41.4	41.4	41.8
C13 - C50	2.6	1.8	1.8	1.9	1.7	1.9

CO conversion, %	5.5	4.6	4.4	4.4	4.4	4.4
rate, g CH ₂ /g cat/hr	0.16	0.14	0.13	0.13	0.13	0.13
CO ₂ formation, %	0.3	0.2	0.2	0.3	0.2	0.2

Performance of Co.026

Dates: 05/30/94 - 05/31/94 Run #1

flow rate = 90.0 cc/min, loading = 0.4 g, WHSV = 6.8 l/hr, H₂/CO ratio in feed = 2

time on stream, hr	21.0	24.0	27.0
reaction temperature, °C	220	220	220
pressure, atm	1.0	1.0	1.0
flow, cc/min	90.0	22.5	22.5

C1 - C15 product distribution, weight %

C1	26.96	22.80	24.70
C2	4.91	4.39	4.45
C3	11.93	7.81	8.48
C4	12.25	12.07	11.85
C5	12.06	12.18	11.87
C6	9.40	10.08	9.78
C7	7.39	8.79	8.55
C8	5.12	6.37	6.06
C9	3.57	4.56	4.45
C10	2.59	3.53	3.14
C11	1.57	2.72	2.51
C12	0.95	1.87	1.58
C13	0.62	1.31	1.27
C14	0.41	0.91	0.85
C15	0.28	0.61	0.47
alpha chain growth probability	0.62	0.67	0.65

C1 - C50 estimated total product distribution, weight %

C1	26.9	22.6	24.7
C2 - C4	29.0	24.1	24.8
C5 - C12	42.3	49.1	47.2
C13 - C50	1.8	4.1	3.2

CO conversion, %	4.4	22.9	19.1
rate, g CH ₂ /g cat/hr	0.13	0.17	0.14
CO ₂ formation, %	0.2	1.5	1.2

Schulz-Flory Plot for Co.026 - Run #1
Time on Stream (hrs)

Schulz-Flory Plot for Co.026 - Run #1
High Conversion Study

Time-on-Stream Plot for Co.026 - Run #1

Co.027 - Run #1

Co wt%	NM wt %	Promotor wt%		Support
20	Ru 0.50			SiO ₂

SUMMARY REACTION DATA.**Reaction Conditions:**

P = 1.0 atm

T = 220 °C

H₂/CO = 2

weight of catalyst = 0.279 g

WHSV = 9.21 1/hr

time on stream = 24.5 hrs

CO₂ (g/g cat/hr) = 0.026CO₂ (% of CO) = 0.2

O/P = 3.44

CO conversion (%)	4.2
rate (g CH ₂ /g cat/hr)	0.17
alpha	0.65
C1 (wt%)	23.0
C2 - C4 (wt%)	26.3
C5 - C12 (wt%)	47.6
C13 + (wt%)	3.1

Co.027 - Run #1

Co wt%	NM wt %	Promotor wt%		Support
20	Ru 0.50			SiO ₂

SUMMARY REACTION DATA*

Reaction Conditions:

P = 1.0 atm

T = 220 °C

H₂/CO = 2

weight of catalyst = 0.279 g

WHSV = 0.97 1/hr

time on stream = 33.5 hrs

CO₂ (g/g cat/hr) = 0.011CO₂ (% of CO) = 1.2

O/P = 0.96

CO conversion (%)	17.8
rate (g CH ₂ /g cat/hr)	0.18
alpha	0.71
C1 (wt%)	19.4
C2 - C4 (wt%)	23.5
C5 - C12 (wt%)	50.2
C13 + (wt%)	6.9

* high conversion study

Performance of Co.027

Dates: 05/27/94 - 05/28/94 Run #1

flow rate = 90.0 cc/min, loading = 0.3 g, WHSV = 9.2 1/hr, H₂/CO ratio in feed = 2

time on stream, hr	0.5	3.5	6.5	9.5	12.5	15.5
reaction temperature, °C	220	220	220	220	220	220
pressure, atm	1.0	1.0	1.0	1.0	1.0	1.0
flow, cc/min	90.0	90.0	90.0	90.0	90.0	90.0

C1 - C15 product distribution, weight %

C1	22.66	23.02	23.75	23.72	23.72	23.77
C2	4.57	4.53	4.67	4.68	4.67	4.69
C3	11.24	10.90	10.89	10.81	10.74	10.74
C4	12.07	11.77	11.71	11.63	11.54	11.61
C5	12.23	12.13	12.03	12.06	12.06	12.07
C6	9.78	9.94	9.92	9.95	9.93	9.79
C7	8.03	8.15	8.08	8.12	8.17	8.14
C8	5.85	5.95	5.88	5.90	5.90	5.92
C9	4.23	4.26	4.19	4.27	4.28	4.28
C10	3.18	3.26	3.14	3.19	3.18	3.15
C11	2.30	2.30	2.07	2.05	2.02	2.13
C12	1.53	1.57	1.56	1.57	1.61	1.60
C13	1.06	1.01	1.01	0.94	1.03	0.98
C14	0.75	0.73	0.64	0.70	0.71	0.70
C15	0.54	0.47	0.43	0.42	0.45	0.43
alpha chain growth probability	0.66	0.65	0.64	0.64	0.65	0.64

C1 - C50 estimated total product distribution, weight %

C1	22.4	22.9	23.7	23.7	23.6	23.7
C2 - C4	27.6	27.1	27.2	27.1	26.8	27.0
C5 - C12	46.5	46.8	46.2	46.5	46.5	46.4
C13 - C50	3.6	3.1	2.9	2.8	3.0	2.9

CO conversion, %	5.7	4.8	4.7	4.4	4.3	4.2
rate, g CH ₂ /g cat/hr	0.23	0.20	0.19	0.18	0.17	0.17
CO ₂ formation, %	0.4	0.2	0.2	0.2	0.2	0.2

Performance of Co.027

Dates: 05/27/94 - 05/28/94 Run #1

flow rate = 90.0 cc/min, loading = 0.3 g, WHSV = 9.2 1/hr, H₂/CO ratio in feed = 2

time on stream, hr	18.5	21.5	24.5	27.5	30.5	33.5
reaction temperature, °C	220	220	220	220	220	220
pressure, atm	1.0	1.0	1.0	1.0	1.0	1.0
flow, cc/min	90.0	90.0	90.0	90.0	90.0	22.5

C1 - C15 product distribution, weight %

C1	23.69	23.28	23.04	23.16	22.95	19.87
C2	4.67	4.62	4.59	4.63	4.60	3.85
C3	10.68	10.52	10.41	10.46	10.37	9.45
C4	11.53	11.40	11.29	11.34	11.25	10.74
C5	11.95	11.91	11.88	11.93	11.87	11.46
C6	9.99	10.00	10.09	10.06	10.02	10.04
C7	8.19	8.33	8.31	8.31	8.47	8.80
C8	5.96	6.13	6.18	6.14	6.23	6.85
C9	4.34	4.48	4.57	4.47	4.58	5.23
C10	3.17	3.34	3.28	3.37	3.40	4.02
C11	2.06	2.16	2.26	2.27	2.28	3.30
C12	1.61	1.51	1.75	1.55	1.62	2.35
C13	1.01	1.10	1.03	1.07	1.02	1.70
C14	0.72	0.74	0.84	0.71	0.87	1.34
C15	0.45	0.49	0.47	0.53	0.47	1.00
alpha chain growth probability	0.65	0.65	0.65	0.66	0.65	0.71

C1 - C50 estimated total product distribution, weight %

C1	23.6	23.1	23.0	22.9	22.9	19.4
C2 - C4	26.8	26.4	26.3	26.2	26.2	23.5
C5 - C12	46.6	47.3	47.6	47.4	47.8	50.2
C13 - C50	3.0	3.3	3.1	3.6	3.2	6.9

CO conversion, %	4.2	4.3	4.2	4.2	4.2	17.8
rate, g CH ₂ /g cat/hr	0.17	0.17	0.17	0.17	0.17	0.18
CO ₂ formation, %	0.2	0.2	0.2	0.2	0.2	1.2

Schulz-Flory Plot for Co.027 - Run #1

Time on Stream (hrs)

hrs.

Schulz-Flory Plot for Co.027 - Run #1
High Conversion Study

Time-on-Stream Plot for Co.027 - Run #1

Co.028 - Run #3 (re-calcine in flow air)

Co wt%	NM wt %	Promotor wt%		Support
20	Ru 0.50	K 0.50		Al ₂ O ₃

SUMMARY REACTION DATA**Reaction Conditions:**

P = 1.0 atm

T = 220 °C

H₂/CO = 2

weight of catalyst = 0.249 g

WHSV = 10.34 1/hr

time on stream = 26.0 hrs

CO₂ (g/g cat/hr) = 0.037CO₂ (% of CO) = 0.2

O/P = 13.49

CO conversion (%)	4.5
rate (g CH ₂ /g cat/hr)	0.21
alpha	0.79
C1 (wt%)	15.5
C2 - C4 (wt%)	16.8
C5 - C12 (wt%)	47.2
C13 + (wt%)	20.5

Performance of Co.028

Dates: 04/18/94 - 04/19/94 Run #3 (re-calcine in flow air)

flow rate = 90.0 cc/min, loading = 0.2 g, WHSV = 10.3 1/hr, H₂/CO ratio in feed = 2

time on stream, hr	0.5	2.5	5.0	8.0	24.0	26.0
reaction temperature, °C	220	220	220	220	220	220
pressure, atm	1.0	1.0	1.0	1.0	1	1
flow, cc/min	90.0	90.0	90.0	90.0	90.0	90.0

C1 - C15 product distribution, weight %

C1	16.80	16.95	16.99	16.92	17.21	17.79
C2	3.21	3.24	3.69	3.79	3.35	3.72
C3	7.56	7.42	7.53	7.46	7.33	7.45
C4	8.55	8.25	8.25	8.18	8.06	8.10
C5	9.52	9.14	9.06	9.10	8.89	8.95
C6	8.87	8.67	8.24	8.69	8.38	8.47
C7	8.49	8.27	8.14	8.16	8.03	8.02
C8	7.48	7.36	7.32	7.28	7.20	7.21
C9	6.48	6.49	6.48	6.41	6.43	6.40
C10	5.65	5.70	5.72	5.67	5.61	5.66
C11	4.75	4.98	4.91	4.94	4.86	4.80
C12	4.08	4.23	4.23	4.26	4.22	4.16
C13	3.38	3.58	3.56	3.49	3.66	3.53
C14	2.78	3.10	3.21	3.05	3.46	3.00
C15	2.40	2.61	2.68	2.61	3.31	2.75
alpha chain growth probability	0.78	0.79	0.79	0.79	0.81	0.79

C1 - C50 estimated total product distribution, weight %

C1	15.1	15.0	15.0	15.0	14.2	15.5
C2 - C4	17.4	16.8	17.1	17.2	15.4	16.8
C5 - C12	49.7	48.6	47.8	48.3	45.6	47.2
C13 - C50	17.8	19.6	20.1	19.6	24.8	20.5

CO conversion, %	6.0	5.4	5.2	5.2	4.7	4.5
rate, g CH ₂ /g cat/hr	0.27	0.25	0.23	0.23	0.21	0.21
CO ₂ formation, %	0.4	0.4	0.3	0.3	0.2	0.2

Performance of Co.028

Dates: 04/18/94 - 04/19/94 Run #3 (re-calcine in flow air)

flow rate = 90.0 cc/min, loading = 0.2 g, WHSV = 10.3 1/hr, H₂/CO ratio in feed = 2

time on stream, hr	30.0
reaction temperature, °C	220
pressure, atm	1
flow, cc/min	90.0

C1 - C15 product distribution, weight %

C1	17.43
C2	4.00
C3	7.50
C4	8.31
C5	9.02
C6	8.61
C7	8.06
C8	7.18
C9	6.38
C10	5.56
C11	4.73
C12	4.03
C13	3.36
C14	2.92
C15	2.91

alpha	chain growth probability	0.80
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C1 - C50 estimated total product distribution, weight %

C1	14.9
C2 - C4	16.9
C5 - C12	46.7
C13 - C50	21.5

CO conversion, %	4.7
rate, g CH ₂ /g cat/hr	0.21
CO ₂ formation, %	0.2

Schulz-Flory Plot for Co.028 - Run #3
Time on Stream (hrs)

Time-on-Stream Plot for Co.028 - Run #3

Co.029 - Run #1

Co wt%	NM wt %	Promotor wt%		Support
30	Ru 0.50	K 0.50		Al ₂ O ₃

SUMMARY REACTION DATA

Reaction Conditions:

P = 1.0 atm

T = 220 °C

H₂/CO = 2

weight of catalyst = 0.184 g

WHSV = 13.99 1/hr

time on stream = 26.0 hrs

CO₂ (g/g cat/hr) = 0.026CO₂ (% of CO) = 0.1

O/P = 25.95

CO conversion (%)	2.8
rate (g CH ₂ /g cat/hr)	0.17
alpha	0.79
C1 (wt%)	15.3
C2 - C4 (wt%)	17.3
C5 - C12 (wt%)	48.0
C13 + (wt%)	19.4

Performance of Co.029

Dates: 05/19/94 - 05/20/94 Run #1

flow rate = 90.0 cc/min, loading = 0.2 g, WHSV = 14.0 1/hr, H₂/CO ratio in feed = 2

time on stream, hr	0.5	3.0	5.5	8.0	24.0	26.0
reaction temperature, °C	220	220	220	220	220	220
pressure, atm	1.0	1.0	1.0	1.0	1.0	1.0
flow, cc/min	90.0	90.0	90.0	90.0	90.0	90.0

C1 - C15 product distribution, weight %

C1	15.57	16.33	16.51	16.67	17.87	17.37
C2	3.49	3.66	3.70	3.86	3.92	3.83
C3	7.19	7.30	7.32	7.37	7.58	7.49
C4	8.31	8.18	8.15	8.21	8.40	8.30
C5	9.46	9.16	9.11	9.00	8.93	9.12
C6	9.02	8.64	8.40	8.51	7.87	8.46
C7	8.73	8.50	8.42	8.30	8.06	8.31
C8	7.66	7.53	7.52	7.40	7.27	7.39
C9	6.67	6.63	6.67	6.61	6.50	6.56
C10	5.81	5.79	5.86	5.88	5.67	5.60
C11	4.88	4.90	4.97	4.96	4.86	4.67
C12	4.19	4.30	4.22	4.18	4.18	3.94
C13	3.53	3.52	3.54	3.46	3.54	3.42
C14	3.03	3.03	3.05	2.99	2.91	2.95
C15	2.46	2.52	2.57	2.60	2.43	2.60
alpha chain growth probability	0.78	0.79	0.79	0.79	0.78	0.79

C1 - C50 estimated total product distribution, weight %

C1	14.0	14.6	14.7	14.8	16.1	15.3
C2 - C4	17.1	17.1	17.0	17.2	17.9	17.3
C5 - C12	50.5	49.3	49.0	48.5	47.7	48.0
C13 - C50	18.5	19.0	19.3	19.5	18.3	19.4

CO conversion, %	4.2	3.8	3.5	3.4	2.7	2.8
rate, g CH ₂ /g cat/hr	0.26	0.23	0.22	0.21	0.16	0.17
CO ₂ formation, %	0.3	0.2	0.1	0.2	0.3	0.1

Performance of Co.029

Dates: 05/19/94 - 05/20/94 Run #1

flow rate = 90.0 cc/min, loading = 0.2 g, WHSV = 14.0 1/hr, H₂/CO ratio in feed = 2

time on stream, hr	28.0
reaction temperature, °C	220
pressure, atm	1.0
flow, cc/min	90.0

C1 - C15 product distribution, weight %

C1	17.61
C2	3.87
C3	7.53
C4	8.35
C5	9.03
C6	8.17
C7	8.19
C8	7.33
C9	6.53
C10	5.64
C11	4.77
C12	4.06
C13	3.48
C14	2.93
C15	2.52
alpha chain growth probability	0.79

C1 - C50 estimated total product distribution, weight %

C1	15.7
C2 - C4	17.6
C5 - C12	47.9
C13 - C50	18.8

CO conversion, %	2.7
rate, g CH ₂ /g cat/hr	0.17
CO ₂ formation, %	0.2

Schulz-Flory Plot for Co.029 - Run #1
Time on Stream (hrs)

Time-on-Stream Plot for Co.029 - Run #1

Co.039 - Run #2

Co wt%	NM wt %	Promotor wt%		Support
12				TiO ₂

SUMMARY REACTION DATA**Reaction Conditions:**

P = 1.0 atm

T = 220 °C

H₂/CO = 2

weight of catalyst = 0.451 g

WHSV = 2.85 1/hr

time on stream = 21.5 hrs

CO₂ (g/g cat/hr) = 0.009CO₂ (% of CO) = 0.2

O/P = 0.95

CO conversion (%)	3.9
rate (g CH ₂ /g cat/hr)	0.05
alpha	0.48
C1 (wt%)	42.4
C2 - C4 (wt%)	34.1
C5 - C12 (wt%)	23.4
C13 + (wt%)	0.2

Performance of Co.039

Dates: 06/01/94 - 06/02/94 Run #2

flow rate = 45.0 cc/min, loading = 0.5 g, WHSV = 2.9 1/hr, H₂/CO ratio in feed = 2

time on stream, hr	0.5	3.5	6.5	9.5	12.5	15.5
reaction temperature, °C	220	220	220	220	220	220
pressure, atm	1.0	1.0	1.0	1.0	1.0	1.0
flow, cc/min	45.0	45.0	45.0	45.0	45.0	45.0

C1 - C15 product distribution, weight %

C1	39.17	40.81	41.38	41.67	41.62	41.84
C2	6.29	6.41	6.42	6.42	6.40	6.40
C3	15.03	14.97	14.99	14.97	15.14	15.23
C4	12.99	12.73	12.63	12.52	12.58	12.60
C5	10.22	9.86	9.73	9.62	9.70	9.65
C6	6.39	6.00	5.90	5.87	5.85	5.96
C7	4.49	4.24	4.16	4.12	4.10	4.05
C8	2.62	2.35	2.38	2.28	2.28	2.19
C9	1.24	1.18	1.11	1.18	1.08	1.05
C10	0.73	0.66	0.62	0.63	0.60	0.60
C11	0.39	0.37	0.31	0.38	0.33	0.29
C12	0.28	0.25	0.24	0.22	0.22	0.13
C13	0.16	0.16	0.12	0.13	0.12	
C14						
C15						
alpha chain growth probability	0.51	0.50	0.49	0.51	0.50	0.49

C1 - C50 estimated total product distribution, weight %

C1	39.2	40.8	41.4	41.6	41.6	41.8
C2 - C4	34.3	34.1	34.0	33.9	34.1	34.2
C5 - C12	26.3	24.9	24.4	24.3	24.1	23.9
C13 - C50	0.3	0.2	0.2	0.3	0.2	0.2

CO conversion, %	4.7	4.5	4.3	4.2	4.1	4.0
rate, g CH ₂ /g cat/hr	0.06	0.06	0.05	0.05	0.05	0.05
CO ₂ formation, %	0.3	0.3	0.2	0.2	0.2	0.2

Performance of Co.039

Dates: 06/01/94 - 06/02/94 Run #2

flow rate = 45.0 cc/min, loading = 0.5 g, WHSV = 2.9 1/hr, H₂/CO ratio in feed = 2

time on stream, hr	18.5	21.5	24.5	27.5
reaction temperature, °C	220	220	220	220
pressure, atm	1.0	1.0	1.0	1.0
flow, cc/min	45.0	45.0	22.5	22.5

C1 - C15 product distribution, weight %

C1	42.24	42.44	43.30	44.13
C2	6.43	6.44	6.60	6.67
C3	15.19	15.23	13.59	13.48
C4	12.48	12.46	12.35	12.16
C5	9.51	9.49	9.56	9.29
C6	5.72	5.67	5.69	5.56
C7	4.16	4.08	4.00	4.05
C8	2.19	2.20	2.32	2.16
C9	1.08	0.98	1.17	1.05
C10	0.58	0.56	0.66	0.62
C11	0.29	0.28	0.30	0.33
C12	0.14	0.16	0.19	0.19
C13			0.14	0.15
C14			0.08	0.10
C15			0.05	0.06
alpha chain growth probability	0.49	0.48	0.49	0.50

C1 - C50 estimated total product distribution, weight %

C1	42.2	42.4	43.4	44.2
C2 - C4	34.0	34.1	32.6	32.3
C5 - C12	23.6	23.4	23.9	23.3
C13 - C50	0.2	0.2	0.2	0.2

CO conversion, %	4.0	3.9	7.7	7.6
rate, g CH ₂ /g cat/hr	0.05	0.05	0.05	0.05
CO ₂ formation, %	0.2	0.2	0.6	0.6

Schulz-Flory Plot for Co.039 - Run #2
Time on Stream (hrs)

Time-on-Stream Plot for Co.039 - Run #2

Co.040 - Run #2

Co wt%	NM wt %	Promotor wt%		Support
12				TiO2

SUMMARY REACTION DATA

Reaction Conditions:

