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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 H2/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, 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

Six new catalysts under subtask 1.2 and one under subtask 1.3 were formulated and prepared during this period in order to investigate the effect of certain promoters such Pd, Ru and Fe on the deactivation properties of Al_2O_3-supported Co during F-T synthesis at high temperatures.

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. Four new catalysts were tested for their F-T synthesis performance. The main focus of the fixed bed testing during this period was the investigation of the deactivation behavior of Co catalysts during F-T synthesis at high temperatures, as well as the effect of certain promoters on this deactivation process. In addition, a couple of runs were carried out using regenerated catalysts used in either the fixed-bed reactor or the slurry bubble column reactor in order to elucidate the nature of the deactivation process as well as the extent of its reversibility.

During this reporting period, a total of 10 runs were performed in the slurry bubble column reactor. Out of these 10 runs, eight were miscellaneous runs carried to evaluate the effects of various promoters on the performance of Co catalysts in F-T synthesis under standard conditions. Some of these runs were also carried out at high temperature in order to evaluate the catalyst resistance to deativation. Two runs were carried out for ca.1000 h for the first one and 500 h for the second one as part of the catalyst aging studies (Task 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 on page 17 with their compositions. The last column of Table 1 indicates whether the catalyst has already been prepared. Of the 89 catalysts listed in Table 1, five new Co catalysts and one Fe catalyst (highlighted in Table 1) were formulated and prepared in-house during this period. The detailed formulations of the new catalysts are given in Appendix A.

Co.066 (with 15% Co, 0.5% Ru, and 5% Fe on alumina), Co.067 (with 20% Co, 2% Pd on alumina), Co.068 (with 20% Co, 1% Pd on alumina), and Co.069 (with 20% Co, 2% Ru on alumina) were prepared this quarter in order to investigate the effect of certain promoters such Pd, Ru and Fe on the deactivation properties of Al_2O_3-supported Co during F-T synthesis at higher temperatures than those usually used with Co catalysts. Carbon deposition resulting from enhanced Boudouard reaction at high temperature is believed to be the main cause of deactivation of the Co F-T catalysts. The choice of the promoters used in these formulations was based on their intrinsic ability to enhance the hydrogenation reactions while slowing down the Boudouard reaction under the conditions used in F-T synthesis. Two different loadings of Pd (1 and 2 wt%) were used, as well as a higher Ru loading (2 wt%) than the one used so far with most of the previously formulated catalysts.

Co.070 (13% Co on alumina) was formulated with lower Co loading than used previously in order to complete the investigation on the effect of Co loading.

One alumina-supported iron catalyst (Fe.01) (30 wt% Fe and 1.5 wt% Cu) was also prepared for comparison purposes.

Under Subtask 1.3, one new FeCo-based catalyst (CoW.13) was prepared during this period. An updated list of all the catalysts formulated so far within Subtask 1.3 (including those catalysts listed in previous quarterly reports) is given in Table 2 on page 23 with their composition. The detailed formulation of the new catalyst is given in Appendix A. The catalyst was formulated with equal loadings of Co and Fe and was promoted with Ru. This catalyst was also formulated in order to investigate the effect of Fe on the catalysts deactivation by carbon deposition under high temperature reaction conditions.

c. Catalyst Characterization (Subtask 1.6)

Physical Properties

Table 3 on page 24 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.

Static Hydrogen Chemisorption

An updated summary of the properties of the Co catalysts as determined by H_2 chemisorption is given in Table 4 on page 27. .

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 on page 27.

B. TASK 2: CATALYST TESTING

a. Subtask 2.1 - Fixed Bed Reaction Studies:

The reaction conditions and procedure were described in previous quarterly reports. Four (4) new catalysts (Co.064, Co.066-Co.068)) were tested for the first time during this reporting period. Catalysts Co.025 (run #2-2a), Co.053 (run #12-14), Co.055 (run #8-8a) and catalyst CoW.05 (run #3-3a) were also retested in order to investigate the effect of reaction temperature on the deactivation of Co catalysts during F-T synthesis and determine the cause of such deactivation. For this purpose, the reaction was initiated at 220°C and allowed to proceed for ca. 20h to reach steady-state. After dilution of the reactant stream with Ar (H_2/CO/Ar = 2/1/1), the temperature was increased to 280°C over a period of 2.5h and CO hydrogenation was continued at 280°C for another 20-40h. The performances of all these catalysts (highlighted in Table 5) at steady state are compared in Table 5 on page 31 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.064, a Ru- and Zr-promoted Co/Al_2O_3 catalyst was tested as part of the study of the effect of promoters on alumina-supported F-T Co catalysts. Previous results with a similar catalyst without the Ru promoter (Co.034) showed that ZrO_2 promotion alone enhanced significantly the activity of Co catalysts for F-T synthesis. It is clear from the results obtained for Co.064 that Ru promotion results in another significant increase in activity from that obtained with Co.034.

