EXECUTIVE SUMMARY

During the 9th quarter of the project, results have led to a number of important conclusions.

Vista B γ-Al$_2$O$_3$ still seems to be the best alumina to use. A catalyst prepared by Calsicat using Condea alumina, which has a better initial particle size distribution for the SBCR requiring less sieving and discarding, was found to exhibit a much lower activity than a similar formulation using Vista B. The exact cause of this difference is not known since the Condea alumina has a suitable level of S impurities, surface area, and pore structure.

All catalysts prepared to date by Calsicat using Vista B have exhibited excellent particle size retention characteristics in the SBCR. Typical particle size reducctions have been in the range of 0.5-2.0%.

SBCR trials made with a Co catalyst prepared by Calsicat, reduced, and coated with Soya confirmed that Soya/wax coating of the reduced catalysts does not protect the Co catalysts sufficiently from reoxidation to eliminate the need for gas phase reduction prior to SBC reaction. Co catalysts appear not to be able to be reduced suitably when suspended in a hydrocarbon liquid phase.

The optimum loading of Zr in Co/SiO$_2$ catalysts in order to promote activity is on the order of 4 wt%. Loadings as high as 15 wt% cause a significant reduction in overall activity. This has been confirmed by both fixed-bed and SBC reaction results. La promotion of Co/SiO$_2$ appears to give a rate enhancement similarily to Zr in the gas phase; however, promotion of Co/SiO$_2$ at the level of 8.5 wt% La gave lower activity in the SBCR than Co/SiO$_2$ without La.

Catalyst pretreatment effects appear to be a function of preparation. For example, catalysts

iv

prepared using an organic solution seem to give higher activity when reduced directly and not calcined.

Co loadings of 30 wt% on alumina exhibit significantly higher activities than 20 wt% Co catalysts in excess of a linear increase. It is suggested that this is due to the fact that a greater percent of the additional Co is reducible to the metal. It is known that there is ca.3 wt% of the Co which goes to form Co aluminates. Another significant portion of the Co is not able to be completely reduced due to interaction with the oxide support. However, these effects are mostly apparent in the initial 10 wt% Co loading.

Using a mixture of Co/Al_2O_3 and a WGS catalyst results in higher activity and Co_2 formation in the SBCR. Using 15 g of the Co catalyst and either 0, 5, or 15 g of CuCr/Al_2O_3 produced CO conversions of 27.1, 29.3, and 35.8%, respectively, and CO_2 selectivities of 0.8, 2.0, and 6.3%, respectively, at 240°C.

Finally, significant work has focussed on pushing conversion to higher levels. This has been achieved by raising the temperature and lowering the flow rate. To date, the maximum conversion obtained has been 62.9% at 260°C and 540 SL/h (20% N_2 in a H_2 + CO mixture). However, low flow rates and higher temperatures result in greater heat being released than can be in many cases adequately removed since the SBCR does not have an internal heat exchanger. This results in difficulties in temperature control. In addition, the highly active and selective catalysts developed to date for use at lower temperatures start to lose activity above 240°C. This loss of activity is especially great above 260°C.

I. 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.

II. 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

1

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.

2

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, pretreatment, 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.

III. 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.

IV. SUMMARY OF WORK ACCOMPLISHED THIS QUARTER

Seven (7) 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. Six (6) new catalysts were tested for their F-T synthesis performance.

An investigation of the effect of pretreatment in various atmospheres (calcination in air or nitrogen prior to reduction in hydrogen, direct reduction without prior calcination, and reduction-oxidation-reduction (ROR)) of a selected number of catalysts upon their performance for F-T synthesis was continued during this period.

A paper on "Zirconia Promotion of Fischer-Tropsch Cobalt catalysts: Behavior in Fixed-Bed and Slurry Bubble Column Reactors" was submitted for the preprints of the 209th ACS National Meeting, Division of Fuel Chemistry, Symposium on Synthesis Gas Chemistry, April 2-6, 1995 in Anaheim, CA.