P = 1.0 atm

T = 220 °C

H₂/CO = 2

weight of catalyst = 0.471 g

WHSV = 2.73 1/hr

time on stream = 21.5 hrs

CO₂ (g/g cat/hr) = 0.007CO₂ (% of CO) = 0.2

O/P = 1.12

CO conversion (%)	2.8
rate (g CH ₂ /g cat/hr)	0.03
alpha	0.46
C1 (wt%)	44.6
C2 - C4 (wt%)	34.5
C5 - C12 (wt%)	20.8
C13 + (wt%)	0.1

Performance of Co.040

Dates: 06/29/94 - 06/30/94 Run #2

flow rate = 45.0 cc/min, loading = 0.5 g, WHSV = 2.7 1/hr, H₂/CO ratio in feed = 2

time on stream, hr	0.5	3.5	6.5	9.5	12.5	15.5
reaction temperature, °C	220	220	220	220	220	220
pressure, atm	1.0	1.0	1.0	1.0	1.0	1.0
flow, cc/min	45.0	45.0	45.0	45.0	45.0	45.0

C1 - C15 product distribution, weight %

C1	39.82	41.94	42.60	42.99	43.79	43.91
C2	6.67	6.81	6.81	6.81	6.83	6.82
C3	15.67	15.67	15.69	15.72	15.75	15.75
C4	12.66	12.33	12.24	12.19	12.11	12.08
C5	9.91	9.41	9.31	9.17	9.10	9.08
C6	6.13	5.70	5.52	5.40	5.24	5.33
C7	4.52	4.10	3.99	3.95	3.81	3.83
C8	2.41	2.36	2.24	2.20	1.86	1.90
C9	1.12	0.98	0.96	0.91	0.90	0.82
C10	0.59	0.45	0.42	0.46	0.40	0.33
C11	0.30	0.25	0.23	0.22	0.20	0.15
C12	0.18					
C13						
C14						
C15						
alpha chain growth probability	0.50	0.48	0.47	0.48	0.47	0.45

C1 - C50 estimated total product distribution, weight %

C1	39.7	41.8	42.5	42.9	43.7	43.8
C2 - C4	34.9	34.7	34.7	34.6	34.6	34.6
C5 - C12	25.1	23.3	22.7	22.4	21.6	21.5
C13 - C50	0.2	0.1	0.1	0.1	0.1	0.1

CO conversion, %	3.6	3.3	3.1	3.0	3.0	2.9
rate, g CH ₂ /g cat/hr	0.04	0.04	0.04	0.04	0.04	0.03
CO ₂ formation, %	0.2	0.2	0.2	0.2	0.2	0.2

Performance of Co.040

Dates: 06/29/94 - 06/30/94 Run #2

flow rate = 45.0 cc/min, loading = 0.5 g, WHSV = 2.7 1/hr, H₂/CO ratio in feed = 2

time on stream, hr	18.5	21.5	24.5	27.5
reaction temperature, °C	220	220	220	220
pressure, atm	1.0	1.0	1.0	1.0
flow, cc/min	45.0	45.0	22.5	22.5

C1 - C15 product distribution, weight %

C1	44.52	44.64	45.52	46.01
C2	6.85	6.87	6.88	6.87
C3	15.73	15.77	14.19	14.19
C4	11.95	11.95	11.82	11.75
C5	8.90	8.82	8.89	8.79
C6	5.23	5.20	5.31	5.27
C7	3.66	3.62	3.77	3.64
C8	1.78	1.77	2.00	1.91
C9	0.84	0.81	0.94	0.89
C10	0.37	0.37	0.46	0.45
C11	0.19	0.19	0.23	0.22
C12				
C13				
C14				
C15				
alpha chain growth probability	0.46	0.46	0.48	0.48

C1 - C50 estimated total product distribution, weight %

C1	44.4	44.6	45.4	45.9
C2 - C4	34.5	34.5	32.8	32.7
C5 - C12	21.0	20.8	21.7	21.3
C13 - C50	0.1	0.1	0.1	0.1

CO conversion, %	2.9	2.8	5.6	5.6
rate, g CH ₂ /g cat/hr	0.03	0.03	0.03	0.03
CO ₂ formation, %	0.2	0.2	0.4	0.4

Schulz-Flory Plot for Co.040 - Run #2
Time on Stream (hrs)

Schulz-Flory Plot for Co.040 - Run #2
High Conversion Study

Time-on-Stream Plot for Co.040 - Run #2

Co.047 - Run #1

Co wt%	NM wt %	Promotor wt%		Support
20	Ru 0.50	K 0.30		Al ₂ O ₃

SUMMARY REACTION DATA

Reaction Conditions:

P = 1.0 atm

T = 220 °C

H₂/CO = 2

weight of catalyst = 0.273 g

WHSV = 9.43 1/hr

time on stream = 22.0 hrs

CO₂ (g/g cat/hr) = 0.040CO₂ (% of CO) = 0.3

O/P = 7.20

E_a = 26.6 kcal/mol

CO conversion (%)	6.4
rate (g CH ₂ /g cat/hr)	0.26
alpha	0.73
C1 (wt%)	21.3
C2 - C4 (wt%)	21.9
C5 - C12 (wt%)	47.4
C13 + (wt%)	9.3

Performance of Co.047

Dates: 04/07/94 - 04/08/94 Run #1

flow rate = 90.0 cc/min, loading = 0.3 g, WHSV = 9.4 l/hr, H₂/CO ratio in feed = 2

time on stream, hr	0.5	2.5	5.0	8.0	20.5	22.0
reaction temperature, °C	220	220	220	220	220	220
pressure, atm	1.0	1.0	1.0	1.0	1	1
flow, cc/min	90.0	90.0	90.0	90.0	90.0	90.0

C1 - C15 product distribution, weight %

C1	20.77	20.32	21.20	21.13	21.52	22.11
C2	4.04	3.95	3.72	4.11	4.20	3.87
C3	10.24	9.48	9.38	9.28	9.20	9.24
C4	10.97	10.18	9.96	9.74	9.62	9.62
C5	11.12	10.68	10.40	10.19	10.05	10.01
C6	8.75	8.72	8.51	8.46	8.14	8.24
C7	8.30	8.43	8.28	8.13	8.17	8.08
C8	6.58	6.81	6.78	6.67	6.68	6.59
C9	5.05	5.40	5.44	5.42	5.53	5.46
C10	4.11	4.50	4.47	4.51	4.61	4.56
C11	3.22	3.63	3.65	3.79	3.70	3.68
C12	2.53	2.82	3.01	3.22	3.07	3.11
C13	1.80	2.22	2.13	2.32	2.29	2.16
C14	1.42	1.65	1.73	1.77	1.82	1.93
C15	1.10	1.22	1.33	1.25	1.42	1.33
alpha chain growth probability	0.71	0.72	0.73	0.72	0.73	0.73

C1 - C50 estimated total product distribution, weight %

C1	20.1	19.7	20.4	20.6	20.6	21.3
C2 - C4	24.4	22.9	22.2	22.5	22.0	21.9
C5 - C12	48.0	48.9	48.2	48.1	47.5	47.4
C13 - C50	7.5	8.4	9.3	8.8	9.9	9.3

CO conversion, %	9.7	8.5	8.2	7.8	6.8	6.4
rate, g CH ₂ /g cat/hr	0.40	0.35	0.34	0.32	0.28	0.26
CO ₂ formation, %	0.4	0.2	0.3	0.4	0.5	0.3

Performance of Co.047

Dates: 04/07/94 - 04/08/94 Run #1

flow rate = 90.0 cc/min, loading = 0.3 g, WHSV = 9.4 1/hr, H₂/CO ratio in feed = 2

time on stream, hr	24.0	26.0	28.0	30.0	32.0
reaction temperature, °C	220	210	240	230	220
pressure, atm	1	1	1	1	1
flow, cc/min	90.0	90.0	90.0	90.0	90.0

C1 - C15 product distribution, weight %

C1	21.45	16.91	37.49	28.17	20.30
C2	3.77	2.98	6.53	5.40	4.08
C3	8.97	7.00	13.47	3.10	8.69
C4	9.34	7.94	10.99	11.11	9.27
C5	9.93	9.05	9.17	11.35	9.97
C6	8.38	8.23	6.55	8.74	8.54
C7	8.20	8.35	5.33	8.04	8.18
C8	6.76	7.50	3.72	6.27	6.81
C9	5.62	6.73	2.38	4.68	5.68
C10	4.68	5.96	1.70	3.95	4.74
C11	3.82	5.13	1.07	3.13	3.89
C12	3.25	4.43	0.89	2.48	3.51
C13	2.30	3.80	0.27	1.55	2.54
C14	2.16	3.20	0.27	1.17	2.12
C15	1.39	2.80	0.16	0.86	1.71
alpha chain growth probability	0.73	0.80	0.59	0.71	0.75

C1 - C50 estimated total product distribution, weight %

C1	20.7	14.8	37.5	27.8	19.1
C2 - C4	21.3	15.6	31.0	19.4	20.7
C5 - C12	48.2	48.3	30.4	46.8	48.0
C13 - C50	9.8	21.3	1.1	6.0	12.2

CO conversion, %	6.6	3.6	17.4	8.6	5.2
rate, g CH ₂ /g cat/hr	0.27	0.15	0.72	0.36	0.21
CO ₂ formation, %	0.6	0.2	0.8	0.4	0.3

Co.047 Arrhenius Plot - Run #1

Schulz-Flory Plot for Co.047 - Run #1
Time on Stream (hrs)

Schulz-Flory Plot for Co.047 - Run #1
Temperature

Time-on-Stream Plot for Co.047 - Run #1

Co.048 - Run #1

Co wt%	NM wt %	Promotor wt%		Support
20	Ru 0.50	K 0.30	Zr 8.50	SiO ₂

SUMMARY REACTION DATA

Reaction Conditions:

P = 1.0 atm

T = 220 °C

H₂/CO = 2

weight of catalyst = 0.245 g

WHSV = 10.48 1/hr

time on stream = 26.0 hrs

CO₂ (g/g cat/hr) = 0.027CO₂ (% of CO) = 0.2

O/P = 17.18

E_a = 28.0 kcal/mol

CO conversion (%)	3.5
rate (g CH ₂ /g cat/hr)	0.16
alpha	0.77
C1 (wt%)	16.3
C2 - C4 (wt%)	18.6
C5 - C12 (wt%)	49.1
C13 + (wt%)	16.0

Performance of Co.048

Dates: 04/14/94 - 04/15/94 Run #1

flow rate = 90.0 cc/min, loading = 0.2 g, WHSV = 10.5 1/hr, H₂/CO ratio in feed = 2

time on stream, hr	1.0	3.0	5.0	8.0	22.0	24.0
reaction temperature, °C	220	220	220	220	220	220
pressure, atm	1.0	1.0	1.0	1.0	1	1
flow, cc/min	90.0	90.0	90.0	90.0	90.0	90.0

C1 - C15 product distribution, weight %

C1	17.11	17.31	16.70	18.11	18.56	18.28
C2	4.06	4.12	3.62	3.91	4.33	4.22
C3	8.27	8.25	7.79	8.36	8.47	8.37
C4	8.97	8.85	8.25	8.90	8.94	8.30
C5	9.51	9.30	9.76	9.34	9.41	9.31
C6	8.26	7.82	7.73	8.08	8.26	8.74
C7	8.38	8.17	8.59	8.16	8.20	8.12
C8	7.33	7.21	7.50	7.12	7.12	7.06
C9	6.30	6.29	6.57	6.15	6.09	6.14
C10	5.44	5.51	5.67	5.32	5.23	5.35
C11	4.62	4.67	4.81	4.53	4.39	4.51
C12	3.85	4.00	4.15	3.93	3.62	3.71
C13	3.15	3.31	3.32	3.17	3.03	3.04
C14	2.56	2.86	2.98	2.62	2.44	2.66
C15	2.19	2.32	2.55	2.30	1.91	2.20
alpha chain growth probability	0.77	0.78	0.78	0.77	0.76	0.77

C1 - C50 estimated total product distribution, weight %

C1	15.8	15.6	14.9	16.6	17.2	16.6
C2 - C4	19.6	19.1	17.6	19.4	20.1	19.0
C5 - C12	49.1	47.8	49.1	48.1	48.2	48.3
C13 - C50	15.5	17.6	18.5	15.9	14.5	16.1

CO conversion, %	5.0	4.7	4.7	4.3	3.4	3.4
rate, g CH ₂ /g cat/hr	0.23	0.21	0.22	0.20	0.16	0.16
CO ₂ formation, %	0.4	0.3	0.2	0.2	0.2	0.3

Performance of Co.048

Dates: 04/14/94 - 04/15/94 Run #1

flow rate = 90.0 cc/min, loading = 0.2 g, WHSV = 10.5 l/hr, H₂/CO ratio in feed = 2

time on stream, hr	26.0	29.0	31.0	33.0	35.0
reaction temperature, °C	220	210	240	230	220
pressure, atm	1	1	1	1	1
flow, cc/min	90.0	90.0	90.0	90.0	90.0

C1 - C15 product distribution, weight %

C1	17.83	15.09	27.91	22.20	18.46
C2	4.14	3.29	6.51	5.41	4.49
C3	8.12	6.59	11.93	9.87	8.27
C4	8.04	6.82	10.55	9.70	8.70
C5	9.58	9.35	9.72	9.58	9.32
C6	8.47	7.92	7.62	8.01	8.50
C7	8.30	8.47	7.24	7.97	8.01
C8	7.24	7.81	5.10	6.22	6.85
C9	6.33	7.10	3.82	5.13	6.04
C10	5.46	6.28	2.96	4.27	5.18
C11	4.60	5.51	2.16	3.41	4.48
C12	3.90	4.94	1.75	2.77	3.74
C13	3.13	4.19	1.15	2.11	3.13
C14	2.63	3.58	0.98	1.81	2.59
C15	2.25	3.05	0.60	1.52	2.23
alpha chain growth probability	0.77	0.80	0.68	0.74	0.78

C1 - C50 estimated total product distribution, weight %

C1	16.3	13.0	27.2	21.1	16.8
C2 - C4	18.6	14.3	28.3	23.7	19.6
C5 - C12	49.1	49.0	39.7	45.2	47.3
C13 - C50	16.0	23.7	4.8	10.0	16.3

CO conversion, %	3.5	2.2	10.0	6.2	3.0
rate, g CH ₂ /g cat/hr	0.16	0.10	0.46	0.29	0.14
CO ₂ formation, %	0.2	0.2	0.5	0.2	0.2

Co.048 Arrhenius Plot - Run #1

Schulz-Flory Plot for Co.048 - Run #1
Time on Stream (hrs)

Performance of Co.049

Dates: 04/24/94 - 04/25/94 Run #1

flow rate = 90.0 cc/min, loading = 0.2 g, WHSV = 11.8 l/hr, H₂/CO ratio in feed = 2

time on stream, hr	0.5	2.5	5.0	8.5	22.0	24.0
reaction temperature, °C	220	220	220	220	220	220
pressure, atm	1.0	1.0	1.0	1.0	1.0	1.0
flow, cc/min	90.0	90.0	90.0	90.0	90.0	90.0

C1 - C15 product distribution, weight %

C1	24.62	24.15	23.41	24.73	23.74	24.33
C2	4.77	4.69	4.58	4.74	4.53	4.21
C3	12.39	12.01	11.43	11.61	10.60	10.55
C4	12.66	12.97	11.91	11.99	10.93	10.87
C5	11.54	11.44	11.49	11.60	10.89	10.77
C6	8.52	8.78	9.17	9.37	8.90	8.66
C7	7.59	7.46	7.75	7.09	7.89	7.91
C8	5.46	5.45	5.78	5.37	6.11	6.12
C9	3.81	3.92	4.26	3.92	4.62	4.66
C10	2.98	3.04	3.29	2.96	3.68	3.70
C11	2.06	2.30	2.45	2.38	2.84	3.04
C12	1.40	1.46	1.79	1.67	1.98	2.06
C13	0.93	1.05	1.20	1.14	1.41	1.34
C14	0.74	0.76	0.85	0.79	1.15	1.04
C15	0.55	0.52	0.64	0.63	0.72	0.74
alpha chain growth probability	0.66	0.65	0.67	0.67	0.68	0.68

C1 - C50 estimated total product distribution, weight %

C1	24.2	23.9	23.1	24.3	23.5	24.0
C2 - C4	29.3	29.4	27.5	27.9	25.8	25.3
C5 - C12	42.9	43.2	45.1	43.6	45.9	45.6
C13 - C50	3.6	3.5	4.2	4.2	4.9	5.0

CO conversion, %	10.5	10.3	9.4	8.8	7.3	7.3
rate, g CH ₂ /g cat/hr	0.54	0.53	0.48	0.45	0.38	0.38
CO ₂ formation, %	0.3	0.4	0.4	0.4	0.3	0.4

Performance of Co.049

Dates: 04/24/94 - 04/25/94 Run #1

flow rate = 90.0 cc/min, loading = 0.2 g, WHSV = 11.8 1/hr, H₂/CO ratio in feed = 2

time on stream, hr	26.0
reaction temperature, °C	220
pressure, atm	1.0
flow, cc/min	90.0

C1 - C15 product distribution, weight %

C1	23.64
C2	4.60
C3	10.57
C4	10.83
C5	10.76
C6	8.85
C7	7.87
C8	6.10
C9	4.72
C10	3.64
C11	2.84
C12	2.24
C13	1.51
C14	1.06
C15	0.76
alpha chain growth probability	0.69

C1 - C50 estimated total product distribution, weight %

C1	23.4
C2 - C4	25.7
C5 - C12	45.8
C13 - C50	5.1

CO conversion, %	7.1
rate, g CH ₂ /g cat/hr	0.37
CO ₂ formation, %	0.2

Schulz-Flory Plot for Co.049 - Run #1
Time on Stream (hrs)

Time-on-Stream Plot for Co.049 - Run #1

Co.049 - Run #2

Co wt%	NM wt %	Promotor wt%		Support
20	Ru 0.50	K 0.10		Al ₂ O ₃

SUMMARY REACTION DATA

Reaction Conditions:

P = 1.0 atm

T = 220 °C

H₂/CO = 2

weight of catalyst = 0.175 g

WHSV = 14.69 1/hr

time on stream = 24.0 hrs

CO₂ (g/g cat/hr) = 0.056CO₂ (% of CO) = 0.3

O/P = 5.93

E_a = 36.0 kcal/mol

CO conversion (%)	6.0
rate (g CH ₂ /g cat/hr)	0.39
alpha	0.68
C1 (wt%)	23.3
C2 - C4 (wt%)	25.8
C5 - C12 (wt%)	46.2
C13 + (wt%)	4.6

Performance of Co.049

Dates: 04/28/94 - 04/29/94 Run #2

flow rate = 90.0 cc/min, loading = 0.2 g, WHSV = 14.7 l/hr, H₂/CO ratio in feed = 2

time on stream, hr	0.5	2.5	5.0	8.0	21.0	24.0
reaction temperature, °C	220	220	220	220	220	220
pressure, atm	1.0	1.0	1.0	1.0	1.0	1.0
flow, cc/min	90.0	90.0	90.0	90.0	90.0	90.0

C1 - C15 product distribution, weight %

C1	23.70	24.24	23.33	24.92	21.93	23.46
C2	4.24	4.22	4.53	4.32	4.31	4.57
C3	12.32	11.98	11.40	11.57	9.98	10.44
C4	12.84	12.47	11.99	11.91	10.46	10.90
C5	11.80	11.65	11.49	11.27	11.57	11.06
C6	8.88	8.85	9.10	8.71	9.44	9.59
C7	7.51	7.59	7.74	7.55	8.29	7.74
C8	5.48	5.60	5.86	5.71	6.48	5.99
C9	3.92	4.03	4.26	4.19	4.89	4.50
C10	2.96	3.10	3.32	3.23	3.90	3.58
C11	2.22	2.16	2.45	2.30	2.95	2.69
C12	1.61	1.65	1.82	1.67	2.29	2.25
C13	1.13	1.14	1.24	1.13	1.56	1.47
C14	0.81	0.76	0.86	0.93	1.11	1.06
C15	0.58	0.55	0.61	0.59	0.85	0.68
alpha chain growth probability	0.66	0.66	0.67	0.66	0.69	0.68

C1 - C50 estimated total product distribution, weight %

C1	23.4	24.0	23.1	24.6	21.5	23.3
C2 - C4	29.0	28.3	27.6	27.5	24.3	25.8
C5 - C12	43.8	44.0	45.2	44.0	48.4	46.2
C13 - C50	3.8	3.7	4.0	4.0	5.8	4.6

CO conversion, %	7.6	7.3	6.7	6.2	6.1	6.0
rate, g CH ₂ /g cat/hr	0.49	0.47	0.43	0.40	0.39	0.39
CO ₂ formation, %	0.3	0.2	0.3	0.3	0.3	0.3

Performance of Co.049

Dates: 04/28/94 - 04/29/94 Run #2

flow rate = 90.0 cc/min, loading = 0.2 g, WHSV = 14.7 1/hr, H₂/CO ratio in feed = 2

time on stream, hr	26.0	28.0	30.0	32.0
reaction temperature, °C	220	220	220	210
pressure, atm	1.0	1.0	1.0	1.0
flow, cc/min	90.0	6.0	6.0	6.0