As reported previously, most of the highly active catalysts deactivated promptly as soon as they were subjected to relatively high temperatures resulting from excessive and uncontrolled release of the heat of reaction. The preliminary investigation of the effect of reaction temperature on the performance of Co catalysts during F-T synthesis described in the previous quarterly report indicated that the Co catalysts tested (Co.005 and Co.053) were very sensitive to temperature and deactivated rather quickly at temperatures above 240°C. In order to elucidate the nature of this deactivation process, the catalysts which had undergone significant deactivation after high temperature (280°C) reaction in either the fixed bed reactor or the slurry bubble column reactor were regenerated and retested in the fixed bed reactor. In one experiment (Co.053, run #13) the catalyst was regenerated *in-situ* by calcination in flowing air at 300°C for 10h, re-reduced in flowing H_2 at 350°C for 10h and the CO hydrogenation carried out again at 220°C to check for the reversibility of the deactivation process. In another experiment (Co.053, run #14), a catalyst which had been run for several days in the slurry bubble column reactor was again regenerated in flowing air 300°C for 10h and re-reduced in flowing H_2 at 350°C for 10h before carrying out CO hydrogenation at 220°C. In both cases the catalysts recovered completely their initial activity. In addition, reactions at very high H_2/CO ratios and high temperatures showed very little deactivation. All these results suggest that the deactivation of the Co catalysts during F-T synthesis at high temperatures above 240°C in both the fixed-bed and the slurry bubble column reactors was mainly the result of carbon deposition on the catalyst surface.

A second series of experiments was carried out to investigate the effect of certain promoters (Zr, La, Cr, and Re) as well as the effect of another support such as silica on the deactivation characteristics of Co catalysts during F-T synthesis. Co.025, Co.055, and CoW.05 were used for this purpose. In addition, preliminary results were also obtained with the newly formulated catalysts containing Pd or Fe (Co.066-Co.068). All these catalysts were tested as indicated, first at 220°C than at 280°C, while monitoring their deactivation. The results suggest that the deactivation process and rate are similar to those of the alumina-supported catalysts tested previously (Co.005 and Co053), and that none of the promoters helps to slow down the rate of carbon formation at high temperatures above 240°C. In addition, promotion with high loadings of Fe or Pd resulted in catalysts with relatively lower activity and higher methane selectivity. The only exception was Co.068 with 1% Pd which had adequate activity and selectivity as well as lower deactivation rate at high temperature. Further investigation of the deactivation characteristics of these Co catalysts using olefin hydrogenation and Boudouard reactions may help in the formulation of new Co catalysts which are more resistant to deactivation at high temperature.

b. Subtask 2.2 - Slurry Bubble Column Reactor Testing

1. Run Chronology

During this reporting period a total of 10 runs were performed in the SBCR's, Runs M3-40 through 47, and M4-33 and 35. 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 conversion and CH_4 selectivities discussed in this chronology were obtained from results obtained at the initial startup conditions -- 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 2 to 47 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 is given in Table VI, Appendix D. Four tables were prepared to compare catalyst activities for Runs 3 to 33 in M4-SBCR at the same run conditions (see Tables VII, VIII, IX, and X in Appendix D). A summary of all runs using catalysts made by Calsicat are given in Table XI, Appendix D.

2. Discussion of Results

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

One run was made with a catalyst containing 20% Co and 8.5% La_2O_3 on alumina support (see Run 40 in M3-SBCR in Table 6). The CO conversion at startup conditions was only 8.7% which is considerably lower than the 28% CO conversion obtained with Catalyst No. Co.058 (Run 38 in M3) that contained 1.0% La_2O_3. Too much La_2O_3 reduced the catalyst activity significantly.

One run was made with a catalyst containing 30% Co with 0.5% Ru and 1.5% K on alumina support (see Run 41 in M3-SBCR in Table 6). The CO conversion was only 6.6% which is considerably lower than that obtained with similar catalysts containing 0.1, 0.3, and 0.5% K. Apparently the amount of K added was too high and reduced catalyst activity significantly.

Another run was made with a catalyst containing 20% Co with 0.5% Ru plus 0.3% K and 8.5% Zr (see Run 42 in M3-SBCR in Table 6). The CO conversion at startup conditions was 27.6%, almost identical to that obtained with Catalyst No. Co.047 which contained no Zr. The total hydrocarbon product rates and CH_4 selectivities were also identical. The addition of Zr to alumina supported catalysts has little or no effect on the catalyst activity.

A fourth run was made with a catalyst containing 13% Co with no promoters on alumina support. The CO conversion at startup conditions was 22.8% with a CH_4 selectivity of 10.9% (see Run 47 in M3-SBCR in Table 6). The CO conversion with a 20% Co catalyst with no promoters was 27.1% and 31.4% with a catalyst containing 30% Co (see Runs M3-15 and M3-34 in Table 6). The catalyst activity does not appear to be directly proportional to the Co concentration.

One run was made with a combination cobalt/water-gas-shift catalyst containing 20% Co, 5.0% Cu and 4.0% Cr on alumina support (see Run 46 in M3-SBCR in Table 6). The CO conversion at startup conditions was quite low, 4.0%, with a CH_4 selectivity of 10.9%. The CO conversion increased to 14.0% at 280°C and 19.4% at 300°C. The CH_4 selectivity increased to 44.2% and 54.4%, respectively. This catalyst is unsatisfactory because of its low activity and high selectivity to lower carbon numbers.