Under subtask 2.2 during this reporting period a total of 11 runs were made in the two slurry bubble column reactors with eleven catalysts, including five on alumina, two from Calsicat, one WGS blend, and three on silica support. Four high CO conversion runs were made. Data were compiled to compare the CO conversions and product selectivities of the methane reduction catalysts.

4

V. 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 given in Table 1 with their compositions. The last column of Table 1 indicates whether the catalyst has already been prepared. Out of the 78 catalysts listed in Table 1, two (CAL.09-CAL.10) were prepared by Calsicat. Seven (7) new Co catalysts (highlighted in Table 1) were formulated and prepared during this period. The detailed formulations of the new catalysts are given in Appendix A.

Co.057, is similar to Co.055, with SiO_2 as the support instead of Al_2O_3. Co.058 and Co.059, both alumina-supported catalysts, are similar to Co.055 and Co.015, but without Re or Ru promoters. Co.063, also an alumina-supported catalyst, is similar to Co.034, but with La_2O_3 replacing ZrO_2 as the oxide promoter. These four catalysts were formulated in order to investigate further the effects of La_2O_3 on the catalytic properties of Co. La_2O_3 addition was found in previous formulations to enhance significantly the activity of cobalt for F-T synthesis.

Co.060-Co.062, all alumina-supported catalysts, were formulated with 30% Co loading in order to achieve higher conversion levels in the slurry bubble column reactor.

CAL.09-CAL.10 were formulated with the same composition as that of Co.047 which was selected as the low methane catalyst for the reproducibility test. They were both prepared in small

5

batches for formulation check and determination of the best pretreatment to adopt for the preparation of the larger batches to be used for the reproducibility tests. CAL.09 was calcined in nitrogen, reduced in hydrogen, and protected in soya instead of the paraffin wax used in some of the previous samples (CAL.07 and CAL.08). CAL.10 was prepared with a different alumina (Condea) than the one (Vista-B) used so far during this project. The Condea alumina was selected for its narrow particle size distribution in the range required for slurry bubble column applications.

Under Subtask 1.3 five (5) new Co catalysts with a water-gas shift component were prepared. CoW.08 and CoW.09 are similar to catalysts which had been prepared previously, but with different loadings of the various metals. CoW.08, similar to CoW.05, but with 30% Co, was prepared by pre-impregnating the alumina with Cu-CrO and calcining this support precursor at 750 °C, before incorporating the cobalt. CoW.09, similar to CoW.06, but with 10% Cu and 8% Cr, was prepared in a similar way. CoW10-CoW12 are all Co-Fe based catalysts with other promoters (Ru and K) on either alumina or silica. The list of these catalysts is given in Table 2 with their composition, and the detailed formulations are included in Appendix A.

c. Catalyst Pretreatment (Subtask 1.5)

The investigation of the effects of pretreatment on the catalytic properties of a selected number of catalysts (Co.004, C0.015, Co.017, Co.053, Co.055 and Co.056) was continued during this period. Except for Co.053, all the catalysts were promoted with La_2O_3 and Ru or Re in the case of Co.055. The effects of pretreatment in various atmosphere (calcination in air or in nitrogen prior to reduction in H_2, direct reduction in H_2 without prior calcination, and reduction-oxidation-reduction (ROR)) were addressed. The results are included in subtask 2.1 which summarizes the results

6

obtained when these catalysts were tested in the fixed bed reactor.

d. Catalyst Characterization (Subtask 1.6)

(1) Physical Properties

Table 3 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 H_2 chemisorption is given in Table 4. Metal dispersions and particle sizes of CAL.09 and CAL.010 were determined by CO chemisorption carried out at Calsicat. Co.004, Co.015, Co.053, and Co.055 were characterized by static hydrogen chemisorption at the University of Pittsburgh following different pretreatments.

(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 a previous quarterly report. All the TPR results obtained so far are summarized in Table 4.