C1 - C15 product distribution, weight %

C1	24.21	31.93	29.76	18.81
C2	4.16	5.56	4.49	3.09
C3	10.51	9.95	10.74	7.42
C4	10.88	11.67	10.30	9.31
C5	10.93	10.47	10.89	10.17
C6	9.13	7.33	6.99	9.15
C7	7.13	7.11	7.74	8.66
C8	6.75	4.87	5.44	7.32
C9	4.56	3.34	4.02	6.23
C10	3.62	2.54	3.02	5.14
C11	2.79	1.87	2.40	4.26
C12	2.13	1.36	1.59	3.46
C13	1.39	0.86	1.19	2.82
C14	1.09	0.67	0.81	2.29
C15	0.72	0.47	0.63	1.87
alpha chain growth probability	0.69	0.65	0.67	0.76

C1 - C50 estimated total product distribution, weight %

C1	24.0	31.6	29.3	17.5
C2 - C4	25.3	26.9	25.1	18.4
C5 - C12	45.8	38.5	41.4	50.5
C13 - C50	4.9	3.1	4.2	13.5

CO conversion, %	5.9	107.0	102.1	50.5
rate, g CH ₂ /g cat/hr	0.38	0.46	0.44	0.22
CO ₂ formation, %	0.3	11.5	10.1	6.3

Schulz-Flory Plot for Co.049 - Run #2
Time on Stream (hrs)

Schulz-Flory Plot for Co.049 - Run #2
High Conversion Study at Different Temperature

Time-on-Stream Plot for Co.049 - Run #2

Co.049 - Run #3

Co wt%	NM wt %	Promotor wt%		Support
20	Ru 0.50	K 0.10		Al ₂ O ₃

SUMMARY REACTION DATA

Reaction Conditions:

P = 1.0 atm

T = 220 °C

H₂/CO = 2

weight of catalyst = 0.184 g

WHSV = 13.96 1/hr

time on stream = 28.0 hrs

CO₂ (g/g cat/hr) = 0.059CO₂ (% of CO) = 0.3

O/P = 4.73

E_a = 30.9 kcal/mol

CO conversion (%)	6.7
rate (g CH ₂ /g cat/hr)	0.41
alpha	0.69
C1 (wt%)	25.2
C2 - C4 (wt%)	26.6
C5 - C12 (wt%)	44.0
C13 + (wt%)	4.2

Performance of Co.049

Dates: 05/02/94 - 05/03/94 Run #3

flow rate = 90.0 cc/min, loading = 0.2 g, WHSV = 14.0 1/hr, H₂/CO ratio in feed = 2

time on stream, hr	0.5	2.5	5.5	8.5	23.0	25.0
reaction temperature, °C	220	220	220	220	220	220
pressure, atm	1.0	1.0	1.0	1.0	1.0	1.0
flow, cc/min	90.0	90.0	90.0	90.0	90.0	90.0

C1 - C15 product distribution, weight %

C1	26.40	26.19	25.72	26.40	24.74	24.57
C2	5.06	5.12	4.94	4.91	4.65	4.36
C3	12.93	12.73	12.27	12.04	11.00	10.90
C4	12.96	12.76	12.38	12.21	11.37	11.30
C5	11.57	11.41	11.29	11.26	11.07	11.06
C6	8.81	8.57	8.52	8.34	8.95	8.85
C7	7.05	7.15	7.35	7.25	7.74	7.80
C8	4.84	5.03	5.28	5.28	5.85	5.92
C9	3.34	3.47	3.86	3.82	4.36	4.37
C10	2.42	2.59	2.75	2.80	3.33	3.45
C11	1.72	1.89	2.08	2.04	2.43	2.53
C12	1.12	1.29	1.42	1.50	1.86	1.95
C13	0.84	0.78	0.93	0.98	1.14	1.29
C14	0.52	0.63	0.71	0.71	0.89	1.02
C15	0.40	0.39	0.49	0.46	0.61	0.63
alpha chain growth probability	0.64	0.64	0.65	0.65	0.67	0.67

C1 - C50 estimated total product distribution, weight %

C1	26.1	26.0	25.5	26.2	24.5	24.4
C2 - C4	30.6	30.4	29.3	28.9	26.7	26.3
C5 - C12	40.6	40.9	42.0	41.8	44.7	45.0
C13 - C50	2.6	2.6	3.2	3.1	4.1	4.2

CO conversion, %	10.8	9.4	8.6	8.7	6.8	6.9
rate, g CH ₂ /g cat/hr	0.66	0.57	0.53	0.53	0.42	0.42
CO ₂ formation, %	0.4	0.3	0.3	0.3	0.3	0.3

Performance of Co.049

Dates: 05/02/94 - 05/03/94 Run #3

flow rate = 90.0 cc/min, loading = 0.2 g, WHSV = 14.0 1/hr, H₂/CO ratio in feed = 2

time on stream, hr	28.0	30.0	32.0	34.0
reaction temperature, °C	220	220	220	210
pressure, atm	1.0	1.0	1.0	1.0
flow, cc/min	90.0	15.0	15.0	15.0

C1 - C15 product distribution, weight %

C1	25.32	25.68	26.75	18.23
C2	4.40	4.63	4.29	3.07
C3	11.06	10.00	9.90	7.83
C4	11.19	11.60	11.33	9.26
C5	10.92	11.01	10.84	10.35
C6	8.66	8.60	8.66	9.69
C7	7.68	7.86	7.81	8.77
C8	5.80	5.93	5.74	7.28
C9	4.26	4.45	4.31	6.03
C10	3.38	3.15	3.32	5.12
C11	2.45	2.41	2.47	4.25
C12	1.93	1.79	1.70	3.40
C13	1.36	1.24	1.29	2.78
C14	0.98	0.99	0.98	2.27
C15	0.61	0.66	0.62	1.69
alpha chain growth probability	0.69	0.68	0.67	0.75

C1 - C50 estimated total product distribution, weight %

C1	25.2	25.3	26.5	17.3
C2 - C4	26.6	25.8	25.3	19.1
C5 - C12	44.0	44.4	44.1	51.5
C13 - C50	4.2	4.4	4.2	12.1

CO conversion, %	6.7	44.6	44.9	24.5
rate, g CH ₂ /g cat/hr	0.41	0.45	0.46	0.25
CO ₂ formation, %	0.3	3.8	3.6	2.2

Schulz-Flory Plot for Co.048 - Run #1
Temperature

Time-on-Stream Plot for Co.048 - Run #1

Co.049 - Run #1

Co wt%	NM wt %	Promotor wt%		Support
20	Ru 0.50	K 0.10		Al ₂ O ₃

SUMMARY REACTION DATA**Reaction Conditions:**

P = 1.0 atm

T = 220 °C

H₂/CO = 2

weight of catalyst = 0.218 g

WHSV = 11.82 1/hr

time on stream = 26.0 hrs

CO₂ (g/g cat/hr) = 0.043CO₂ (% of CO) = 0.2

O/P = 5.63

CO conversion (%)	7.1
rate (g CH ₂ /g cat/hr)	0.37
alpha	0.69
C1 (wt%)	23.4
C2 - C4 (wt%)	25.7
C5 - C12 (wt%)	45.8
C13 + (wt%)	5.1

Schulz-Flory Plot for Co.049 - Run #3
Time on Stream (hrs)

Schulz-Flory Plot for Co.049 - Run #3
High Conversion Study at Different Temperature

Time-on-Stream Plot for Co.049 - Run #3

Co.049 - Run #3

Co wt%	NM wt %	Promotor wt%		Support
20	Ru 0.50	K 0.10		Al ₂ O ₃

SUMMARY REACTION DATA*

Reaction Conditions:

P = 1.0 atm

T = 220 °C

H₂/CO = 2

weight of catalyst = 0.184 g

WHSV = 2.33 1/hr

time on stream = 30.0 hrs

CO₂ (g/g cat/hr) = 0.131CO₂ (% of CO) = 3.8

O/P = 0.67

E_a = 30.9 kcal/mol

CO conversion (%)	44.6
rate (g CH ₂ /g cat/hr)	0.45
alpha	0.68
C1 (wt%)	25.3
C2 - C4 (wt%)	25.8
C5 - C12 (wt%)	44.4
C13 + (wt%)	4.4

* high conversion study

Co.053 - Run #1

Co wt%	NM wt %	Promotor wt%		Support
20	Ru 0.50			Al ₂ O ₃

SUMMARY REACTION DATA

Reaction Conditions:

P = 1.0 atm
 T = 220 °C
 H₂/CO = 2
 weight of catalyst = 0.192 g
 WHSV = 13.37 1/hr
 time on stream = 24.5 hrs

CO₂ (g/g cat/hr) = 0.049
 CO₂ (% of CO) = 0.2
 O/P = 3.07

CO conversion (%)	7.0
rate (g CH ₂ /g cat/hr)	0.41
alpha	0.62
C1 (wt%)	27.3
C2 - C4 (wt%)	31.3
C5 - C12 (wt%)	39.4
C13 + (wt%)	2.1

Co.053 - Run #1

Co wt%	NM wt %	Promotor wt%		Support
20	Ru 0.50			Al ₂ O ₃

SUMMARY REACTION DATA*

Reaction Conditions:

P = 1.0 atm

T = 220 °C

H₂/CO = 2

weight of catalyst = 0.192 g

WHSV = 3.34 1/hr

time on stream = 31.0 hrs

CO₂ (g/g cat/hr) = 0.081CO₂ (% of CO) = 1.6

O/P = 0.79

CO conversion (%)	28.5
rate (g CH ₂ /g cat/hr)	0.42
alpha	0.64
C1 (wt%)	26.8
C2 - C4 (wt%)	28.4
C5 - C12 (wt%)	41.9
C13 + (wt%)	2.9

* high conversion study

Performance of Co.053

Dates: 05/16/94 - 05/17/94 Run #1

flow rate = 90.0 cc/min, loading = 0.2 g, WHSV = 13.4 1/hr, H₂/CO ratio in feed = 2

time on stream, hr	0.5	2.5	5.0	8.0	24.5	26.5
reaction temperature, °C	220	220	220	220	220	220
pressure, atm	1.0	1.0	1.0	1.0	1.0	1.0
flow, cc/min	90.0	90.0	90.0	90.0	90.0	90.0

C1 - C15 product distribution, weight %

C1	25.80	26.60	25.34	26.77	27.52	28.43
C2	5.02	5.11	4.89	5.16	5.27	5.03
C3	13.60	13.61	12.92	13.44	13.31	12.93
C4	13.54	13.42	12.81	13.26	13.00	12.71
C5	11.94	11.79	11.37	11.71	11.54	11.33
C6	8.94	8.61	8.49	8.89	8.47	8.35
C7	6.91	6.96	7.99	6.92	6.86	6.67
C8	4.76	4.74	5.47	4.65	4.74	4.76
C9	3.16	3.10	3.63	3.12	3.22	3.17
C10	2.23	2.23	2.62	2.20	2.30	2.32
C11	1.51	1.47	1.74	1.49	1.51	1.73
C12	1.11	1.04	1.07	1.05	0.99	1.25
C13	0.67	0.64	0.83	0.61	0.58	0.59
C14	0.48	0.41	0.48	0.43	0.37	0.45
C15	0.34	0.26	0.35	0.29	0.32	0.27
alpha chain growth probability	0.63	0.61	0.63	0.62	0.62	0.61

C1 - C50 estimated total product distribution, weight %

C1	25.6	26.5	25.2	26.6	27.3	28.5
C2 - C4	31.9	32.1	30.4	31.7	31.3	30.7
C5 - C12	40.3	39.7	42.1	39.8	39.4	39.0
C13 - C50	2.2	1.8	2.3	1.9	2.1	1.8

CO conversion, %	8.7	8.0	7.8	7.7	7.0	6.8
rate, g CH ₂ /g cat/hr	0.51	0.47	0.46	0.45	0.41	0.40
CO ₂ formation, %	0.3	0.3	0.2	0.2	0.2	0.2

Performance of Co.053

Dates: 05/16/94 - 05/17/94 Run #1

flow rate = 90.0 cc/min, loading = 0.2 g, WHSV = 13.4 1/hr, H₂/CO ratio in feed = 2

time on stream, hr	29.0	31.0	33.0	35.0
reaction temperature, °C	220	220	210	220
pressure, atm	1.0	1.0	1.0	1.0
flow, cc/min	90.0	22.5	22.5	22.5

C1 - C15 product distribution, weight %

C1	28.10	27.11	19.99	28.61
C2	5.18	4.77	3.52	5.07
C3	13.18	11.38	9.66	11.64
C4	12.92	12.66	11.21	12.70
C5	11.49	11.60	11.53	11.28
C6	8.45	8.94	9.86	8.19
C7	6.73	7.43	8.49	7.18
C8	4.70	5.16	6.63	4.95
C9	3.20	3.58	5.13	3.45
C10	2.31	2.52	4.03	2.33
C11	1.50	1.68	3.06	1.74
C12	1.04	1.32	2.45	1.13
C13	0.57	0.79	2.07	0.81
C14	0.41	0.62	1.36	0.57
C15	0.23	0.44	1.01	0.36
alpha chain growth probability	0.60	0.64	0.70	0.63

C1 - C50 estimated total product distribution, weight %

C1	28.1	26.8	19.5	28.5
C2 - C4	31.3	28.4	23.8	29.3
C5 - C12	39.0	41.9	49.8	39.9
C13 - C50	1.6	2.9	6.8	2.4

CO conversion, %	6.8	28.5	16.6	26.3
rate, g CH ₂ /g cat/hr	0.40	0.42	0.24	0.38
CO ₂ formation, %	0.2	1.6	1.0	1.4

Schulz-Flory Plot for Co.053 - Run #1
Time on Stream (hrs)

Schulz-Flory Plot for Co.053 - Run #1
High Conversion Study at Different Temperature

Time-on-Stream Plot for Co.053 - Run #1

Co.053 - Run #2

Co wt%	NM wt %	Promotor wt%		Support
20	Ru 0.50			Al ₂ O ₃

SUMMARY REACTION DATA

Reaction Conditions:

P = 1.0 atm

T = 220 °C

H₂/CO = 2

weight of catalyst = 0.171 g

WHSV = 15.03 1/hr

time on stream = 25.5 hrs

CO₂ (g/g cat/hr) = 0.052CO₂ (% of CO) = 0.2

O/P = 2.35

CO conversion (%)	6.6
rate (g CH ₂ /g cat/hr)	0.43
alpha	0.63
C1 (wt%)	23.4
C2 - C4 (wt%)	27.4
C5 - C12 (wt%)	46.6
C13 + (wt%)	2.6

Performance of Co.053

Dates: 05/23/94 - 05/24/94 Run #2

flow rate = 90.0 cc/min, loading = 0.2 g, WHSV = 15.0 l/hr, H₂/CO ratio in feed = 2

time on stream, hr	0.5	3.0	5.0	7.0	23.0	25.5
reaction temperature, °C	220	220	220	220	220	220
pressure, atm	1.0	1.0	1.0	1.0	1.0	1.0
flow, cc/min	90.0	90.0	90.0	90.0	90.0	90.0

C1 - C15 product distribution, weight %

C1	25.54	22.61	22.33	24.20	22.89	23.57
C2	4.95	4.55	4.41	5.50	4.40	4.51
C3	12.50	11.85	11.52	13.97	11.30	11.43
C4	12.76	12.55	12.16	14.24	11.66	11.64
C5	10.99	11.25	11.01	12.49	10.54	10.28
C6	7.76	8.63	8.03	8.88	7.54	7.28
C7	8.23	9.28	10.73	7.23	11.11	10.91
C8	5.74	6.46	7.10	4.82	7.43	7.33
C9	3.88	4.32	4.55	3.15	4.85	4.78
C10	2.77	3.13	3.21	2.05	3.25	3.27
C11	1.82	2.02	2.07	1.49	2.08	2.05
C12	1.21	1.49	1.22	0.85	1.34	1.23
C13	0.86	0.84	0.79	0.52	0.73	0.79
C14	0.56	0.59	0.51	0.35	0.52	0.54
C15	0.44	0.43	0.36	0.25	0.37	0.39
alpha chain growth probability	0.64	0.64	0.63	0.60	0.63	0.63

C1 - C50 estimated total product distribution, weight %

C1	25.2	22.4	22.3	24.1	22.8	23.4
C2 - C4	29.8	28.7	28.0	33.6	27.3	27.4
C5 - C12	42.1	46.0	47.4	40.7	47.5	46.6
C13 - C50	2.9	2.9	2.4	1.6	2.4	2.6

CO conversion, %	7.1	6.7	6.5	6.3	6.4	6.6
rate, g CH ₂ /g cat/hr	0.47	0.44	0.43	0.42	0.42	0.43
CO ₂ formation, %	0.2	0.2	0.2	0.2	0.2	0.2

Performance of Co.053

Dates: 05/23/94 - 05/24/94 Run #2

flow rate = 90.0 cc/min, loading = 0.2 g, WHSV = 15.0 l/hr, H₂/CO ratio in feed = 2

time on stream, hr	27.5
reaction temperature, °C	220
pressure, atm	1.0
flow, cc/min	90.0

C1 - C15 product distribution, weight %

C1	24.31
C2	4.64
C3	11.85
C4	12.09
C5	10.69
C6	7.71
C7	9.95
C8	6.73
C9	4.37
C10	2.97
C11	1.88
C12	1.25
C13	0.72
C14	0.48
C15	0.36
alpha chain growth probability	0.63

C1 - C50 estimated total product distribution, weight %

C1	24.2
C2 - C4	28.4
C5 - C12	45.0
C13 - C50	2.4

CO conversion, %	6.7
rate, g CH ₂ /g cat/hr	0.44
CO ₂ formation, %	0.2

Schulz-Flory Plot for Co.053 - Run #2
Time on Stream (hrs)

Time-on-Stream Plot for Co.053 - Run #2

Co.053 - Run #3

Co wt%	NM wt %	Promotor wt%		Support
20	Ru 0.50			Al ₂ O ₃

SUMMARY REACTION DATA

Reaction Conditions:

P = 1.0 atm
 T = 220 °C
 H₂/CO = 2
 weight of catalyst = 0.194 g
 WHSV = 13.25 1/hr
 time on stream = 24.5 hrs

CO₂ (g/g cat/hr) = 0.027
 CO₂ (% of CO) = 0.1
 O/P = 1.67

CO conversion (%)	7.8
rate (g CH ₂ /g cat/hr)	0.45
alpha	0.62
C1 (wt%)	27.6
C2 - C4 (wt%)	30.4
C5 - C12 (wt%)	40.1
C13 + (wt%)	1.9

Co.053 - Run #3

Co wt%	NM wt %	Promotor wt%		Support
20	Ru 0.50			Al ₂ O ₃

SUMMARY REACTION DATA*

Reaction Conditions:

P = 1.0 atm

T = 220 °C

H₂/CO = 2

weight of catalyst = 0.194 g

WHSV = 3.31 1/hr

time on stream = 27.5 hrs

CO₂ (g/g cat/hr) = 0.044CO₂ (% of CO) = 0.9

O/P = 0.52

CO conversion (%)	31.5
rate (g CH ₂ /g cat/hr)	0.46
alpha	0.65
C1 (wt%)	25.4
C2 - C4 (wt%)	28.1
C5 - C12 (wt%)	43.6
C13 + (wt%)	3.0

• high conversion study

Performance of Co.053

Dates: 06/27/94 - 06/28/94 Run #3

flow rate = 90.0 cc/min, loading = 0.2 g, WHSV = 13.3 1/hr, H₂/CO ratio in feed = 2

time on stream, hr	0.5	3.5	6.5	9.5	12.5	15.5
reaction temperature, °C	220	220	220	220	220	220
pressure, atm	1.0	1.0	1.0	1.0	1.0	1.0
flow, cc/min	90.0	90.0	90.0	90.0	90.0	90.0

C1 - C15 product distribution, weight %

C1	27.29	27.67	28.27	28.14	28.27	27.99
C2	4.93	4.91	4.96	4.92	4.92	4.86
C3	13.49	13.44	13.42	13.37	13.32	13.23
C4	13.34	13.22	13.17	13.14	13.06	12.96
C5	12.05	12.10	11.87	11.96	11.91	11.96
C6	8.98	9.09	8.87	9.04	8.97	9.09
C7	6.96	7.07	6.89	6.95	6.95	7.05
C8	4.60	4.57	4.56	4.63	4.64	4.71
C9	2.91	2.87	2.91	2.86	2.91	2.97
C10	1.96	1.86	1.92	1.96	1.97	2.02
C11	1.34	1.30	1.21	1.19	1.24	1.29
C12	0.77	0.77	0.84	0.78	0.80	0.82
C13	0.59	0.47	0.48	0.47	0.44	0.45
C14	0.43	0.37	0.35	0.32	0.33	0.33
C15	0.35	0.27	0.27	0.26	0.27	0.27
alpha chain growth probability	0.63	0.61	0.61	0.61	0.61	0.61

C1 - C50 estimated total product distribution, weight %

C1	26.8	27.4	28.0	27.9	28.0	27.7
C2 - C4	31.2	31.3	31.2	31.1	31.0	30.8
C5 - C12	39.6	39.5	39.0	39.3	39.3	39.7
C13 - C50	2.3	1.8	1.8	1.7	1.8	1.8

CO conversion, %	10.2	8.9	8.8	8.4	8.4	8.1
rate, g CH ₂ /g cat/hr	0.59	0.51	0.51	0.49	0.49	0.47
CO ₂ formation, %	0.2	0.2	0.2	0.2	0.2	0.2

Performance of Co.053

Dates: 06/27/94 - 06/28/94 Run #3

flow rate = 90.0 cc/min, loading = 0.2 g, WHSV = 13.3 1/hr, H₂/CO ratio in feed = 2

time on stream, hr	18.5	21.5	24.5	27.5	30.5
reaction temperature, °C	220	220	220	220	210
pressure, atm	1.0	1.0	1.0	1.0	1.0
flow, cc/min	90.0	90.0	90.0	22.5	22.5

C1 - C15 product distribution, weight %

C1	28.04	27.90	27.82	25.66	20.13
C2	4.86	4.83	4.80	4.63	3.30
C3	13.21	13.12	13.03	11.21	9.45
C4	12.93	12.91	12.81	12.57	10.87
C5	11.89	11.87	11.80	12.01	11.57
C6	9.07	9.08	9.04	9.50	10.08
C7	7.02	7.08	7.11	7.79	8.73
C8	4.70	4.78	4.85	5.42	6.82
C9	3.03	3.05	3.13	3.63	5.19
C10	2.08	2.14	2.08	2.50	4.19
C11	1.30	1.32	1.44	2.06	3.22
C12	0.75	0.87	0.97	1.24	2.44
C13	0.52	0.46	0.50	0.77	1.76
C14	0.34	0.33	0.35	0.57	1.32
C15	0.26	0.27	0.29	0.45	0.92
alpha chain growth probability	0.61	0.61	0.62	0.65	0.70

C1 - C50 estimated total product distribution, weight %

C1	27.8	27.7	27.6	25.4	19.8
C2 - C4	30.7	30.6	30.4	28.1	23.2
C5 - C12	39.7	40.0	40.1	43.6	50.7
C13 - C50	1.7	1.8	1.9	3.0	6.3

CO conversion, %	8.0	7.9	7.8	31.5	17.5
rate, g CH ₂ /g cat/hr	0.47	0.46	0.45	0.46	0.25
CO ₂ formation, %	0.2	0.1	0.1	0.9	0.5

Schulz-Flory Plot for Co.053 - Run #3
Time on Stream (hrs)

Schulz-Flory Plot for Co.053 - Run #3
High Conversion Study at Different Temperature

Time-on-Stream Plot for Co.053 - Run #3

Co.054 - Run #1

Co wt%	NM wt %	Promotor wt%		Support
20		K 0.30	Zr 8.50	SiO ₂

SUMMARY REACTION DATA

Reaction Conditions:

P = 1.0 atm

T = 220 °C

H₂/CO = 2

weight of catalyst = 0.333 g

WHSV = 7.73 1/hr

time on stream = 24.5 hrs

CO₂ (g/g cat/hr) = 0.014CO₂ (% of CO) = 0.1

O/P = 16.35

CO conversion (%)	1.2
rate (g CH ₂ /g cat/hr)	0.04
alpha	0.79
C1 (wt%)	17.8
C2 - C4 (wt%)	19.0
C5 - C12 (wt%)	44.2
C13 + (wt%)	19.0

Performance of Co.054

Dates: 06/03/94 - 06/04/94 Run #1

flow rate = 90.0 cc/min, loading = 0.3 g, WHSV = 7.7 1/hr, H₂/CO ratio in feed = 2

time on stream, hr	0.5	3.5	6.5	9.5	12.5	15.5
reaction temperature, °C	220	220	220	220	220	220
pressure, atm	1.0	1.0	1.0	1.0	1.0	1.0
flow, cc/min	90.0	90.0	90.0	90.0	90.0	90.0

C1 - C15 product distribution, weight %

C1	16.65	17.85	18.66	19.40	19.41	18.78
C2	4.02	4.27	4.43	4.56	4.52	4.34
C3	8.03	8.16	8.32	8.56	8.43	8.17
C4	8.29	8.02	8.22	8.30	8.23	8.02
C5	9.09	8.97	8.93	8.83	8.95	9.23
C6	7.45	7.12	6.27	6.53	6.38	6.18
C7	8.28	7.96	7.90	7.58	7.69	8.02
C8	7.24	7.15	7.03	6.81	6.92	7.09
C9	6.51	6.35	6.23	6.12	6.19	6.31
C10	5.68	5.71	5.61	5.46	5.50	5.61
C11	4.96	4.86	4.82	4.69	4.57	4.93
C12	4.19	4.29	4.24	4.10	4.10	4.22
C13	3.84	3.60	3.64	3.51	3.58	3.56
C14	3.12	3.08	3.10	3.02	2.93	2.93
C15	2.64	2.60	2.60	2.54	2.61	2.64
alpha chain growth probability	0.79	0.79	0.80	0.79	0.80	0.80

C1 - C50 estimated total product distribution, weight %

C1	14.7	15.8	16.5	17.2	17.1	16.5
C2 - C4	18.0	18.1	18.6	19.0	18.6	18.0
C5 - C12	47.1	46.2	45.0	44.4	44.4	45.2
C13 - C50	20.2	20.0	20.0	19.4	19.9	20.2

CO conversion, %	1.8	1.5	1.4	1.3	1.3	1.3
rate, g CH ₂ /g cat/hr	0.06	0.05	0.05	0.04	0.04	0.04
CO ₂ formation, %	0.2	0.2	0.1	0.1	0.1	0.1

Performance of Co.054

Dates: 06/03/94 - 06/04/94 Run #1

flow rate = 90.0 cc/min, loading = 0.3 g, WHSV = 7.7 1/hr, H₂/CO ratio in feed = 2

time on stream, hr	18.5	21.5	24.5	27.5	30.5
reaction temperature, °C	220	220	220	220	220
pressure, atm	1.0	1.0	1.0	1.0	1.0
flow, cc/min	90.0	90.0	90.0	22.5	22.5

C1 - C15 product distribution, weight %

C1	19.43	19.92	20.08	20.33	20.82
C2	4.48	4.58	4.61	4.25	4.29
C3	8.30	8.42	8.45	8.31	8.42
C4	8.55	8.31	8.44	8.36	8.44
C5	8.90	8.87	8.82	8.93	9.00
C6	6.40	6.51	6.47	7.97	8.04
C7	7.62	7.57	7.64	7.40	7.42
C8	7.03	6.85	6.78	6.54	6.46
C9	6.16	6.09	6.04	5.92	5.69
C10	5.53	5.45	5.38	5.18	5.10
C11	4.69	4.60	4.49	4.48	4.40
C12	4.17	4.00	4.09	3.92	3.69
C13	3.47	3.45	3.38	3.24	3.16
C14	2.90	2.91	2.82	2.79	2.77
C15	2.36	2.47	2.50	2.38	2.31
alpha chain growth probability	0.79	0.79	0.79	0.79	0.78

C1 - C50 estimated total product distribution, weight %

C1	17.5	17.7	17.8	18.2	18.7
C2 - C4	19.3	19.0	19.0	18.7	19.0
C5 - C12	45.1	44.5	44.2	45.1	45.0
C13 - C50	18.1	18.8	19.0	17.9	17.3

CO conversion, %	1.2	1.2	1.2	5.2	5.3
rate, g CH ₂ /g cat/hr	0.04	0.04	0.04	0.04	0.05
CO ₂ formation, %	0.1	0.1	0.1	0.6	0.6

Schulz-Flory Plot for Co.054 - Run #1

Time on Stream (hrs)

Time-on-Stream Plot for Co.054 - Run #1

CAL.01 - Run #3 (re-reduced)

Co wt%	NM wt %	Promotor wt%		Support
20	Ru 0.50			Al ₂ O ₃

SUMMARY REACTION DATA

Reaction Conditions:

P = 1.0 atm

T = 220 °C

H₂/CO = 2

weight of catalyst = 0.170 g

WHSV = 15.09 1/hr

time on stream = 25.5 hrs

CO₂ (g/g cat/hr) = 0.052CO₂ (% of CO) = 0.2

O/P = 4.97

CO conversion (%)	2.5
rate (g CH ₂ /g cat/hr)	0.16
alpha	0.63
C1 (wt%)	25.6
C2 - C4 (wt%)	31.7
C5 - C12 (wt%)	40.5
C13 + (wt%)	2.2

Performance of CAL.01

Dates: 03/31/94 - 04/01/94 Run #3 (re-reduced)

flow rate = 90.0 cc/min, loading = 0.2 g, WHSV = 15.1 l/hr, H₂/CO ratio in feed = 2

time on stream, hr	0.5	6.5	21.5	25.5
reaction temperature, °C	220	220	220	220
pressure, atm	1.0	1.0	1.0	1.0
flow, cc/min	90.0	90.0	90.0	90.0

C1 - C15 product distribution, weight %

C1	23.88	25.35	25.81	25.78
C2	5.11	5.35	5.41	5.40
C3	12.59	12.61	12.42	12.44
C4	13.56	13.32	14.00	14.04
C5	12.41	12.13	12.02	11.97
C6	8.79	8.72	8.29	8.30
C7	7.32	7.10	7.26	7.21
C8	5.07	4.94	4.93	4.91
C9	3.49	3.36	3.37	3.35
C10	2.58	2.44	2.34	2.42
C11	1.79	1.63	1.55	1.52
C12	1.28	1.15	1.08	1.06
C13	0.89	0.76	0.70	0.72
C14	0.70	0.57	0.49	0.51
C15	0.54	0.56	0.31	0.35
alpha chain growth probability	0.64	0.63	0.62	0.63

C1 - C50 estimated total product distribution, weight %

C1	23.7	25.3	25.7	25.6
C2 - C4	31.0	31.2	31.7	31.7
C5 - C12	42.5	41.3	40.6	40.5
C13 - C50	2.8	2.3	2.1	2.2

CO conversion, %	2.5	2.8	2.5	2.5
rate, g CH ₂ /g cat/hr	0.17	0.19	0.16	0.16
CO ₂ formation, %	0.2	0.2	0.2	0.2

Schulz-Flory Plot for CAL.01 - Run #3 (re-reduced)
Time on Stream (hrs)

Time-on-Stream Plot for CAL.01 - Run #4

CAL.01 - Run #4 (re-calcine)

Co wt%	NM wt %	Promotor wt%		Support
20	Ru 0.50			Al ₂ O ₃

SUMMARY REACTION DATA

Reaction Conditions:

P = 1.0 atm

T = 220 °C

H₂/CO = 2

weight of catalyst = 0.170 g

WHSV = 15.09 1/hr

time on stream = 25.0 hrs

CO₂ (g/g cat/hr) = 0.098CO₂ (% of CO) = 0.4

O/P = 1.21

CO conversion (%)	7.3
rate (g CH ₂ /g cat/hr)	0.48
alpha	0.57
C1 (wt%)	35.8
C2 - C4 (wt%)	33.3
C5 - C12 (wt%)	30.1
C13 + (wt%)	0.9

Performance of CAL.01

Dates: 04/04/94 - 04/05/94 Run #4 (re-calcine)

flow rate = 90.0 cc/min, loading = 0.2 g, WHSV = 15.1 l/hr, H₂/CO ratio in feed = 2

time on stream, hr	0.5	2.5	5.0	8.0	23.0	25.0
reaction temperature, °C	220	220	220	220	220	220
pressure, atm	1.0	1.0	1.0	1.0	1	1
flow, cc/min	90.0	90.0	90.0	90.0	90.0	90.0

C1 - C15 product distribution, weight %

C1	34.89	37.36	34.50	35.31	35.20	35.95
C2	6.46	6.73	6.29	6.41	5.77	5.75
C3	13.83	13.98	14.02	14.07	14.02	14.25
C4	13.77	13.54	13.75	13.54	13.32	13.48
C5	11.20	10.60	11.36	10.78	10.59	10.75
C6	7.56	6.76	6.26	6.96	8.49	6.71
C7	4.68	4.24	5.21	4.90	4.87	5.02
C8	2.89	2.66	3.27	3.07	3.09	3.17
C9	1.83	1.63	2.06	1.90	1.84	1.92
C10	1.07	0.95	1.28	1.21	1.20	1.26
C11	0.74	0.64	0.85	0.74	0.67	0.69
C12	0.46	0.39	0.49	0.52	0.38	0.47
C13	0.27	0.22	0.30	0.26	0.24	0.26
C14	0.20	0.16	0.20	0.18	0.17	0.18
C15	0.14	0.12	0.14	0.13	0.15	0.13
alpha chain growth probability	0.59	0.58	0.58	0.58	0.58	0.57

C1 - C50 estimated total product distribution, weight %

C1	34.7	37.2	34.3	35.1	34.9	35.8
C2 - C4	33.8	34.1	33.9	33.9	32.8	33.3
C5 - C12	30.5	28.0	30.8	30.1	31.3	30.1
C13 - C50	1.0	0.8	1.0	0.9	1.0	0.9

CO conversion, %	7.4	7.4	7.5	7.7	7.3	7.3
rate, g CH ₂ /g cat/hr	0.49	0.49	0.50	0.51	0.48	0.48
CO ₂ formation, %	0.7	0.4	0.4	0.7	0.4	0.4

Performance of CAL.01

Dates: 04/04/94 - 04/05/94 Run #4 (re-calcine)

flow rate = 90.0 cc/min, loading = 0.2 g, WHSV = 15.1 l/hr, H₂/CO ratio in feed = 2

time on stream, hr	28.0
reaction temperature, °C	220
pressure, atm	1
flow, cc/min	90.0

C1 - C15 product distribution, weight %

C1	39.99
C2	7.04
C3	16.23
C4	1.99
C5	12.09
C6	7.79
C7	5.70
C8	3.61
C9	2.13
C10	1.49
C11	0.87
C12	0.45
C13	0.30
C14	0.20
C15	0.12
alpha chain growth probability	0.57

C1 - C50 estimated total product distribution, weight %

C1	39.9
C2 - C4	25.2
C5 - C12	34.1
C13 - C50	0.8

CO conversion, %	6.6
rate, g CH ₂ /g cat/hr	0.44
CO ₂ formation, %	0.3

Schulz-Flory Plot for CAL.01 - Run #4 (re-calcine)
Time on Stream (hrs)

7/11/94

Time-on-Stream Plot for CAL.01 - Run #4

CAL.02 - Run #1

Co wt%	NM wt %	Promotor wt%		Support
20	Ru 0.50			Al ₂ O ₃

SUMMARY REACTION DATA

Reaction Conditions:

P = 1.0 atm

T = 220 °C

H₂/CO = 2

weight of catalyst = 0.182 g

WHSV = 14.11 1/hr

time on stream = 25.0 hrs

CO₂ (g/g cat/hr) = 0.040CO₂ (% of CO) = 0.2

O/P = 3.04

CO conversion (%)	6.1
rate (g CH ₂ /g cat/hr)	0.38
alpha	0.63
C1 (wt%)	27.3
C2 - C4 (wt%)	30.7
C5 - C12 (wt%)	39.7
C13 + (wt%)	2.3

Performance of CAL.02

Dates: 05/05/94 - 05/06/94 Run #1

flow rate = 90.0 cc/min, loading = 0.2 g, WHSV = 14.1 1/hr, H₂/CO ratio in feed = 2

time on stream, hr	0.5	2.5	5.0	8.0	23.0	25.0
reaction temperature, °C	220	220	220	220	220	220
pressure, atm	1.0	1.0	1.0	1.0	1.0	1.0
flow, cc/min	90.0	90.0	90.0	90.0	90.0	90.0

C1 - C15 product distribution, weight %

C1	24.79	25.50	26.34	26.49	27.02	27.35
C2	4.86	5.01	4.64	5.16	5.15	4.71
C3	13.17	13.25	13.34	13.38	13.18	13.14
C4	13.31	13.28	13.29	13.28	12.97	12.93
C5	11.76	11.75	11.68	11.63	11.48	11.37
C6	8.63	8.69	8.52	8.29	8.30	8.29
C7	7.02	6.95	6.87	6.87	6.82	6.77
C8	5.00	4.87	4.82	4.84	4.88	4.81
C9	3.53	3.37	3.31	3.34	3.33	3.26
C10	2.54	2.42	2.45	2.28	2.36	2.61
C11	2.00	1.84	1.74	1.76	1.68	1.96
C12	1.33	1.23	1.23	1.05	1.19	1.17
C13	0.85	0.80	0.82	0.72	0.80	0.77
C14	0.63	0.60	0.54	0.54	0.49	0.51
C15	0.57	0.43	0.41	0.37	0.35	0.34
alpha chain growth probability	0.66	0.64	0.64	0.63	0.63	0.63

C1 - C50 estimated total product distribution, weight %

C1	24.2	25.2	26.1	26.2	26.8	27.3
C2 - C4	30.6	31.2	30.9	31.5	31.1	30.7
C5 - C12	41.4	40.8	40.3	39.8	39.7	39.7
C13 - C50	3.8	2.8	2.7	2.5	2.3	2.3

CO conversion, %	7.4	7.5	7.0	6.8	6.0	6.1
rate, g CH ₂ /g cat/hr	0.45	0.46	0.43	0.42	0.37	0.38
CO ₂ formation, %	0.3	0.3	0.3	0.2	0.2	0.2

Schulz-Flory Plot for CAL01 - Run #1
Time on Stream (hrs)

Time-on-Stream Plot for CAL.02 - Run #1

CAL.03 - Run #1

Co wt%	NM wt %	Promotor wt%		Support
20	Ru 0.50			Al ₂ O ₃

SUMMARY REACTION DATA

Reaction Conditions:

P = 1.0 atm

T = 220 °C

H₂/CO = 2

weight of catalyst = 0.178 g

WHSV = 14.46 1/hr

time on stream = 27.0 hrs

CO₂ (g/g cat/hr) = 0.048CO₂ (% of CO) = 0.2

O/P = 2.59

CO conversion (%)	7.3
rate (g CH ₂ /g cat/hr)	0.46
alpha	0.60
C1 (wt%)	29.0
C2 - C4 (wt%)	31.9
C5 - C12 (wt%)	37.5
C13 + (wt%)	1.6

Performance of CAL.03

Dates: 05/09/94 - 05/11/94 Run #1

flow rate = 90.0 cc/min, loading = 0.2 g, WHSV = 14.5 1/hr, H₂/CO ratio in feed = 2

time on stream, hr	1.0	3.0	5.0	9.0	21.0	23.0
reaction temperature, °C	220	220	220	220	220	220
pressure, atm	1.0	1.0	1.0	1.0	1.0	1.0
flow, cc/min	90.0	90.0	90.0	90.0	90.0	90.0

C1 - C15 product distribution, weight %

C1	28.62	29.32	28.89	28.38	28.84	29.33
C2	4.93	5.00	4.93	4.86	5.28	5.33
C3	13.79	13.94	13.81	13.61	13.57	13.59
C4	13.45	13.49	13.43	13.36	13.12	13.01
C5	11.43	11.34	11.42	11.58	11.34	11.11
C6	8.16	7.88	8.02	8.45	8.24	7.98
C7	6.47	6.35	6.46	6.53	6.52	6.44
C8	4.40	4.32	4.38	4.52	4.48	4.41
C9	2.92	2.89	2.97	3.02	2.96	2.97
C10	2.07	2.01	2.02	2.12	2.11	2.14
C11	1.34	1.36	1.43	1.47	1.44	1.49
C12	1.02	0.86	0.99	0.93	0.91	0.96
C13	0.61	0.61	0.60	0.54	0.57	0.62
C14	0.42	0.35	0.39	0.36	0.36	0.33
C15	0.36	0.29	0.26	0.25	0.26	0.27
alpha chain growth probability	0.63	0.61	0.61	0.61	0.61	0.61

C1 - C50 estimated total product distribution, weight %

C1	28.2	29.0	28.8	28.3	28.7	29.2
C2 - C4	31.7	32.1	32.0	31.7	31.8	31.8
C5 - C12	37.8	36.9	37.4	38.3	37.8	37.2
C13 - C50	2.4	1.9	1.7	1.6	1.7	1.8

CO conversion, %	9.9	8.9	8.4	8.2	7.7	7.1
rate, g CH ₂ /g cat/hr	0.63	0.56	0.53	0.52	0.49	0.45
CO ₂ formation, %	0.4	0.3	0.4	0.4	0.3	0.3

Performance of CAL.03

Dates: 05/09/94 - 05/11/94 Run #1

flow rate = 90.0 cc/min, loading = 0.2 g, WHSV = 14.5 l/hr, H₂/CO ratio in feed = 2

time on stream, hr	25.0	27.0	29.0	31.0	33.0	46.0
reaction temperature, °C	220	220	220	210	220	220
pressure, atm	1.0	1.0	1.0	1.0	1.0	1.0
flow, cc/min	90.0	90.0	22.5	22.5	22.5	90.0