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 previous quarterly reports. Six (6) new catalysts (Co.044, Co.045, Co.056, Co.057, Co.060, CAL.10) were tested for the first time during this reporting period. Catalysts Co.004 (run #6-8), Co.015 (run #3), Co.017 (run #3), Co.053 (run #4-6), and Co.055 (run #4-7) were also retested following the different pretreatment procedures described in Subtask 1.5.

The performances of all these catalysts (highlighted in Table 5) at steady state are compared in Table 5 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.044 and Co.045 were tested in order to investigate the effect of Zr loading on the catalytic properties of promoted Co/SiO$_2$ catalysts. These results and those obtained previously with similar formulations but different Zr loadings, indicate that Zr enhanced the activity of cobalt for F-T synthesis when it is pre-impregnated on the support. However, Zr loadings greater than 4 wt% did not seem to provide any significant effect beyond what was observed at the 4% level. Co.045 with its 15 wt% of Zr showed even lower activity for F-T synthesis than the catalysts containing 4 (Co.045) or 8.5 wt% (Co.024) of Zr.

Co.056 and Co.057, both SiO$_2$-supported catalysts, were tested in order to investigate the effect of La$_2$O$_3$ promotion on the catalytic properties of Co. The fixed-bed reactor results show that

8

La$_2$O$_3$ promotion had a similar enhancing effect on the activity of Co/SiO$_2$ catalysts for F-T synthesis to the effect observed with Zr promotion.

Co.060 was tested as part of an ongoing study of the effect of Co loading. The preliminary results indicate that, as the Co loading is increased beyond the 20 wt% level used in most of the catalysts formulated so far in this project, the additional cobalt interacts less with the support, thus resulting in a higher rate of syngas conversion per unit weight of Co.

Co.004, Co.015, Co.017, Co.053 and Co.055 were retested following various pretreatments prior to the standard reduction and reaction procedures. The results indicate that not only the pretreatment environment but also the preparation method (aqueous vs organic) may play a major role in determining the activity of these catalysts. For the catalysts prepared entirely by aqueous impregnation, the pretreatment environment (air, nitrogen, hydrogen, or ROR) did not seem to have any effect on the catalysts activity. However, when at least on step in the catalyst preparation involved an impregnation with an organic solution of one of the metal precursors, the catalyst exhibited a very high activity when it was directly reduced without prior calcination.

Finally, the last trial catalyst prepared at Calsicat, CAL.10, was also tested using the standard reaction conditions. It had a lower activity than that obtained with similar catalysts prepared with Vista-B alumina (e.g. CAL.05 or Co.047). The reason for such a behavior is not yet understood.

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

1. Run Chronolgy

During this reporting period a total of 11 runs were performed in the SBCR's, Runs M3-30 through 34 and M4-22 through 27. A chronology of the experimental runs performed in the two

slurry bubble column reactors - M3 and M4 - is given in Appendix C. All comparisons of CO conversions and CH_4 selectivities discussed in this chronology were obtained from results obtained at the initial startup conditions, i.e. 240°C temperature, 450 psi pressure, and 2/1 H_2/CO feed gas ratio.

A complete summary of all runs made in the M3-SBCR is given in Table I in Appendix D. Four tables of data were prepared in order to compare catalyst activities for Runs 30 to 34 in M3-SBCR at the same run conditions (see Tables II, III, IV, and V in Appendix D).

A complete summary of all runs made in the M4-SBCR are given in Table VI, Appendix D. Four tables were prepared to compare catalyst activities for Runs 22 to 27 in M4-SBCR at the same run conditions (see Tables VII, VIII, IX, and X in Appendix D).

2. Discussion of Results

(a) Water-Gas Shift Activity Test

Run 22 was made in the M4-SBCR to evaluate the effect of adding a blend of equal amounts of two catalysts: 15.5 gm of Catalyst No. WGS.09 (water-gas shift catalyst) and 15.0 gm of Catalyst No. Co.005 (methane reduction). The CO conversion at startup conditions was considerably higher than observed with Catalyst Blend A in Run 14 in M4-SBCR, 35.6% vs. 29.3% (see Table 6). Also, the CO_2 selectivity was much higher, 6.3% vs. 2.0%. Some water-gas shift activity has occurred with this catalyst blend as demonstrated by the higher CO_2 yield and increase in CO conversion. Water-gas shift activity was also observed at all other run conditions.