C1 - C15 product distribution, weight %

C1	29.19	29.09	28.45	20.40	29.21	27.64
C2	5.34	5.31	5.07	3.60	5.09	5.14
C3	13.61	13.60	11.47	9.81	11.27	13.18
C4	13.04	13.12	12.76	11.41	12.54	12.86
C5	11.10	11.30	11.34	11.62	11.32	11.55
C6	7.98	8.21	8.34	10.00	8.62	9.17
C7	6.46	6.49	7.16	8.53	7.02	6.70
C8	4.41	4.53	4.91	6.54	4.79	4.95
C9	2.92	3.03	3.56	5.08	3.41	3.14
C10	2.19	1.99	2.22	3.81	2.31	2.18
C11	1.61	1.35	1.84	3.04	1.64	1.30
C12	0.94	0.90	1.13	2.23	1.17	0.93
C13	0.54	0.50	0.77	1.72	0.72	0.54
C14	0.40	0.36	0.60	1.32	0.48	0.37
C15	0.29	0.23	0.38	0.88	0.39	0.36
alpha chain growth probability	0.62	0.60	0.63	0.69	0.64	0.63

C1 - C50 estimated total product distribution, weight %

C1	29.0	29.0	28.3	20.0	28.9	27.2
C2 - C4	31.8	31.9	29.1	24.4	28.6	30.7
C5 - C12	37.3	37.5	40.1	49.6	40.0	39.8
C13 - C50	1.9	1.6	2.5	6.0	2.6	2.3

CO conversion, %	7.1	7.3	29.3	17.0	28.9	7.4
rate, g CH ₂ /g cat/hr	0.45	0.46	0.46	0.27	0.46	0.47
CO ₂ formation, %	0.2	0.2	1.9	1.2	1.9	0.4

Schulz-Flory Plot for CAL.03 - Run #1
Time on Stream (hrs)

Schulz-Flory Plot for CAL.03 - Run #1
High Conversion Study at Different Temperature

Time-on-Stream Plot for CAL.03 - Run #1

CAL.03 - Run #1

Co wt%	NM wt %	Promotor wt%		Support
20	Ru 0.50			Al ₂ O ₃

SUMMARY REACTION DATA*

Reaction Conditions:

P = 1.0 atm

T = 220 °C

H₂/CO = 2

weight of catalyst = 0.178 g

WHSV = 3.62 1/hr

time on stream = 29.0 hrs

CO₂ (g/g cat/hr) = 0.105CO₂ (% of CO) = 1.9

O/P = 0.76

CO conversion (%)	29.3
rate (g CH ₂ /g cat/hr)	0.46
alpha	0.63
C1 (wt%)	28.3
C2 - C4 (wt%)	29.1
C5 - C12 (wt%)	40.1
C13 + (wt%)	2.5

* high conversion study

CoW01 - Run #2

Co wt%		WGS Promotors wt%		Support
20		Cu 4.00	Zn 10.00	Al ₂ O ₃

SUMMARY REACTION DATA

Reaction Conditions:

P = 1.0 atm

T = 220 °C

H₂/CO = 2

weight of catalyst = 0.800 g

WHSV = 3.21 1/hr

time on stream = 12.5 hrs

CO₂ (g/g cat/hr) = 0.006CO₂ (% of CO) = 0.1

O/P = 3.78

CO conversion (%)	1.2
rate (g CH ₂ /g cat/hr)	0.02
alpha	0.58
C1 (wt%)	30.2
C2 - C4 (wt%)	40.9
C5 - C12 (wt%)	27.9
C13 + (wt%)	1.0

Performance of CoW01

Dates: 06/06/94 - 06/08/94 Run #2

flow rate = 90.0 cc/min, loading = 0.8 g, WHSV = 3.2 1/hr, H₂/CO ratio in feed = 2

time on stream, hr	0.5	3.5	6.5	9.5	12.5
reaction temperature, °C	220	220	220	220	220
pressure, atm	1.0	1.0	1.0	1.0	1.0
flow, cc/min	90.0	90.0	90.0	90.0	90.0

C1 - C15 product distribution, weight %

C1	31.26	31.18	30.89	30.34	30.20	rereduce 350C
C2	9.17	9.30	9.27	9.10	9.05	
C3	17.18	17.41	17.36	17.07	16.90	
C4	14.52	14.70	15.01	14.94	14.94	
C5	11.80	11.96	11.94	12.14	12.18	
C6	2.25	1.93	2.44	2.77	2.95	
C7	4.66	4.68	4.57	4.74	4.86	
C8	2.93	2.90	2.70	2.95	3.01	
C9	1.98	1.77	1.88	1.97	2.00	
C10	1.29	1.19	1.29	1.28	1.33	
C11	0.93	0.95	0.79	0.86	0.73	
C12	0.69	0.53	0.52	0.56	0.58	
C13	0.58	0.46	0.44	0.42	0.43	
C14	0.41	0.40	0.37	0.37	0.36	
C15	0.25	0.34	0.31	0.29	0.28	
alpha chain growth probability	0.58	0.57	0.57	0.58	0.58	

C1 - C50 estimated total product distribution, weight %

C1	31.3	31.4	31.0	30.4	30.2
C2 - C4	40.9	41.7	41.8	41.3	40.9
C5 - C12	26.7	26.0	26.3	27.4	27.9
C13 - C50	1.1	0.9	0.8	0.9	1.0

CO conversion, %	1.1	1.1	1.1	1.1	1.2
rate, g CH ₂ /g cat/hr	0.02	0.02	0.02	0.02	0.02
CO ₂ formation, %	0.2	0.2	0.1	0.1	0.1

Performance of CoW01

Dates: 06/06/94 - 06/08/94 Run #2

flow rate = 90.0 cc/min, loading = 0.8 g, WHSV = 3.2 1/hr, H₂/CO ratio in feed = 2

time on stream, hr	15.0	1.5	4.5
reaction temperature, °C	220	220	220
pressure, atm	1.0	1.0	1.0
flow, cc/min	90.0	20.0	20.0

C1 - C15 product distribution, weight %

C1	42.19	40.16	40.39
		inc. conv.	
C2	12.83	11.20	11.26
C3	19.26	17.70	17.71
C4	11.69	12.35	12.27
C5	8.77	8.26	8.18
C6	0.00	4.08	3.83
C7	2.55	2.49	2.46
C8	1.21	1.47	1.46
C9	0.59	0.80	0.88
C10	0.29	0.55	0.50
C11	0.23	0.33	0.30
C12	0.19	0.25	0.24
C13	0.19	0.20	0.19
C14		0.15	0.14
C15			0.11
alpha chain growth probability	0.51	0.53	0.53

C1 - C50 estimated total product distribution, weight %

C1	42.1	40.1	40.4
C2 - C4	43.7	41.2	41.3
C5 - C12	13.9	18.3	18.0
C13 - C50	0.2	0.3	0.3

CO conversion, %	0.5	2.3	2.3
rate, g CH ₂ /g cat/hr	0.01	0.01	0.01
CO ₂ formation, %	0.1	0.4	0.4

Schulz-Flory Plot for CoW01 - Run #2
Time on Stream (hrs)

Schulz-Flory Plot for CoW01 - Run #1 S2
Time on Stream (hrs)

CoW01 - Run #3

Co wt%		WGS Promotors wt%		Support
20		Cu 4.00	Zn 10.00	Al ₂ O ₃

SUMMARY REACTION DATA

Reaction Conditions:

P = 1.0 atm

T = 220 °C

H₂/CO = 2

weight of catalyst = 0.400 g

WHSV = 6.43 1/hr

time on stream = 21.5 hrs

CO₂ (g/g cat/hr) = 0.006CO₂ (% of CO) = 0.1

O/P = 11.32

CO conversion (%)	0.2
rate (g CH ₂ /g cat/hr)	0.01
alpha	0.51
C1 (wt%)	40.9
C2 - C4 (wt%)	50.4
C5 - C12 (wt%)	8.5
C13 + (wt%)	0.2

Performance of CoW01

Dates: 06/09/94 - 06/10/94 Run #3

flow rate = 90.0 cc/min, loading = 0.4 g, WHSV = 6.4 l/hr, H₂/CO ratio in feed = 2

time on stream, hr	0.5	3.5	6.5	21.5	25.0	28.0
reaction temperature, °C	220	220	220	220	220	220
pressure, atm	1.0	1.0	1.0	1.0	1.0	1.0
flow, cc/min	90.0	90.0	90.0	90.0	90.0	90.0

C1 - C15 product distribution, weight %

C1	42.10	42.07	41.17	41.18	39.23	39.71
C2	13.11	15.03	15.00	15.30	14.57	14.66
C3	18.24	20.29	20.40	21.45	20.45	20.52
C4	12.55	13.95	14.34	14.04	14.46	13.48
C5	8.07	5.57	6.05	5.52	7.72	7.85
C6	0.00	0.00	0.00	0.00	0.00	0.00
C7	2.47	1.57	1.75	1.39	1.87	1.80
C8	1.16	0.64	0.68	0.77	1.04	0.97
C9	0.67	0.23	0.21	0.19	0.26	0.46
C10	0.55	0.24	0.21	0.15	0.21	0.21
C11	0.47	0.26	0.18		0.19	0.21
C12	0.39	0.17				0.14
C13	0.22					
C14						
C15						
alpha chain growth probability	0.52	0.50	0.51	0.51	0.52	0.50

C1 - C50 estimated total product distribution, weight %

C1	42.2	42.0	40.9	40.9	39.0	39.6
C2 - C4	44.0	49.2	49.5	50.4	49.2	48.5
C5 - C12	13.5	8.7	9.4	8.5	11.6	11.7
C13 - C50	0.3	0.2	0.2	0.2	0.3	0.2

CO conversion, %	0.3	0.2	0.2	0.2	0.2	0.2
rate, g CH ₂ /g cat/hr	0.01	0.01	0.01	0.01	0.01	0.01
CO ₂ formation, %	0.1	0.1	0.1	0.1	0.1	0.1

Schulz-Flory Plot for CoW.01 - Run #3
Time on Stream (hrs), Comment: rereduced at 350 C

CoW.02 - Run #1

Co wt%	NM wt %	Promotor wt%		Support
20	Cu 5.00	Cr 4.00		Al ₂ O ₃

SUMMARY REACTION DATA

Reaction Conditions:

P = 1.0 atm

T = 220 °C

H₂/CO = 2

weight of catalyst = 0.400 g

WHSV = 6.43 1/hr

time on stream = 21.0 hrs

CO₂ (g/g cat/hr) = 0.008CO₂ (% of CO) = 0.1

O/P = 4.94

CO conversion (%)	0.3
rate (g CH ₂ /g cat/hr)	0.01
alpha	0.60
C1 (wt%)	25.6
C2 - C4 (wt%)	40.8
C5 - C12 (wt%)	32.2
C13 + (wt%)	1.3

Performance of CoW.02

Dates: 06/12/94 - 06/13/94 Run #1

flow rate = 90.0 cc/min, loading = 0.4 g, WHSV = 6.4 1/hr, H₂/CO ratio in feed = 2

time on stream, hr	3.0	6.0	9.0	12.0	15.0	18.0
reaction temperature, °C	220	220	220	220	220	220
pressure, atm	1.0	1.0	1.0	1.0	1.0	1.0
flow, cc/min	90.0	90.0	90.0	90.0	90.0	90.0

C1 - C15 product distribution, weight %

C1	22.66	24.39	24.78	27.78	24.95	25.39
C2	8.50	9.01	9.09	10.31	9.32	9.51
C3	16.64	17.39	16.18	18.29	16.50	16.48
C4	14.80	16.04	13.96	15.73	14.14	14.14
C5	12.69	10.67	12.47	9.39	12.74	12.68
C6	5.77	6.07	4.91	5.25	4.65	4.23
C7	6.00	5.34	5.78	4.15	5.65	5.63
C8	3.85	3.40	3.83	2.72	3.66	3.57
C9	2.73	2.33	2.71	1.91	2.56	2.52
C10	1.85	1.62	1.86	1.35	1.78	1.76
C11	1.27	1.11	1.16	0.79	1.18	1.17
C12	0.99	0.83	0.83	0.71	0.77	0.94
C13	0.72	0.58	0.74	0.51	0.66	0.63
C14	0.66	0.48	0.65	0.45	0.58	0.58
C15	0.49	0.45	0.65	0.39	0.50	0.49
alpha chain growth probability	0.60	0.59	0.60	0.57	0.60	0.60

C1 - C50 estimated total product distribution, weight %

C1	22.9	24.6	25.0	28.0	25.1	25.6
C2 - C4	40.4	42.8	39.6	44.7	40.3	40.5
C5 - C12	35.3	31.4	33.9	26.4	33.2	32.6
C13 - C50	1.5	1.1	1.5	0.9	1.4	1.4

CO conversion, %	0.4	0.4	0.3	0.3	0.3	0.3
rate, g CH ₂ /g cat/hr	0.01	0.01	0.01	0.01	0.01	0.01
CO ₂ formation, %	0.1	0.1		0.1	0.1	0.1

Performance of CoW.02

Dates: 06/12/94 - 06/13/94 Run #1

flow rate = 90.0 cc/min, loading = 0.4 g, WHSV = 6.4 l/hr, H₂/CO ratio in feed = 2

time on stream, hr	21.0
reaction temperature, °C	220
pressure, atm	1.0
flow, cc/min	90.0

C1 - C15 product distribution, weight %

C1	25.44
C2	9.53
C3	16.38
C4	14.58
C5	12.65
C6	3.99
C7	5.63
C8	3.65
C9	2.42
C10	1.73
C11	1.09
C12	0.74
C13	0.65
C14	0.58
C15	0.50

alpha	chain growth probability	0.60
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C1 - C50 estimated total product distribution, weight %

C1	25.6
C2 - C4	40.8
C5 - C12	32.2
C13 - C50	1.3

CO conversion, %	0.3
rate, g CH ₂ /g cat/hr	0.01
CO ₂ formation, %	0.1

Schulz-Flory Plot for CoW.02 - Run #1
Time on Stream (hrs)

WATER-GAS SHIFT

Performance of Cu/ZnO Commercial

Dates: 04/5/94 - 04/6/94 Run#1

flow rate = 157 cc/min, loading = 0.04g, WHSV = 91/hr, H₂O/CO ratio in feed = 1.5

time on stream, hr	0.1	1.5	2.1	3.8	5.0	13.0
reaction temperature, °C	171	171	171	171	171	171
pressure, atm	1.0	1.0	1.0	1.0	1.0	1.0
flow, cc/min	157.0	157.0	157.0	157.0	157.0	157.0
CO conversion, %	4.1	2.8	2.5	1.8	1.8	1.5
rate, g CO/g cat/hr	0.60	0.39	0.35	0.25	0.25	0.24

Performance of Cu/ZnO Commercial

Dates: 04/5/94 - 04/6/94 Run#1

flow rate = 156 cc/min, loading = 0.04g, WHSV = 91/hr, H₂O/CO ratio in feed = 1.5

E_{app} = 10 kcal/mol

time on stream, hr	14.0
reaction temperature, °C	171.0
pressure, atm	1.0
flow, cc/min	157.0

CO conversion, %	1.60
rate, g CO/g cat/hr	0.25

Performance of WGS Cu-Chromite Commercial

Dates: 04/11/94 - 04/12/94 Run #2

flow rate = 157 cc/min, loading = 0.04g, WHSV = 91/hr, H₂O/CO ratio in feed = 1.5

time on stream, hr	init rate	1.5
reaction temperature, °C	171	171
pressure, atm	1.0	1.0
flow, cc/min	157.0	157.0

CO conversion, %	14.4	14.9
rate, g CO/g cat/hr	2.47	2.49

Performance of WGS.01

Dates: 04/8/94 - 04/9/94 Run#2

flow rate = 157 cc/min, loading = 0.04g, WHSV = 91/hr, H₂O/CO ratio in feed = 1.5

time on stream, hr	0.1	1.5	8.5
reaction temperature, °C	171	171	171
pressure, atm	1.0	1.0	1.0
flow, cc/min	157.0	157.0	157.0

CO conversion, %	3.4	2.7	1.8
rate, g CO/g cat/hr	0.62	0.48	0.36

Performance of WGS.02

Dates: 4/9/94 - 4/10/94 Run #2

flow rate = 157 cc/min, loading = 0.04g, WHSV = 91/hr, H₂O/CO ratio in feed = 1.5

time on stream, hr	0.1	1.5
reaction temperature, °C	171	171
pressure, atm	1.0	1.0
flow, cc/min	157	157

CO conversion, %	3.9	3.2
rate, g CO/g cat/hr	0.73	0.60

Performance of WGS.03

Dates: 04/10/94 - 04/11/94

flow rate = 157 cc/min, loading = 0.04g, WHSV = 91/hr, H₂O/CO ratio in feed = 1.5

time on stream, hr	0.1	1.5
reaction temperature, °C	171	171
pressure, atm	1.0	1.0
flow, cc/min	157.0	157.0

CO conversion, %	5.3	4.7
rate, g CO/g cat/hr	0.89	0.79

Performance of WGS.03

Dates: 06/15/94 - 06/16/94 Run#2

flow rate = 157 cc/min, loading = 0.04g, WHSV = 91/hr, H₂O/CO ratio in feed = 1.5

time on stream, hr	0.1	1.5	2.1	17.0	19.0
reaction temperature, °C	220	220	220	220	220
pressure, atm	1.0	1.0	1.0	1.0	1.0
flow, cc/min	157.0	157.0	157.0	157.0	157.0

CO conversion, %	13.0	9.4	8.4	5.4	5.3
rate, g CO/g cat/hr	2.02	1.43	1.36	9.08	8.81

Performance of WGS.06

Dates: 04/17/94 - 04/18/94 Run#1

flow rate = 157 cc/min, loading = 0.04g, WHSV = 91/hr, H₂O/CO ratio in feed = 1.5

time on stream, hr	0.1	1.5	4.0	8.0	9.5
reaction temperature, °C	171	171	171	171	171
pressure, atm	1.0	1.0	1.0	1.0	1.0
flow, cc/min	157.0	157.0	157.0	157.0	157.0

CO conversion, %	*	1.5	1.3	1.1	1.1
rate, g CO/g cat/hr	*	0.24	0.21	0.19	0.18

* was not measured.

Performance of CoW.02

Dates: 06/11/94 - 06/13/94

flow rate = 157 cc/min, loading = 0.04g, WHSV = 91/hr, H₂O/CO ratio in feed = 1.5

time on stream, hr	0.1	1.5	2.1	17.1	19.0
reaction temperature, °C	220	220	220	220	220
pressure, atm	1.0	1.0	1.0	1.0	1.0
flow, cc/min	157.0	157.0	157.0	157.0	157.0

CO conversion, %	3.4	1.8	1.7	1.3	1.1
rate, g CO/g cat/hr	0.61	0.32	0.28	0.19	0.17

Performance of CoW.03

Dates: 06/16/94 - 06/17/94 Run#1

flow rate = 157 cc/min, loading = 0.04g, WHSV = 91/hr, H₂O/CO ratio in feed = 1.5

time on stream, hr	0.1	1.5	2.1	17.0	19.0
reaction temperature, °C	220	220	220	220	220
pressure, atm	1.0	1.0	1.0	1.0	1.0
flow, cc/min	157.0	157.0	157.0	157.0	157.0

CO conversion, %	3.4	2.5	2.3	1.5	1.6
rate, g CO/g cat/hr	0.56	0.39	0.34	0.21	0.21

APPENDIX C

SLURRY BUBBLE COLUMN REACTOR DATA

Table I

SUMMARY OF M3 SBCR RUN RESULTS

Unless otherwise noted, total flow is ca.15 L/min. STP, or 3 cm/sec linear gas flow.

Conversion is total CO conversion over the period (X).

Conversion and selectivities are calculated using N2 as an internal standard in the GC analysis of the offgas.

Prod. rate: Rate for production of total hydrocarbons, C1+ (kg/kg cat., hr).

Alpha: Based on GC analysis of offgas and liquid product.

Cat. No	Cat. wt, g	Per No	Time Start	Time Stop	Temp C	Pres psi	H2: CO	Synfld cc/hr	Conv. %	Prod. Rate	Selectivity			Alpha		Olefin/Paraf		Olefins	Comments
											IC4	IC2H6	IC3+	GC	Liq	C3	C4	C5-C18, X	
CO.001	16.5	1	162	177	225	450	2.0	20	15.9	0.70	2.3	0.81	96.4	0.98	0.88	5.00	2.27	25.2	
CO.001	16.5	2	202	228	200	450	2.0	20	3.9	0.17	0.0	0.01	99.9	0.81	0.91	0.00	0.00	21.7	
CO.001	16.5	3	254	280	240	450	2.0	20	30.9	1.36	11.7	1.77	85.5	0.87	0.77	2.63	1.64	22.4	
CO.001	16.5	4	302	323	225	450	1.2	20	9.9	0.59	0.7	0.31	98.4	0.76	0.90	0.00	7.14	29.4	
CO.001	16.5	5	350	372	225	450	2.0	20	15.3	0.68	6.0	0.98	92.5	0.84	0.88	4.00	2.70	23.1	
CO.001	16.5	6	398	420	225	300	2.0	20	12.5	0.55	6.1	1.13	92.2	0.79	0.86	4.35	2.86	21.7	
CO.001	16.5	7	446	468	240	300	2.0	20	22.9	1.02	16.5	0.81	81.5	0.71	0.79	3.03	1.79	22.4	
CO.001	16.5	8	494	516	240	600	2.0	20	29.9	1.33	12.6	1.55	85.0	0.76	0.82	2.63	1.69	22.4	
CO.001	16.5	9	517	540	240	600	2.0	0	29.5	1.31	12.0	1.72	85.3	0.76	--	2.50	1.56	22.4	
CO.001	16.5	9	541	564	240	600	2.0	0	28.4	1.26	10.4	1.66	87.1	0.77	--	3.03	1.72	--	
CO.001	16.5	9	565	588	240	600	2.0	0	27.9	1.27	11.1	1.74	86.2	0.76	--	3.03	1.72	--	
CO.001	16.5	9	589	612	240	600	2.0	0	27.0	1.20	10.7	1.72	86.7	0.76	0.82	2.78	2.00	--	
CO.001	16.5	10	637	660	240	600	2.0	20	26.4	1.17	11.0	1.67	86.4	0.77	0.83	2.86	1.96	22.4	G.C.Calib
CO.001	16.5	11	684	706	225	450	2.0	20	11.6	0.51	5.4	1.00	93.0	0.81	0.87	5.26	3.45	23.8	
CO.005	19.5	1	12	36	240	450	2.0	20	33.2	1.23	5.6	1.61	91.8	0.80	0.81	2.04	1.27	23.1	G.C.Calib
CO.005	19.5	2	60	84	220	450	2.0	20	15.0	0.56	2.9	0.61	96.2	0.86	0.87	4.55	3.23	21.7	
CO.005	19.5	3	108	132	240	450	1.2	20	18.5	0.94	6.9	0.97	91.3	0.81	--	5.88	3.85	26.6	
CO.005	19.5	4	156	179	240	450	2.0	20	29.6	1.11	11.5	1.80	85.8	0.76	0.78	2.22	1.39	21.7	
CO.002	20.1	1	37	59	240	450	2.0	20	36.1	1.32	22.9	3.22	72.4	0.66	0.77	0.65	0.31	16.8	
CO.002	20.1	2	85	106	220	450	2.0	20	16.6	0.60	3.8	1.13	94.7	0.84	0.88	2.44	0.89	--	
CO.002	20.1	3	133	149	210	600	1.0	20	5.2	0.28	0.0	0.00	99.1	0.89	0.94	0.00	0.00	--	Power Fail
CO.003	15.1	1	15	35	240	450	2.0	20	31.7	1.53	16.7	2.37	79.8	0.71	--	1.30	0.60	18.2	G.C.Calib
CO.003	15.1	2	61	83	220	450	2.0	20	13.2	0.63	5.1	0.99	93.4	0.82	0.90	4.55	1.89	--	
CO.003	15.1	3	88	107	240	450	2.0	20	28.4	1.37	15.1	2.37	81.4	0.75	--	1.45	0.97	--	
CO.003	15.1	4	133	155	240	450	1.0	20	13.1	0.95	4.2	1.24	93.3	0.83	0.88	6.67	3.70	--	
CO.003	15.1	5	181	203	240	600	1.0	20	13.4	0.97	3.9	1.09	93.7	0.81	--	5.26	3.45	30.1	
CO.003	15.1	6	217	227	240	450	2.0	20	25.4	1.23	14.9	2.35	81.7	0.73	--	1.89	1.19	--	
CO.011	15.3	1	13	35	240	450	2.0	20	14.3	0.67	7.6	1.58	89.4	0.78	0.83	4.17	2.57	21.7	
CO.011	15.3	2	61	83	220	450	2.0	20	5.1	0.23	0.0	0.00	97.2	0.87	0.82	--	--	--	
CO.011	15.3	3	88	107	240	450	2.0	20	13.5	0.63	5.4	1.70	91.1	0.79	--	4.00	2.83	--	
CO.011	15.3	4	133	155	240	450	1.0	20	6.3	0.44	0.4	1.02	95.5	0.82	0.88	--	--	--	
CO.011	15.3	5	181	203	240	600	1.0	20	6.7	0.46	0.2	0.88	96.0	0.84	0.89	12.00	3.67	27.3	G.C.Calib
CO.011	15.3	6	217	226	240	450	2.0	20	12.0	0.57	5.9	1.78	90.4	0.78	--	4.40	2.43	--	

Table I
(Continued)

SUMMARY OF M3 SBCR RUN RESULTS

Unless otherwise noted, total flow is ca.15 L/min. STP, or 3 cm/sec linear gas flow.

Conversion is total CO conversion over the period (X).

Conversion and selectivities are calculated using N2 as an internal standard in the GC analysis of the offgas.

Prod. rate: Rate for production of total hydrocarbons, C1+ (kg/kg cat.,hr).

Alpha: Based on GC analysis of offgas and liquid product.

Cat. No	Cat. wt,g	Per No	Time Start	Time Stop	Temp C	Pres psi	H2: CO	Synfld cc/hr	Conv. %	Prod. Rate	Selectivity			Alpha GC	Alpha Liq	Olefin/Paraf		Olefins C6-C18,X	Comments
											XC4	XC2H6	XC3+			C3	C4		
CO.012	15.8	1	14	36	240	450	2.0	20	13.9	0.63	6.1	1.51	90.6	0.80	0.89	4.00	2.57	17.5	
CO.012	15.8	2	62	84	220	450	2.0	20	5.1	0.23	0.0	0.18	97.8	0.89	0.90	--	2.50	--	
CO.012	15.8	3	88	92	240	450	2.0	20	13.1	0.59	6.1	1.71	90.4	0.80	--	5.00	2.25	--	Power Fail
CO.012	15.8	4	134	156	240	450	1.0	20	3.9	0.26	4.8	2.28	86.3	0.70	0.85	16.00	3.50	--	
CO.012	15.8	5	182	204	240	600	1.0	20	4.3	0.28	0.1	2.08	91.6	0.75	0.82	8.50	3.50	30.8	
CO.012	15.8	6	218	227	240	450	2.0	20	7.2	0.32	7.3	3.16	85.1	0.70	--	5.00	3.17	--	
CO.015	15.0	1	14	35	240	450	2.0	20	28.3	1.37	12.7	2.00	84.1	0.76	0.80	1.61	1.07	19.6	G.C.Calib
CO.015	15.0	2	61	83	220	450	2.0	20	11.5	0.56	4.4	0.95	93.9	0.81	0.89	3.60	2.14	--	
CO.015	15.0	3	97	106	240	450	2.0	20	26.4	1.28	13.2	2.11	83.5	0.75	--	1.69	1.20	--	
CO.015	15.0	4	133	155	240	450	1.0	20	11.5	0.83	4.8	1.17	92.5	0.80	0.85	5.60	3.29	--	
CO.015	15.0	5	181	191	240	600	1.0	20	12.4	0.90	4.9	0.84	93.6	0.84	0.85	5.20	3.14	30.8	Power Fail
CO.011	15.0	1	13	35	240	450	2.0	20	18.5	0.89	8.8	1.69	88.8	0.78	0.83	3.18	1.85	20.3	G.C.Calib
CO.011	15.0	2	61	82	220	450	2.0	20	6.3	0.31	0.0	1.00	98.6	0.88	0.93	12.00	1.80	--	
CO.011	15.0	3	97	107	240	450	2.0	20	16.6	0.80	8.4	2.07	88.7	0.77	--	3.30	2.00	--	
CO.011	15.0	4	133	155	240	450	1.0	20	8.0	0.58	1.3	1.31	96.3	0.82	0.87	7.00	2.83	--	
CO.011	15.0	5	181	203	240	600	1.0	20	8.7	0.63	1.4	1.10	96.4	0.83	0.87	5.00	2.67	30.5	
CO.011	15.0	6	228	229	240	450	2.0	20	14.7	0.71	7.9	2.16	89.1	0.78	--	3.78	1.67	--	Power Fail
CO.017	15.0	1	9	31	240	450	2.0	20	27.2	1.32	11.2	1.77	85.9	0.77	0.80	2.09	1.20	30.8	
CO.017	15.0	2	55	79	220	450	2.0	20	11.4	0.55	5.0	0.00	94.8	0.88	0.90	5.00	3.20	--	
CO.017	15.0	3	81	103	240	450	2.0	20	25.9	1.26	11.7	1.61	85.6	0.77	--	1.95	1.26	--	
CO.017	15.0	4	129	151	240	450	1.0	20	11.6	0.84	5.0	0.00	93.9	0.82	0.86	25.0	2.88	--	
CO.017	15.0	5	177	199	240	600	1.0	20	11.6	0.84	4.2	0.00	94.7	0.86	0.86	24.0	1.63	21.0	G.C.Calib
CO.017	15.0	6	213	221	240	450	2.0	20	24.3	1.20	12.1	1.38	86.4	0.78	--	2.47	1.64	--	
CO.018	15.6	1	13	35	240	450	2.0	20	33.8	1.56	9.7	2.01	86.6	0.75	0.85	1.81	1.13	21.0	G.C.Calib
CO.018	15.6	2	61	80	220	450	2.0	20	12.6	0.59	2.8	0.00	97.1	0.90	0.88	--	--	--	
CO.018	15.6	3	97	107	240	450	2.0	20	27.9	1.30	9.4	1.86	87.7	0.75	--	2.65	2.17	--	
CO.018	15.6	4	133	155	240	450	1.0	20	12.4	0.86	3.3	0.00	95.0	0.80	0.86	--	--	--	
CO.018	15.6	5	181	203	240	600	1.0	20	13.0	0.90	3.2	0.00	94.9	0.80	0.85	--	--	38.5	
CO.018	15.6	6	217	226	240	450	2.0	20	26.4	1.22	10.1	1.38	86.8	0.73	--	2.89	2.05	--	

Table I
(Continued)

SUMMARY OF M3 SBCR RUN RESULTS

Unless otherwise noted, total flow is ca.15 L/min. STP, or 3 cm/sec linear gas flow.

Conversion is total CO conversion over the period (%).

Conversion and selectivities are calculated using N2 as an internal standard in the GC analysis of the offgas.

Prod. rate: Rate for production of total hydrocarbons, C1+ (kg/kg cat., hr).

Alpha: Based on GC analysis of offgas and liquid product.

Cat. No	Cat. wt, g	Per No	Time Start	Time Stop	Temp C	Pres psi	H2: CO	Synfld cc/hr	Conv. %	Prod. Rate	Selectivity			Alpha GC	Alpha Liq	Olefin/Paraf		Olefins C6-C18, %	Comments
											ZCH4	ZC2H6	ZC3+			C3	C4		
CO.016	14.7	1	16	35	240	450	2.0	20	26.4	1.31	8.3	1.71	89.3	0.78	0.81	2.00	1.41	21.7	G.C.Calib
CO.016	14.7	2	65	83	220	450	2.0	20	9.7	0.48	0.0	0.01	99.9	0.91	0.88	--	--	--	TCD weak.
CO.016	14.7	3	89	105	240	450	2.0	20	25.2	1.25	9.2	1.72	88.6	0.78	--	2.10	1.41	--	CH4 peaks
CO.016	14.7	4	134	155	240	450	1.0	20	10.9	0.81	1.2	0.79	97.7	0.84	0.86	--	--	--	are lower
CO.016	14.7	5	181	203	240	600	1.0	20	11.4	0.85	0.0	0.49	99.3	0.92	0.86	--	--	32.2	than
CO.016	14.7	6	210	226	240	450	2.0	20	22.7	1.12	3.8	1.98	93.7	0.79	--	2.37	1.41	--	expected.
CO.019	15.2	1	14	35	240	450	2.0	20	13.9	0.66	0.4	1.68	97.2	0.80	0.86	5.33	2.67	26.6	G.C.Calib
CO.019	15.2	2	66	83	220	450	2.0	20	3.8	0.18	0.0	1.71	96.7	0.88	--	--	--	--	New TCD
CO.019	15.2	3	88	105	240	450	2.0	20	12.2	0.57	0.0	2.03	96.3	0.80	--	5.60	3.80	--	
CO.019	15.2	4	133	155	240	450	1.0	20	--	--	--	--	--	--	--	--	--	--	Repair G.C
CO.019	15.2	5	169	178	240	600	1.0	20	5.9	0.41	0.0	1.49	96.1	0.80	--	8.50	13.00	--	Valve Leak
CO.019	15.2	6	193	203	240	450	2.0	20	10.2	0.48	0.8	2.23	95.0	0.79	--	4.80	3.40	--	CH4 peaks
CO.019	15.2	7	217	226	240	450	1.0	20	5.1	0.36	0.0	1.56	95.4	0.80	--	--	--	--	undetected
CO.005	14.7	1	25	35	240	450	2.0	20	27.1	1.34	7.9	1.60	89.7	0.79	0.82	2.30	1.38	23.1	G.C.Calib
CO.005	14.7	2	62	83	220	450	2.0	20	10.7	0.53	0.0	0.94	98.4	0.83	0.88	4.25	3.25	--	
CO.005	14.7	3	86	105	240	450	2.0	20	25.3	1.25	7.6	1.79	89.6	0.78	--	2.42	1.50	--	
CO.005	14.7	4	134	155	240	450	1.0	20	11.6	0.85	0.0	1.12	97.5	0.82	0.85	7.00	4.60	--	
CO.005	14.7	5	182	203	240	600	1.0	20	12.3	0.90	0.0	0.95	97.7	0.83	0.85	7.00	4.40	--	
CO.005	14.7	6	210	226	240	450	2.0	20	23.0	1.13	5.9	1.79	91.4	0.78	--	3.20	2.00	--	
CO.002	15.4	1	14	35	240	450	2.0	20	30.1	1.42	12.5	2.52	83.9	0.75	0.80	1.00	0.66	17.5	
CO.002	15.4	2	67	83	220	450	2.0	20	12.8	0.60	4.2	1.30	93.9	0.80	0.86	2.57	1.63	--	G.C.Calib
CO.002	15.4	3	91	107	240	450	2.0	20	28.2	1.34	17.3	2.91	78.8	0.71	--	0.93	0.65	--	
CO.002	15.4	4	136	155	240	450	1.0	20	12.6	0.89	4.4	1.61	92.8	0.79	0.84	4.43	2.88	--	
CO.002	15.4	5	182	198	240	600	1.0	20	13.1	0.92	3.6	1.36	93.9	0.81	0.84	4.29	2.75	25.2	
CO.002	15.4	6	209	227	240	450	2.0	20	25.6	1.22	17.4	3.10	78.7	0.71	--	1.00	0.66	--	
CO.025	15.6	1	21	35	240	450	2.0	20	26.6	1.24	10.7	2.08	86.4	0.76	0.82	2.25	1.47	21.7	G.C.Calib
CO.025	15.6	2	62	83	220	450	2.0	20	8.4	0.39	0.0	1.12	96.9	0.82	0.92	6.50	3.00	--	
CO.025	15.6	3	90	107	240	450	2.0	20	21.5	1.00	9.0	2.03	88.0	0.77	--	2.64	1.64	--	
CO.025	15.6	4	134	155	240	450	1.0	20	10.3	0.71	0.8	1.17	96.7	0.82	0.93	7.67	4.25	--	
CO.025	15.6	5	181	203	240	600	1.0	20	11.7	0.81	1.3	1.12	96.5	0.83	0.88	8.00	4.25	32.9	
CO.025	15.6	6	217	226	240	450	2.0	20	19.9	0.93	9.3	2.16	87.7	0.76	--	2.92	1.85	--	
CO.004	15.0	1	20	39	240	450	2.0	20	33.9	1.64	15.3	2.38	80.9	0.74	0.79	1.17	0.78	20.3	Repair G.C
CO.004	15.0	2	66	87	220	450	2.0	20	15.1	0.73	4.1	1.61	94.0	0.81	0.85	3.83	2.25	--	
CO.004	15.0	3	92	111	240	450	2.0	20	32.7	1.59	15.7	2.56	80.2	0.73	--	1.20	0.80	--	
CO.004	15.0	4	138	159	240	450	1.0	20	14.7	1.06	4.1	1.24	93.2	0.80	0.83	6.17	3.75	--	
CO.004	15.0	5	186	207	240	600	1.0	20	15.0	1.09	3.6	1.13	94.1	0.82	0.83	5.67	4.00	33.6	
CO.004	15.0	6	214	230	240	450	2.0	20	28.4	1.38	14.9	2.46	86.5	0.73	--	1.58	1.03	--	

Unless otherwise noted, total flow is ca.15 L/min. STP, or 3 cm/sec linear gas flow.

Conversion is total CO conversion over the period (2).

Conversion and selectivities are calculated using N2 as an internal standard in the GC analysis of the offgas.

Prod. rate: Rate for production of total hydrocarbons, C1+ (kg/kg cat., hr).

Alpha: Based on GC analysis of offgas and liquid product.

Cat. No	Cat. wt, g	Per No	Time Start	Time Stop	Temp C	Pres psi	H2: CO	Synfl cc/hr	Conv. %	Prod. Rate	Selectivities				Alpha GC	Alpha Liq	Olefin/Paraf		Olefins C5-18, X	Comments
											ICH4	IC2	IC3+	IC02			C3	C4		
CO.021	15.6	1	16	35	240	450	2.0	20	23.2	1.08	9.4	2.0	88.0	0.73	0.77	0.82	2.56	1.54	20.3	
CO.021	15.6	2	62	83	220	450	2.0	20	8.3	0.38	0.0	1.3	98.2	0.51	0.82	0.88	4.33	3.33	--	
CO.021	15.6	3	90	107	240	450	2.0	20	21.8	1.02	10.2	2.2	86.7	0.95	0.76	--	2.50	1.53	--	
CO.021	15.6	4	134	155	240	450	1.0	20	9.9	0.69	1.7	1.6	95.5	1.41	0.81	0.83	6.00	3.80	--	
CO.021	15.6	5	182	203	240	600	1.0	20	11.5	0.80	1.8	1.2	95.8	1.16	0.83	0.85	6.50	3.80	30.8	
CO.021	15.6	6	210	226	240	450	2.0	20	19.9	0.93	9.6	2.3	87.2	0.95	0.76	--	2.31	1.38	--	
CO.041	15.8	1	17	37	240	450	2.0	20	25.3	1.16	11.0	2.1	86.0	0.88	0.76	0.84	2.94	1.61	20.3	
CO.041	15.8	2	66	75	220	450	2.0	20	9.1	0.41	0.0	1.5	97.8	0.65	0.82	0.91	8.00	2.75	--	
CO.041	15.8	3	90	109	240	450	2.0	20	26.3	1.21	9.5	1.9	87.8	0.82	0.78	--	2.81	1.71	--	
CO.041	15.8	4	136	148	240	450	1.0	20	12.7	0.88	1.9	1.2	95.9	0.95	0.83	0.86	9.00	4.20	--	
CO.041	15.8	5	169	178	240	600	1.0	20	13.2	0.91	2.0	1.0	96.1	0.93	0.84	--	7.00	3.50	--	
CO.041	15.8	6	193	203	240	450	2.0	20	24.6	1.13	9.4	1.8	87.9	0.92	0.78	--	2.93	1.75	--	
CO.014	15.1	1	24	38	240	450	2.0	20	8.5	0.40	8.3	3.5	85.8	2.43	0.74	0.83	2.75	1.67	17.5	G.C. Calib
CO.014	15.1	2	68	86	220	450	2.0	20	3.2	0.15	0.0	2.3	93.4	4.31	0.76	0.86	3.50	3.00	--	
CO.014	15.1	3	93	110	240	450	2.0	20	7.1	0.34	8.7	3.0	85.9	2.46	0.71	--	3.00	2.00	--	
CO.014	15.1	4	138	157	240	450	1.0	20	2.2	0.15	0.0	2.8	89.3	7.92	0.67	0.84	9.00	4.00	--	
CO.014	15.1	5	186	206	240	600	1.0	20	2.1	0.15	0.0	2.6	94.8	2.68	0.71	0.81	4.50	3.50	--	
CO.040	14.5	1	19	32	240	450	2.0	20	1.8	0.09	0.0	4.0	94.1	1.89	0.71	0.82	2.50	2.00	--	G.C. Calib
CO.040	14.5	2	43	63	220	450	2.0	20	0.7	0.03	0.0	0.7	97.1	2.17	0.91	--	1.00	2.00	--	Shut down
CO.047	15.8	1	21	39	240	450	2.0	20	28.2	1.29	7.7	1.5	89.3	1.47	0.79	0.84	3.14	1.69	24.5	
CO.047	15.8	2			220	450	2.0	20	--	--	--	--	--	--	--	--	--	--	--	Repair G.C
CO.047	15.8	3	94	111	240	450	2.0	20	25.6	1.17	8.9	1.5	88.2	1.38	0.78	--	3.15	2.00	--	
CO.047	15.8	4	141	159	240	450	1.0	20	11.9	0.81	2.9	0.9	94.1	2.13	0.82	0.88	7.33	4.75	--	
CO.047	15.8	5	187	207	240	600	1.0	20	11.8	0.81	2.6	0.8	94.6	2.01	0.82	0.87	7.00	3.60	--	
CO.047	15.8	6	215	226	240	450	2.0	20	24.0	1.10	10.7	1.9	85.7	1.71	0.75	--	3.54	2.13	--	
CO.049	15.6	1	19	39	240	450	2.0	20	30.6	1.41	10.9	1.8	85.7	1.66	0.76	0.82	2.09	1.30	14.0	
CO.049	15.6	2	71	87	220	450	2.0	20	12.0	1.07	2.7	0.9	95.3	1.09	0.81	0.95	4.25	3.25	--	
CO.049	15.6	3	95	111	240	450	2.0	20	29.5	1.37	9.5	1.6	87.6	1.30	0.78	--	2.32	1.40	--	
CO.049	15.6	4	139	159	240	450	1.0	20	12.6	0.87	3.1	1.0	94.1	1.80	0.81	0.86	8.33	4.20	--	
CO.049	15.6	5	187	207	240	600	1.0	20	13.4	0.93	2.6	0.9	94.8	1.68	0.82	0.88	8.33	4.20	37.8	
CO.049	15.6	6	211	231	240	450	2.0	20	24.9	1.16	10.4	1.7	86.5	1.36	0.76	--	2.75	1.75	--	
CO.047	15.6	1	19	33	240	450	2.0	20	28.1	1.30	8.8	1.6	88.1	1.50	0.78	0.85	2.93	1.88	25.9	Repeat R23
CO.047	15.6	2	55	69	220	450	2.0	20	7.4	0.34	1.5	1.2	96.3	1.02	0.76	0.89	3.00	4.67	--	
CO.047	15.6	3	93	159	240	450	2.0	20	25.6	1.19	8.9	1.6	87.8	1.48	0.77	--	3.14	2.00	--	
CO.047	15.6	4	143	159	240	450	1.0	20	10.8	0.75	3.0	1.0	94.2	1.84	0.81	0.94	8.00	4.75	--	
CO.047	15.6	5	189	207	240	600	1.0	20	12.4	0.86	2.2	0.8	95.6	1.39	0.83	0.86	7.33	4.50	36.4	
CO.047	15.6	6	215	231	240	450	2.0	20	23.2	1.08	9.6	1.7	87.4	1.28	0.77	--	3.50	2.07	--	
CO.031	15.9	1	19	39	240	450	2.0	20	30.9	1.41	12.1	1.9	84.9	1.12	0.75	0.83	1.83	1.14	22.4	
CO.031	15.9	2	67	87	220	450	2.0	20	13.6	0.62	3.9	0.9	94.6	0.49	0.80	0.85	4.20	2.67	--	
CO.031	15.9	3	93	111	240	450	2.0	20	29.5	1.35	12.2	2.1	84.6	1.15	0.75	--	1.97	1.25	--	
CO.031	15.9	4	141	159	240	450	1.0	20	12.9	0.88	3.6	1.1	94.3	1.11	0.80	0.88	7.75	4.00	--	
CO.031	15.9	5	189	207	240	600	1.0	20	13.9	0.95	3.5	1.0	94.4	1.12	0.81	0.85	6.80	3.71	30.1	
CO.031	15.9	6	221	230	240	450	2.0	20	26.6	1.22	12.0	2.2	84.9	0.96	0.74	--	2.30	1.43	--	

Table I
(Continued)

SUMMARY OF M3 SBCR RUN RESULTS

)Unless otherwise noted, total flow is ca.15 L/min. STP, or 3 cm/sec linear gas flow.