(b) High CO Conversion Runs

Four high CO conversion runs were made during this reporting period. Three runs were made with a larger charge of catalyst, approximately 30 gm of Catalyst No. CO.053, and one run was made

10

with a normal charge of 15 gm of CALSICAT Catalyst No. CAL.10.

Run No. 30 in the M3-SBCR was started with a charge of 29.6 gm of Catalyst No. Co.053. The CO conversion at startup conditions was 41.8%, the same as observed in Run 29. CO conversion increased to 46.9% at 260°C, but dropped to 41.4% at 280°C. The CO conversion did not change even at temperatures up to 320°C. The run was terminated when the gas preheater plugged when the heater temperature reached 550°C. It is speculated that the catalyst activity began to decrease above 260°C. Both recovered catalysts from Runs 29 and 30 contained small amounts of iron that came from carbonyls in the CO feed gas. The lead oxide filtration beds need to be changed more frequently to prevent iron from poisoning the catalysts. A summary of the data for Run 30 is given in Table 7.

Run No. 24 in the M4-SBCR was started with 28.5 gm of Catalyst No. Co.053, see Table 8. The CO conversion at startup conditions was 50.4%, which was the highest conversion observed to date. Raising the temperature to 260°C increased the CO conversion only to 55.3% (see Period 3). Lowering the total gas rate from 900 to 540 standard liters per hour ("SLH") with 20% N_2 in the feed gas yielded a CO conversion of 62.9% with a methane selectivity of 23.2%. At this point, the reactor temperature could not be controlled since there is no way to remove the heat of reaction from inside the SBCR reactor because there is no internal heat removal device. The heat of reaction can be removed only by lowering the feed gas temperature or increasing the inert gas (N_2) flow or some combination of both.

Run No. 33 in the M3-SBCR was started with 31.4 gm of a third batch of Catalyst No. Co.053. The CO conversion at startup conditions was 41.4%, which was the same as Runs 29 and 30 in the M3-SBCR. Several run periods were made in which the reactor pressure was lowered to

11

300 psi, the total feed gas rate was lowered to 400 SLH, and finally the reactor temperature was raised to 260°C (see Table 9). The CO conversion reached a maximum of only 49.2%. The conversion dropped to 16.1% when the reactor was returned to startup conditions. It is believed that most of the catalyst activity was lost at the higher temperature, 260°C. Alumina based catalysts have been found to be more sensitive to higher temperatures.

Run No. 26 in the M4-SBCR was started with a charge of 15.6 gm of Catalyst No. CAL.10. This catalyst which was received from Calsicat contained 20 wt% Co with 0.5% K and 0.5% Ru on Condea alumina. The initial CO conversion was only 21.9% which was 5% lower than other Calsicat catalysts made with Vista B alumina support. Several run periods were made to investigate the effect of lowering the total gas flow from 900 to 436 SLH and nitrogen concentration in the feed gas from 60% to 6% (see Table 10). The CO conversion decreased rather than increased as expected. This run will be repeated with a larger amount of a more active catalyst.

A lot has been learned from these five runs about obtaining high CO conversion levels. To obtain high conversions in the SBCR, the following recommendations should be investigated:

o Operate at the lowest total gas feed rate that can keep the catalyst

suspended.

o Operate at the lowest N_2 feed rate. Some N_2 is necessary since it is

used as an internal standard for calculating conversions.

o Investigate higher cobalt loading on the catalyst.

o Increase catalyst loading in the SBCR.

o Determine maximum reaction temperature where catalyst begins to deactivate.

Further attempts to operate at higher CO conversions will be made during the next reporting

period using the above recommendations.

(c) Calsicat Catalyst Test Run

One run was made with a catalyst supplied by Calsicat that was hydrogen reduced and coated with Soya. The CO conversion at the initial startup conditions was only 17.4% (see Run 23 in M4-SBCR of Table 11). All of the wax coated catalysts supplied by Calsicat have shown low catalyst activity.