)Conversion is total CO conversion over the period (Z).

)Conversion and selectivities are calculated using N2 as an internal standard in the GC analysis of the offgas.

)Prod. rate: Rate for production of total hydrocarbons, C1+ (kg/kg cat., hr).

)Alpha: Based on GC analysis of offgas and liquid product.

Run No	Cat. No	Cat. wt, g	Per No	Time Start	Time Stop	Temp C	Pres psi	H2: CO	Synfl cc/hr	Conv. %	Prod. Rate	Selectivities				Alpha GC	Alpha Liq	Olefin C3	Paraffin C4	Olefins C5-18, %	Comments
27	CO.029	15.9	1	23	39	240	450	2.0	20	28.3	1.27	8.3	1.6	87.9	2.21	0.77	0.84	3.40	2.20	27.3	
27	CO.029	15.9	2	71	87	220	450	2.0	20	9.5	0.43	1.7	1.1	96.0	1.23	0.80	0.89	5.67	3.00	--	
27	CO.029	15.9	3	99	111	240	450	2.0	20	25.7	1.16	7.7	1.6	88.8	1.86	0.78	--	4.00	2.36	--	
27	CO.029	15.9	4	150	159	240	450	1.0	20	12.0	0.82	1.9	0.9	95.4	1.88	0.83	0.90	8.33	4.75	--	
27	CO.029	15.9	5	191	207	240	600	1.0	20	12.1	0.82	1.7	0.9	95.6	1.75	0.83	0.89	7.67	4.75	39.9	
27	CO.029	15.9	6	222	230	240	450	2.0	20	23.7	1.08	8.2	1.7	88.5	1.60	0.78	--	3.92	2.67	--	
28	COW.01	15.0	1	19	36	240	450	2.0	20	1.1	0.05	0.0	12.	83.9	4.23	0.58	--	3.33	2.50	--	Shut down

Table II

DATE: 06/29/94

M3 SBCR RUN RESULTS

COMPARISON OF CATALYST ACTIVITY AT SIMILAR RUN CONDITIONS

Period No.	Temp.	Pres.	H2/CO Ratio
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1	240 C	450psi	2.0

a) Total flow is ca.15 L/min. STP, or 3 cm/sec linear gas flow.

Flows: N2-563 SLH, H2-225 SLH, CO-112.5 SLH

b) Conversion is total CO conversion over the period (%).

c) Conversion and selectivities are calculated using N2 as an internal standard in the GC analysis of the offgas.

d) Prod. rate: Rate for production of total hydrocarbons, C1+ (kg/kg cat.,hr)

e) Alpha: Based on GC analysis of offgas and liquid product.

Run No	Cat. No	Cat. wt,g	Conv. %	Prod. Rate	Selectivities %C1	%C2	%C3+	%CO2	Alpha GC	Alpha Liq	Olefin/Paraf C3	C4	Olefins C6-18,%
5	CO.003	15.1	31.7	1.53	16.7	2.4	79.8	1.2	0.71	--	1.30	0.60	18.2
6	CO.011	15.3	14.3	0.67	7.6	1.6	89.4	1.4	0.78	0.83	4.17	2.57	21.7
7	CO.012	15.8	13.9	0.63	6.1	1.5	90.6	1.7	0.80	0.89	4.00	2.57	17.5
8	CO.015	15.0	28.3	1.37	12.7	2.0	84.1	1.2	0.76	0.80	1.61	1.07	19.6
9	CO.011	15.0	18.5	0.89	8.8	1.7	88.8	0.8	0.78	0.83	3.18	1.85	20.3
11	CO.017	15.0	27.2	1.32	11.2	1.8	85.9	1.1	0.77	0.80	2.09	1.20	30.8
12	CO.018	15.6	33.8	1.56	9.7	2.0	86.6	1.7	0.75	0.85	1.81	1.13	21.0
13	CO.016	14.7	26.4	1.31	(1)	1.7	89.3	0.7	0.78	0.81	2.00	1.41	21.7
14	CO.019	15.2	13.9	0.66	(2)	1.7	97.2	0.7	0.80	0.86	5.33	2.67	26.6
15	CO.005	14.7	27.1	1.34	7.9	1.6	89.7	0.8	0.79	0.82	2.30	1.38	23.1
16	CO.002	15.4	30.1	1.42	12.5	2.5	83.9	1.1	0.75	0.80	1.00	0.66	17.5
17	CO.025	15.6	26.6	1.24	10.7	2.1	86.4	0.8	0.76	0.82	2.25	1.47	21.7
18	CO.004	15.0	33.9	1.64	15.3	2.4	80.9	1.4	0.74	0.79	1.17	0.78	20.3
19	CO.021	15.6	23.2	1.08	9.4	2.0	88.0	0.7	0.77	0.82	2.56	1.54	20.3
20	CO.041	15.8	25.3	1.16	11.0	2.1	86.0	0.9	0.76	0.84	2.94	1.61	20.3
21	CO.014	15.1	8.5	0.40	8.3	3.5	85.8	2.4	0.74	0.83	2.75	1.67	17.5
22	CO.040	14.5	1.8	0.09	0.0	4.0	94.1	1.9	0.71	0.82	2.50	2.00	--
23	CO.047	15.8	28.2	1.29	7.7	1.5	89.3	1.5	0.79	0.84	3.14	1.69	24.5
24	CO.049	15.6	30.6	1.41	10.9	1.8	85.7	1.7	0.76	0.82	2.09	1.30	14.0
25	CO.047	15.6	28.1	1.30	8.8	1.6	88.1	1.5	0.78	0.85	2.93	1.88	25.9
26	CO.031	15.9	30.9	1.41	12.1	1.9	84.9	1.1	0.75	0.83	1.83	1.14	22.4
27	CO.029	15.9	28.3	1.27	8.3	1.6	87.9	2.2	0.77	0.84	3.40	2.20	27.3
28	COW.01	15.0	1.1	0.05	0.0	12.	83.9	4.2	0.58	--	3.33	2.50	--

Note: Catalyst Run 9 screened thru 170 x 400 mesh.

Catalysts For Runs 11 thru 20, and 23 thru 28 screened thru 150 x 400 mesh.

Catalysts for Runs 21 and 22 screened thru 100 x 400 mesh.

(1) Weak TCD filaments in G.C. CH4 peaks smaller than expected.

(2) Internal valve in G.C. leaked. CH4 peak undetected.

Table III

DATE: 06/29/94

M3 SBCR RUN RESULTS

COMPARISON OF CATALYST ACTIVITY AT SIMILAR RUN CONDITIONS

Period No.	Temp.	Pres.	H ₂ /CO Ratio
-----	-----	-----	-----
2	220 C	450psi	2.0

a) Total flow is ca.15 L/min. STP, or 3 cm/sec linear gas flow.

Flows: N₂-563 SLH, H₂-225 SLH, CO-112.5 SLH

b) Conversion is total CO conversion over the period (%).

c) Conversion and selectivities are calculated using N₂ as an internal standard in the GC analysis of the offgas.

d) Prod. rate: Rate for production of total hydrocarbons, C₁+ (kg/kg cat.,hr)

e) Alpha: Based on GC analysis of offgas and liquid product.

Run No	Cat. No	Cat. wt,g	Conv. %	Prod. Rate	Selectivities				Alpha GC	Alpha Liq	Olefin/Paraf		Olefin
					%CH ₄	%C ₂	%C ₃ +	%CO ₂			C ₃	C ₄	C ₆ -18,
5	CO.003	15.1	13.2	0.63	5.1	1.0	93.4	0.5	0.82	0.90	4.55	1.89	--
6	CO.011	15.3	5.1	0.23	0.0	0.0	97.2	2.8	0.87	0.82	--	--	--
7	CO.012	15.8	5.1	0.23	0.0	0.2	97.8	2.0	0.89	0.90	--	2.50	--
8	CO.015	15.0	11.5	0.56	4.4	1.0	93.9	0.8	0.81	0.89	3.60	2.14	--
9	CO.011	15.0	6.3	0.31	0.0	1.0	98.6	0.4	0.88	0.93	12.00	1.80	--
11	CO.017	15.0	11.4	0.55	5.0	0.0	94.8	0.2	0.88	0.90	5.00	3.20	--
12	CO.018	15.6	12.6	0.59	2.8	0.0	97.1	0.1	0.90	0.88	--	--	--
13	CO.016	14.7	9.7	0.48	(1)	0.1	99.9	0.0	0.91	0.88	--	--	--
14	CO.019	15.2	3.8	0.18	(2)	1.7	96.7	1.6	0.88	--	--	--	--
15	CO.005	14.7	10.7	0.53	0.0	0.9	98.4	0.7	0.83	0.88	4.25	3.25	--
16	CO.002	15.4	12.8	0.60	4.2	1.3	93.9	0.7	0.80	0.86	2.57	1.63	--
17	CO.025	15.6	8.4	0.39	0.0	1.1	96.9	1.9	0.82	0.92	6.50	3.00	--
18	CO.004	15.0	15.1	0.73	4.1	1.6	94.0	0.3	0.81	0.85	3.83	2.25	--
19	CO.021	15.6	8.3	0.38	0.0	1.3	98.2	0.5	0.82	0.88	4.33	3.33	--
20	CO.041	15.8	9.1	0.41	0.0	1.5	97.8	0.7	0.82	0.91	8.00	2.75	--
21	CO.014	15.1	3.2	0.15	0.0	2.3	85.8	4.3	0.76	0.86	3.50	3.00	--
22	CO.040	14.5	0.7	0.35	0.0	0.7	97.1	2.2	0.91	--	1.00	2.00	--
23	CO.047	15.8	---	---	(3)	---	---	---	---	---	---	---	--
24	CO.049	15.6	12.0	1.07	2.7	0.9	95.3	1.1	0.81	0.95	4.25	3.25	--
25	CO.047	15.6	7.4	0.34	1.5	1.2	96.3	1.0	0.76	0.89	3.00	4.67	--
26	CO.031	15.9	13.6	0.62	3.9	0.9	94.6	0.5	0.80	0.85	4.20	2.67	--
27	CO.029	15.9	9.5	0.43	1.7	1.1	96.0	1.2	0.80	0.89	5.67	3.00	--

Note: Catalyst Run 9 screened thru 170 x 400 mesh.

Catalysts for Runs 11 thru 27 (except Runs 21 and 22) screened through 150 x 400 mesh.

Catalysts for Runs 21 and 22 screened thru 100 x 400.

(1) Weak TCD filaments in G.C. CH₄ peaks smaller than expected.

(2) Internal valve in G.C. leaked. CH₄ peak undetected.

(3) Replaced dual column restrictor valve.

Table IV

DATE: 06/29/94

M3 SBCR RUN RESULTS

COMPARISON OF CATALYST ACTIVITY AT SIMILAR RUN CONDITIONS

Period No.	Temp.	Pres.	H ₂ /CO Ratio
-----	-----	-----	-----
4	240 C	450psi	1.0

a) Total flow is ca. 15 L/min. STP, or 3 cm/sec linear gas flow.

Flows: N₂-562 SLH, H₂-119 SLH, CO-119 SLH

b) Conversion is total CO conversion over the period (%).

c) Conversion and selectivities are calculated using N₂ as an internal standard in the GC analysis of the offgas.

d) Prod. rate: Rate for production of total hydrocarbons, C₁+ (kg/kg cat., hr)

e) Alpha: Based on GC analysis of offgas and liquid product.

Run	Cat.	Cat.	Conv.	Prod.	Selectivities				Alpha	Alpha	Olefin/Paraf		Olefin
No	No	wt, g	%	Rate	%CH ₄	%C ₂	%C ₃ +	%CO ₂	GC	Liq	C ₃	C ₄	C ₆ -18,
---	---	---	---	---	---	---	---	---	---	---	---	---	---
5	CO.003	15.1	13.1	0.95	4.2	1.2	93.3	1.2	0.83	0.88	6.67	3.70	--
6	CO.011	15.3	6.3	0.44	0.4	1.0	95.5	3.1	0.82	0.88	--	--	--
7	CO.012	15.8	3.9	0.26	4.8	2.3	86.3	6.6	0.70	0.85	16.00	3.50	--
8	CO.015	15.0	11.5	0.83	4.8	1.2	92.5	1.5	0.80	0.85	5.60	3.29	--
9	CO.011	15.0	8.0	0.58	1.3	1.3	96.3	1.2	0.82	0.87	7.00	2.83	--
11	CO.017	15.0	11.6	0.84	5.0	0.0	93.9	1.2	0.82	0.86	25.00	2.88	--
12	CO.018	15.6	12.4	0.86	3.3	0.0	95.0	1.7	0.80	0.86	--	--	--
13	CO.016	14.7	10.9	0.81	(1)	0.8	97.7	0.3	0.84	0.86	--	--	--
14	CO.019	15.2	--	--	(2)	--	--	--	0.80	--	--	--	--
15	CO.005	14.7	11.6	0.85	0.0	1.1	97.5	1.4	0.82	0.85	7.00	4.60	--
16	CO.002	15.4	12.6	0.89	4.4	1.6	92.8	1.2	0.79	0.84	4.43	2.88	--
17	CO.025	15.6	10.3	0.71	0.8	1.2	96.7	1.3	0.82	0.93	7.67	4.25	--
18	CO.004	15.0	14.7	1.06	4.1	1.2	93.2	1.4	0.80	0.83	6.17	3.75	--
19	CO.021	15.6	9.9	0.69	1.7	1.4	95.5	1.4	0.81	0.83	6.00	3.80	--
20	CO.041	15.8	12.7	0.88	1.9	1.2	95.9	1.0	0.83	0.86	9.00	4.20	--
21	CO.014	15.1	2.2	0.15	0.0	2.8	89.3	7.9	0.67	0.84	9.00	4.00	--
23	CO.047	15.8	11.9	0.81	2.9	0.9	94.1	2.1	0.82	0.88	7.33	4.75	--
24	CO.049	15.6	12.6	0.87	3.1	1.0	94.1	1.8	0.81	0.86	8.33	4.20	--
25	CO.047	15.6	10.8	0.75	3.0	1.0	94.2	1.8	0.81	0.90	8.00	4.75	--
26	CO.031	15.9	12.9	0.88	3.6	1.1	94.3	1.1	0.80	0.88	7.75	4.00	--
27	CO.029	15.9	12.0	0.82	1.9	0.9	95.4	1.9	0.83	0.90	8.33	4.75	--

Note: Catalyst Run 9 screened thru 170 x 400 mesh.

Catalysts for Runs 11 thru 20 and Run 27 (except Runs 21 and 22) screened thru 150 x 400 mesh.

Catalysts for Runs 21 and 22 screened thru 100 x 400 mesh.

(1) Weak TCD filaments in G.C. CH₄ peaks smaller than expected.

(2) Internal valve in G.C. leaked. CH₄ peak undetected.

Table V

DATE: 06/29/94

M3 SBCR RUN RESULTS

COMPARISON OF CATALYST ACTIVITY AT SIMILAR RUN CONDITIONS

Period No.	Temp.	Pres.	H2/CO Ratio
-----	-----	-----	-----
5	240 C	600psi	1.0

a) Total flow is ca.15 L/min. STP, or 3 cm/sec linear gas flow.

Flows: N2-562 SLH, H2-119 SLH, CO-119 SLH

b) Conversion is total CO conversion over the period (%).

c) Conversion and selectivities are calculated using N2 as an internal standard in the GC analysis of the offgas.

d) Prod. rate: Rate for production of total hydrocarbons, C1+ (kg/kg cat.,hr)

e) Alpha: Based on GC analysis of offgas and liquid product.

Run No	Cat. No	Cat. wt,g	Conv. %	Prod. Rate	Selectivities				Alpha GC	Alpha Liq	Olefin/Paraf Olefin		
---	---	---	---	---	%CH4	%C2	%C3+	%CO2	---	---	C3	C4	C6-18, %
5	CO.003	15.1	13.4	0.97	3.9	1.1	93.7	1.3	0.81	--	5.26	3.45	30.1
6	CO.011	15.3	6.7	0.46	0.2	0.9	96.0	2.9	0.84	0.89	12.00	3.67	27.3
7	CO.012	15.8	4.3	0.28	0.1	2.1	91.6	6.3	0.75	0.82	8.50	3.50	--
8	CO.015	15.0	12.4	0.90	4.9	0.8	93.6	0.7	0.84	0.85	5.20	3.14	30.8
9	CO.011	15.0	8.7	0.63	1.4	1.1	96.4	1.1	0.83	0.87	5.00	2.67	30.5
11	CO.017	15.0	11.6	0.84	4.2	0.0	94.7	1.2	0.86	0.86	24.00	1.63	21.0
12	CO.018	15.6	13.0	0.90	3.2	0.0	94.9	1.9	0.80	0.85	--	--	38.5
13	CO.016	14.7	11.4	0.85	(1)	0.5	99.2	0.3	0.92	0.86	--	--	32.2
14	CO.019	15.2	5.9	0.41	(2)	1.5	96.1	2.4	0.80	--	--	--	--
15	CO.005	14.7	23.0	0.90	0.0	1.0	97.7	1.3	0.83	0.85	7.00	4.40	36.4
16	CO.002	15.4	13.1	0.92	3.6	1.4	93.9	1.1	0.81	0.84	4.29	2.75	25.2
17	CO.025	15.6	19.9	0.81	9.3	1.1	96.5	1.1	0.83	0.88	8.00	4.25	32.9
18	CO.004	15.0	15.0	1.09	3.6	1.1	94.1	1.2	0.82	0.83	5.67	4.00	33.6
19	CO.021	15.6	11.5	0.80	1.8	1.2	95.8	1.2	0.83	0.85	6.50	3.80	30.8
20	CO.041	15.8	13.2	0.91	2.0	1.0	96.1	0.9	0.84	0.87	7.00	3.50	31.5
21	Co.014	15.1	2.1	0.15	0.0	2.6	94.8	2.7	0.71	0.81	4.50	3.50	23.1
23	CO.047	15.8	11.8	0.80	2.6	0.8	94.6	2.0	0.82	0.87	7.00	3.60	38.5
24	CO.049	15.6	13.4	0.92	2.6	0.9	94.8	1.7	0.82	0.88	8.33	4.20	37.8
25	CO.047	15.6	12.4	0.86	2.2	0.8	95.6	1.3	0.83	0.86	7.33	4.50	36.4
26	CO.031	15.9	13.9	0.95	3.5	1.0	94.4	1.1	0.81	0.85	6.80	3.71	30.1
27	CO.029	15.9	12.1	0.82	1.7	0.9	95.6	1.8	0.83	0.89	7.67	4.75	39.9

Note: Catalyst Run 9 screened thru 170 x 400 mesh.

Catalysts for Runs 11 thru 27 (except Runs 21 and 22) screened thru 150 x 400 mesh.

Catalyst for Run 21 screened thru 100 x 400 mesh.

(1) Weak TCD filaments in G.C. CH4 peaks smaller than expected.

(2) Internal valve in G.C. leaked. CH4 peak undetected.

Table VI

SUMMARY OF M4 SBCR RUN RESULTS

Unless otherwise noted, total flow is ca.15 L/min. STP, or 3 cm/sec linear gas flow.

Conversion is total CO conversion over the period (%).

Conversion and selectivities are calculated using N2 as an internal standard in the GC analysis of the offgas.

Prod. rate: Rate for production of total hydrocarbons, C1+ (kg/kg cat., hr).

Alpha: Based on GC analysis of offgas and liquid product.

Cat. No	Cat. wt, g	Per No	Time Start	Time Stop	Temp C	Pres psi	H2: CO	Synfl cc/hr	Conv. %	Prod. Rate	Selectivities				Alpha GC	Alpha Liq	Olefin/Paraf		Olefins C6-18, %	Comments
											IC4	IC2	IC3+	IC02			C3	C4		
C0.002	15.2	1	25	35	240	450	2.0	20	29.4	1.42	17.3	2.2	79.4	1.01	0.73	0.82	0.91	0.60	17.5	
C0.002	15.2	2	73	83	220	450	2.0	20	11.8	0.56	4.7	1.0	93.7	0.59	0.81	0.90	2.71	1.63	--	G.C.Calib
C0.002	15.2	3	97	107	240	450	2.0	20	26.4	1.28	16.0	3.1	80.1	0.88	0.73	--	0.98	0.66	--	
C0.002	15.2	4	145	155	240	450	1.0	20	11.6	0.83	3.9	2.4	92.8	0.84	0.81	0.87	4.29	3.14	--	G.C.Calib
C0.002	15.2	5	182	203	240	600	1.0	20	12.9	0.92	4.0	1.5	93.5	0.91	0.81	0.82	4.29	2.75	24.5	
C0.002	15.2	6	217	226	240	450	2.0	20	24.2	1.17	17.1	3.1	79.0	0.83	0.71	--	1.03	0.70	--	
C0.024	15.4	1	20	37	240	450	2.0	20	25.5	1.21	8.6	2.0	89.0	0.43	0.79	0.84	2.93	1.93	21.7	
C0.024	15.4	2	68	85	220	450	2.0	0	9.5	0.45	0.0	2.1	97.6	0.27	0.83	0.91	5.33	4.00	--	No Synfl
C0.024	15.4	3	92	109	240	450	2.0	0	23.7	1.13	9.5	2.1	88.0	0.45	0.77	--	2.81	1.88	--	
C0.024	15.4	4	140	157	240	450	1.0	0	10.3	0.73	0.5	1.6	97.2	0.71	0.83	0.87	8.33	4.75	--	
C0.024	15.4	5	188	205	240	600	1.0	0	11.3	0.80	0.9	1.5	97.0	0.65	0.83	0.87	6.50	3.80	36.4	
C0.024	15.4	6	212	229	240	450	2.0	0	21.5	1.02	9.3	2.3	87.9	0.50	0.76	--	2.93	2.07	--	
C0.035	15.4	1	16	37	240	450	2.0	20	24.8	1.18	8.5	2.1	89.0	0.47	0.78	0.84	3.13	1.94	23.1	
C0.035	15.4	2	68	85	220	450	2.0	20	8.8	0.42	0.0	2.3	97.4	0.31	0.82	--	5.33	4.00	--	
C0.035	15.4	3	99	109	240	450	2.0	20	23.5	1.11	8.7	2.1	88.6	0.61	0.77	--	3.07	1.94	--	
C0.035	15.4	4	136	157	240	450	1.0	20	10.4	0.73	0.9	0.0	98.4	0.65	--	0.83	--	--	--	G.C.Calib
C0.035	15.4	5	184	205	240	600	1.0	20	10.7	0.76	0.7	1.4	97.1	0.75	0.84	0.88	6.25	4.50	27.3	
C0.035	15.4	6	212	228	240	450	2.0	20	19.4	0.92	7.8	2.3	89.4	0.56	0.79	--	3.08	1.77	--	
C0.028	15.4	1	23	40	240	450	2.0	20	21.2	1.00	6.1	1.6	91.3	1.01	0.81	0.83	4.86	3.00	28.7	
C0.028	15.4	2	67	88	220	450	2.0	20	6.6	0.31	0.0	1.9	97.4	0.72	0.83	0.90	5.50	4.00	--	
C0.028	15.4	3	95	112	240	450	2.0	20	20.1	0.94	5.8	1.6	91.6	1.02	0.81	--	4.25	2.67	--	
C0.028	15.4	4	139	160	240	450	1.0	20	9.2	0.65	0.0	1.3	97.3	1.46	0.85	0.88	9.50	3.75	--	
C0.028	15.4	5	189	208	240	600	1.0	20	9.5	0.67	0.0	1.1	97.5	1.36	0.85	0.88	6.00	3.50	40.6	
C0.028	15.4	6	213	232	240	450	2.0	20	18.0	0.84	5.7	1.6	91.5	1.12	0.80	--	4.57	2.88	--	
C0.043	15.4	1	18	39	240	450	2.0	20	13.0	0.61	3.7	1.8	93.4	1.06	0.79	0.85	5.60	3.17	27.3	
C0.043	15.4	2	53	63	220	450	2.0	20	4.3	0.20	0.0	1.4	96.3	2.25	0.81	0.91	4.00	3.00	--	
C0.043	15.4	3	94	111	240	450	2.0	20	12.3	0.58	3.0	1.5	93.9	1.58	0.80	--	5.00	2.83	--	
C0.043	15.4	4	138	159	240	450	1.0	20	5.2	0.37	0.0	0.0	99.4	0.64	0.83	0.89	7.00	5.00	--	
C0.043	15.4	5	191	207	240	600	1.0	20	5.9	0.41	0.0	2.2	94.8	2.99	0.82	0.89	6.00	3.75	30.1	G.C.Calib
C0.043	15.4	6	215	231	240	450	2.0	20	10.2	0.47	4.7	2.1	91.4	1.79	0.78	--	5.50	3.20	--	Repair G.C
C0.006	15.0	1	19	40	240	450	2.0	20	2.7	0.13	0.1	0.2	98.8	1.75	0.67	0.85	3.33	2.33	16.1	Shut down

Table VI
(Continued)

SUMMARY OF M4 SBCR RUN RESULTS

a) Unless otherwise noted, total flow is ca. 15 L/min. STP, or 3 cm/sec linear gas flow.

b) Conversion is total CO conversion over the period (%).

c) Conversion and selectivities are calculated using N2 as an internal standard in the GC analysis of the offgas.

d) Prod. rate: Rate for production of total hydrocarbons, C1+ (kg/kg cat., hr).

e) Alpha: Based on GC analysis of offgas and liquid product.

Run No	Cat. No	Cat. wt., g	Per No	Time Start	Time Stop	Temp C	Pres psi	H2: CO	Synfl cc/hr	Conv. %	Prod. Rate	Selectivities				Alpha GC	Alpha Liq	Olefin/Paraf		Olefins C6-18, %	Comments
												ZCH4	ZC2	ZC3+	ZCO2			C3	C4		
9	CO.048	15.4	1	19	40	240	450	2.0	12	19.1	0.90	9.9	1.6	87.4	1.05	0.77	0.88	3.60	2.09	20.3	
9	CO.048	15.4	2	70	84	220	450	2.0	12	6.1	0.28	1.8	1.0	95.2	1.93	0.80	0.91	3.67	3.00	--	
9	CO.048	15.4	3	93	111	240	450	2.0	20	17.8	0.84	10.1	1.7	86.9	1.33	0.77	--	3.30	2.10	--	
9	CO.048	15.4	4	139	159	240	450	1.0	20	8.2	0.57	2.3	1.0	93.8	2.98	0.82	0.90	8.50	4.33	--	
9	CO.048	15.4	5	189	207	240	600	1.0	20	11.9	0.83	2.7	0.9	94.4	1.93	0.84	0.89	5.75	3.20	14.0	
9	CO.048	15.4	6	217	226	240	450	2.0	20	24.2	1.17	17.1	3.1	79.0	0.83	0.71	--	1.03	0.70	--	
10	CAL.02	15.9	1	19	40	240	450	2.0	20	34.5	1.58	12.9	2.0	83.9	1.23	0.75	0.84	1.66	1.06	21.0	
10	CAL.02	15.9	2	69	88	220	450	2.0	20	14.9	0.68	4.6	0.9	94.0	0.47	0.81	0.88	4.40	2.29	--	
10	CAL.02	15.9	3	91	112	240	450	2.0	20	34.2	1.57	12.6	2.0	84.4	1.00	0.75	--	1.71	1.06	--	
10	CAL.02	15.9	4	139	160	240	450	1.0	20	14.6	1.00	4.6	1.1	93.3	0.97	0.80	0.88	7.20	4.00	--	
10	CAL.02	15.9	5	187	201	240	600	1.0	20	16.4	1.12	4.2	1.0	94.0	0.89	0.82	0.86	5.83	3.86	35.7	
10	CAL.02	15.9	6	215	230	240	450	2.0	20	30.9	1.42	13.3	2.1	83.7	0.90	0.74	--	1.90	1.21	--	
11	CAL.03	15.6	1	19	40	240	450	2.0	20	29.7	1.39	13.5	2.1	83.4	1.08	0.74	0.86	1.65	1.03	18.2	ShutDown
12	CO.053	15.9	1	22	40	240	450	2.0	20	34.2	1.56	12.6	2.0	84.2	1.23	0.75	0.83	1.60	1.00	24.5	
12	CO.053	15.9	2	69	88	220	450	2.0	20	14.4	0.66	4.3	1.0	94.3	0.48	0.81	0.89	4.20	2.67	--	
12	CO.053	15.9	3	93	112	240	450	2.0	20	34.0	1.56	13.4	2.2	83.2	1.21	0.74	--	1.50	0.94	--	
12	CO.053	15.9	4	150	152	240	450	1.0	20	13.3	0.91	4.3	1.2	93.3	1.18	0.80	0.89	6.60	3.71	--	
12	CO.053	15.9	5	189	208	240	600	1.0	20	15.6	1.06	4.0	0.9	94.0	1.01	0.82	0.87	5.50	3.57	32.2	
12	CO.053	15.9	6	223	231	240	450	2.0	20	29.8	1.37	12.8	2.0	84.3	0.94	0.75	--	1.89	1.10	--	
13	CO.054	15.7	1	23	40	240	450	2.0	20	10.4	0.48	4.7	1.8	92.3	1.17	0.78	0.86	5.75	4.00	25.9	
13	CO.054	15.7	2	71	88	220	450	2.0	20	0.2	0.01	0.0	19.	60.8	19.5	0.33	0.94	8.00	5.00	--	
13	CO.054	15.7	3	102	112	240	450	2.0	20	10.6	0.49	4.5	1.5	92.8	1.23	0.79	--	5.50	3.75	--	
13	CO.054	15.7	4	143	160	240	450	1.0	20	5.2	0.36	0.0	1.2	97.0	1.85	0.83	0.95	6.00	4.50	--	
13	CO.054	15.7	5	191	208	240	600	1.0	20	5.0	0.34	0.0	1.3	96.9	1.78	0.82	0.93	6.50	3.33	30.8	
13	CO.054	15.7	6	223	230	240	450	2.0	20	8.8	0.40	4.7	2.0	91.7	1.54	0.78	--	5.00	3.50	--	

Table VII

DATE: 07/01/94

M4 SBCR RUN RESULTS

COMPARISON OF CATALYST ACTIVITY AT SIMILAR RUN CONDITIONS

Period No.	Temp.	Pres.	H2/CO Ratio
-----	-----	-----	-----
1	240 C	450psi	2.0

a) Total flow is ca. 15 L/min. STP, or 3 cm/sec linear gas flow.

Flows: N2-563 SLH, H2-225 SLH, CO-112.5 SLH

b) Conversion is total CO conversion over the period (%).

c) Conversion and selectivities are calculated using N2 as an internal standard in the GC analysis of the offgas.

d) Prod. rate: Rate for production of total hydrocarbons C1+ (kg/kg cat., hr).

e) Alpha: Based on GC analysis of offgas and liquid product.

Run No	Cat. No	Cat. wt, g	Conv. %	Prod. Rate	Selectivities				Alpha GC	Alpha Liq	Olefin/Paraf		Olefin C6-18, %
					%CH4	%C2	%C3+	%CO2			C3	C4	
3	CO.002	15.2	29.4	1.42	17.3	2.3	79.4	1.01	0.73	0.82	0.91	0.60	17.5
4	CO.024	15.4	25.5	1.21	8.6	2.0	89.0	0.43	0.79	0.84	2.93	1.93	21.7
5	CO.035	15.4	24.8	1.18	8.5	2.1	89.0	0.47	0.78	0.84	3.13	1.94	23.1
6	CO.028	15.4	21.2	1.00	6.1	1.6	91.3	1.01	0.81	0.83	4.86	3.00	28.7
7	CO.043	15.4	13.0	0.61	3.7	1.8	93.4	1.06	0.79	0.85	5.60	3.17	27.3
8	CO.006	15.0	2.7	0.25	0.1	0.2	98.8	1.75	0.67	0.85	3.33	2.33	16.1
9	CO.048	15.4	19.1	0.90	9.9	1.6	87.4	1.05	0.77	0.88	3.60	2.09	20.3
10	CAL.02	15.9	34.5	1.58	12.9	2.0	83.9	1.23	0.75	0.81	1.66	1.06	21.0
11	CAL.03	15.6	29.7	1.39	13.5	2.1	83.4	1.08	0.74	0.86	1.65	1.03	18.2
12	CO.053	15.9	34.2	1.56	12.6	2.0	84.2	1.23	0.75	0.83	1.60	1.00	24.5
13	CO.054	15.7	10.4	0.48	4.7	1.8	92.3	1.17	0.78	0.86	5.75	4.00	25.9

Note: Catalysts for Runs 3 thru 13 (except 8) screened through 150 x 400 mesh.

Catalyst for Run 8 screened thru 100 x 400 mesh.

Table VIII

DATE: 07/01/94

M4 SBCR RUN RESULTS

COMPARISON OF CATALYST ACTIVITY AT SIMILAR RUN CONDITIONS

Period No.	Temp.	Pres.	H ₂ /CO Ratio
-----	-----	-----	-----
2	220 C	450psi	2.0

a) Total flow is ca.15 L/min. STP, or 3 cm/sec linear gas flow.

Flows: N₂-563 SLH, H₂-225 SLH, CO-112.5 SLH

b) Conversion is total CO conversion over the period (%).

c) Conversion and selectivities are calculated using N₂ as an internal standard in the GC analysis of the offgas.

d) Prod. rate: Rate for production of total hydrocarbons C₁+ (kg/kg cat.,hr).

e) Alpha: Based on GC analysis of offgas and liquid product.

Run No	Cat. No	Cat. wt,g	Conv. %	Prod. Rate	Selectivities				Alpha GC	Alpha Liq	Olefin/Paraf		Olefin
---	---	---	---	---	%CH ₄	%C ₂	%C ₃ +	%CO ₂	---	---	C ₃	C ₄	C ₆₋₁₈ , %
3	CO.002	15.2	11.8	0.56	4.7	1.0	93.7	0.59	0.81	0.90	2.71	1.63	--
4	CO.024	15.4	9.5	0.45	0.0	2.1	97.6	0.27	0.83	0.91	5.33	4.00	--
5	CO.035	15.4	8.8	0.42	0.0	2.3	97.4	0.31	0.82	--	5.33	4.00	--
6	CO.028	15.4	6.6	0.31	0.0	1.9	97.4	0.72	0.83	0.90	5.50	4.00	--
7	CO.043	15.4	4.3	0.20	0.0	1.4	96.3	2.25	0.81	0.91	4.00	3.00	--
9	CO.048	15.4	6.1	0.28	1.8	1.0	95.2	1.93	0.80	0.91	3.67	3.00	--
10	CAL.02	15.9	14.9	0.68	4.6	0.9	94.0	0.47	0.81	0.88	4.40	2.29	--
12	CO.053	15.9	14.4	0.66	4.3	1.0	94.3	0.48	0.81	0.89	4.20	2.67	--
13	CO.054	15.7	0.2	0.01	0.0	20.	60.8	19.5	0.33	0.94	8.00	5.00	--

Note: Catalysts for Runs 3 through 12 screened thru 150 x 400 mesh.

Table IX

DATE: 07/01/94

M4 SBCR RUN RESULTS

COMPARISON OF CATALYST ACTIVITY AT SIMILAR RUN CONDITIONS

Period No.	Temp.	Pres.	H ₂ /CO Ratio
-----	-----	-----	-----
4	240 C	450psi	1.0

a) Total flow is ca.15 L/min. STP, or 3 cm/sec linear gas flow.

Flows: N₂-562 SLH, H₂-119 SLH, CO-119 SLH

b) Conversion is total CO conversion over the period (%).

c) Conversion and selectivities are calculated using N₂ as an internal standard in the GC analysis of the offgas.

d) Prod. rate: Rate for production of total hydrocarbons C₁+ (kg/kg cat.,hr).

e) Alpha: Based on GC analysis of offgas and liquid product.

Run No	Cat. No	Cat. wt,g	Conv. %	Prod. Rate	Selectivities				Alpha GC	Alpha Liq	Olefin/Paraf Olefin		
					%CH ₄	%C ₂	%C ₃ +	%CO ₂			C ₃	C ₄	C ₆₋₁₈ , %
3	CO.002	15.2	11.6	0.83	3.9	2.4	92.8	0.84	0.81	0.87	4.29	3.14	--
4	CO.024	15.4	10.3	0.73	0.5	1.6	97.2	0.71	0.83	0.87	8.33	4.75	--
5	CO.035	15.4	10.4	0.73	0.9	0.0	98.4	0.65	--	0.83	--	--	--
6	CO.028	15.4	9.2	0.65	0.0	1.3	97.3	1.46	0.85	0.88	9.50	3.75	--
7	CO.043	15.4	5.2	0.37	0.0	0.0	99.4	0.64	0.83	0.89	7.00	5.00	--
9	CO.048	15.4	8.2	0.57	2.3	1.0	93.8	3.00	0.82	0.90	8.50	4.33	--
10	CAL.02	15.9	14.6	1.00	4.6	1.0	93.3	0.97	0.80	0.88	7.20	4.00	--
12	CO.053	15.9	13.3	0.91	4.3	1.2	93.3	1.18	0.80	0.89	6.60	3.71	--
13	CO.054	15.7	5.2	0.36	0.0	1.2	97.0	1.85	0.83	0.95	6.00	4.50	--

Note: Catalysts for Runs 3 through 13 screened thru 150 x 400 mesh.

Table X

DATE: 07/01/94

M4 SBCR RUN RESULTS

COMPARISON OF CATALYST ACTIVITY AT SIMILAR RUN CONDITIONS

Period No.	Temp.	Pres.	H2/CO Ratio
-----	-----	-----	-----
5	240 C	600psi	1.0

a) Total flow is ca. 15 L/min. STP, or 3 cm/sec linear gas flow.

b) Conversion is total CO conversion over the period (%).

Flows: N2-562 SLH, H2-119 SLH, CO-119 SLH

c) Conversion and selectivities are calculated using N2 as an internal standard in the GC analysis of the offgas.

d) Prod. rate: Rate for production of total hydrocarbons C1+ (kg/kg cat., hr).

e) Alpha: Based on GC analysis of offgas and liquid product.

Run	Cat.	Cat.	Conv.	Prod.	Selectivities				Alpha	Alpha	Olefin/Paraf Olefin		
No	No	wt, g	%	Rate	%CH4	%C2	%C3+	%CO2	GC	Liq	C3	C4	C6-18, %
3	CO.002	15.2	12.9	0.92	4.0	1.5	93.5	0.91	0.81	0.82	4.29	2.75	24.5
4	CO.024	15.4	11.3	0.80	0.9	1.5	97.0	0.65	0.83	0.87	6.50	3.80	36.4
5	CO.035	15.4	10.7	0.76	0.7	1.4	97.1	0.75	0.84	0.88	6.25	4.50	27.3
6	CO.028	15.4	9.5	0.67	0.0	1.1	97.5	1.36	0.85	0.88	6.00	3.50	40.6
7	CO.043	15.4	5.9	0.41	0.0	2.2	94.8	2.99	0.82	0.89	6.00	3.75	30.1
9	CO.048	15.4	11.9	0.83	2.7	0.9	94.4	1.93	0.84	0.89	5.75	3.20	14.0
10	CAL.02	15.9	16.4	1.12	4.2	1.0	94.0	0.89	0.82	0.86	5.83	3.86	35.7
12	CO.053	15.9	15.6	1.06	4.0	0.9	94.0	1.0	0.82	0.87	5.50	3.57	32.2
13	CO.054	15.7	5.0	0.34	0.0	1.3	96.9	1.78	0.82	0.93	6.50	3.33	30.8

Note: Catalysts for Runs 3 through 13 screened thru 150 x 400 mesh.