(d) Miscellaneous Runs Made to Evaluate the Effects of Various Promoters

One run was made with a catalyst similar to base case Catalyst No. Co.001 (20% Co, 1% Re, 1% La_2O_3, plus 0.13% K on alumina) but without K (see Run 31 in M3-SBCR in Table 12). The CO conversion was high, 30% as expected, but the CH_4 selectivity was also high, 23.7%. The addition of K should reduce the methane selectivity, but would also reduce catalyst activity as reported previously.

A run was made with a catalyst containing 20% cobalt plus 8.5% La_2O_3 on silica support. The initial CO conversion was only 11.4%, see Run 25 in M4-SBCR in Table 6. The addition of a large amount of La_2O_3 had a negative effect on the catalyst activity, reducing the CO conversion about 7% (see Run No. 9 in M3 on Table 12).

One run was made to determine the effect of adding a larger amount of Zr on a cobalt-silica catalyst. Using a 15% Zr promoted catalyst yielded a 21% CO conversion compared to 25% CO conversion with an 8.5% Zr promoted catalyst, and 23.2% CO conversion with 0.7%Zr promoter (see Runs 17, 19, and 32 in M3-SBCR, Table 12). Adding a larger amount of Zr decreased catalyst activity. The optimum concentration of Zr needed can be determined by testing additional catalysts with Zr concentrations in the range of 0.7% to 15 wt%.

13

Another run was made to evaluate the effect of K concentration on catalyst activity. Catalyst No. Co.050 which contained 20% Co, 0.5% Ru, 8.5% Zr, and 0.1% K on silica yielded a CO conversion of 20.4%. The CO conversion and CH_4 selectivity were the same as obtained with Catalyst Co.048 that contained 0.3% K, see Runs 9 and 27 in the M4-SBCR on Table 6. The optimum amount of K to add for methane reduction without significantly lowering catalyst activity is somewhere between 0.1 and 0.3 wt%. Adding 0.5% K decreased catalyst activity significantly, see Run 7 in Table 6.

The last catalyst tested this period was a 30 wt% Co on alumina support with no additives or promoters. The CO conversion was high, 31.4%, but the CH_4 selectivity was also high, 14%, which is also in the expected range (see Run 34 in M3-SBCR on Table 12). This will be used as a basis for comparing similar catalysts with various additives and promoters.

3. Catalyst Recovery Analyses

The catalysts charged for all runs, except for Run 20 in M3 and 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 13. 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 reduction in particle size are also given in Table 13. The particle size at the lower 10% pass-through point of the sample for both the charged and recovered catalysts are also given in Table 13.

A comparison of the mean volume diameters of the total feed and recovered samples 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 titanium supported catalyst had the highest reaction, 18.2% (see Run 8 in the M4-SBCR in Table 13).

Seven catalysts prepared by Calsicat have been tested in the SBCR and the particle size reduction was very low, 0.5% for CAL.08 and 1.6% for CAL.05. All these catalysts were prepared on a Vista B gamma-alumina catalyst support which has shown good resistance to attrition in the SBCR's.

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 catalyts, 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 13). 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.

VI. 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. The fixed-bed reactor testing of the series of Al_2O_3- and SiO_2 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;

15

- X-ray diffraction before reduction, after reduction, and after slurry bubble column reaction;

- Temperature programmed reduction (TPR);

- Temperature programmed desorption (TPD).

C. New catalyst formulations will be generated in order to pursue the effect of selectivity promoters.

D. The investigation of the effect of pretreatment conditions including calcination and reduction will be completed.

E. Additional runs will be made in the SBCR's to maximize the CO conversion.

F. Reproducibility tests and aging runs will be made on catalyst obtained from Calsicat.

G. Several catalyst formulations and mixtures will be tested for water-gas shift activity.

VII. ASSESSMENT OF PROSPECTS FOR FUTURE PROGRESS

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

17