The following conclusions can be made on the effects of adding various promoters based on the preceding experiments:

- The addition of a large amount of La_2O_3 on an alumina supported catalyst considerably reduced the catalyst activity.
- The addition of a high amount of K (1.5 wt%) greatly reduced the catalyst activity.
- The addition of Zr to alumina supported catalysts has little or no effect on catalyst activity.
- The catalyst activity is not directly proportional to the amount of Co added.

(b) Catalysts Containing Cobalt and Iron

One run was made with a catalyst (CoW.12) containing 10% Co, 10% Fe, and 0.5% Ru on silica support (see Run 43 in M3-SBCR in Table 6). The initial CO conversion was only 6.1% with a CH_4 selectivity of 20.3% and CO_2 selectivity of 7.3%. The CO conversion increased to 24.5% at

280°C with a CH_4 selectivity of 25.6% and CO_2 selectivity of 11%. The combination Co plus Fe catalyst gave low CO conversion levels plus high CH_4 and CO_2 selectivities on the silica support.

A second run was made with a catalyst (CoW.11) containing 10% Co, 10% Fe, with 0.5% Ru and 0.5% K on an alumina support (see Run 44 in M3-SBCR in Table 6). The CO conversion at startup conditions was lower, 4.7%, as expected. CO conversion increased to 25.1% at 280°C while the CH_4 selectivity increased to 25.6%. The addition of K reduced the CO conversion slightly, but also reduced the CH_4 selectivity significantly.

A third run was made with a catalyst (Fe.01) containing 30% Fe plus 1.5% Cu on a silica support (see Run 45 in M3-SBCR in Table 6). This was the only iron catalyst without Co that has been tested. The initial CO conversion was very low, 3.4%, while the CH_4 selectivity was too low to detect by our GC. The CO conversion increased to 14.5% at 280°C with a CH_4 selectivity of 23.3%, and a CO conversion of 19.0% and CH_4 selectivity of 26.7% at 300°C reaction temperature. In general, the iron catalyst had much lower activity and produced more CH_4 and CO_2 than cobalt catalysts in the slurry bubble catalytic reactors.

(c) Investigation of the Effect of Temperature on Catalyst Deactivation

Several of the catalysts from the SBCR runs were submitted for total carbon analysis (see Table 7). All catalysts were run at 240°C, except Run 3029 which was run at 260°C and Run 3030 had reached 320°C reaction temperature. In general, most recovered catalysts contained 5 to 9% carbon. The high temperature run, Run 3030, contained 13.5% carbon. One silica supported catalyst, containing 8.5% Zr, contained only 0.52% carbon. It has been demonstrated in fixed bed reactor studies that Co catalysts are very sensitive to temperature. They deactivate very fast at temperatures at or above 240°C. A test was made in the fixed bed reactor where one of these catalysts was recalcined and H_2 reduced, and yielded catalyst activity similar to the fresh catalyst charge.

3. Catalyst Recovery Analyses

The catalysts charged for all runs, except for Runs 4, 20, and 29 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 8. 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 8. 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 8.

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 reduction, 18.2% (see Run 8 in the M4-SBCR in Table 8).

Eleven 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 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 8). 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.

B. TASK 4: CATALYST AGING STUDIES

a. First Aging Test at 240°C

Run No. 33 in M4-SBCR was started on March 6th with a charge of 15.9 gm of Calsicat Catalyst No. CAL.13 and shut down on April 20th after 1069 hours on stream (see Table 9). The initial CO conversion at startup conditions was 28.1% with a CH_4 selectivity of 6.4% and a THC production rate of 1.28 gm C_1+/g cat/hr. The CO conversion dropped steadily over the first 600 hours, and then leveled off for the remainder of the run, see Figure 1. The production rate loss paralleled the CO conversion loss (see Figure 2), but the CH_4 selectivity rose from 6.5 to 9.5% over the run duration (see Figure 3). The average catalyst deactivation rate based on the total CO converted over the entire run was 30.1 gm CO/Kg catalyst/hr.

b. Second Aging Test at 212°C

Run No. 35 in M4-SBCR was started on June 14th with a charge of 25.0 gm of Calsicat Catalyst No. CAL.13 to attempt a catalyst aging run at lower reaction temperatures (see Table 10). The CO conversion was a little too high at 220°C (17.2%), so the reaction temperature was held at 212°C where the initial CO conversion averaged 8.9%. After 240 hours on-stream the CO conversion leveled out at 7.4% for the remainder of the run, a total of 524 hours on-stream (see Figure 4). The production rate started at 0.26 gm C_1+/gm cat/hr at initial startup, but leveled out at 0.22 g/g/hr at

225 hours for the remainder of the run (see Figure 5). The CH_4 selectivity at 212°C was too low to measure, so it was reported as 0% (see Figure 6). The average rate of deactivation of the catalyst was about 5.96 gm CO/Kg cat/hr per Kg CO converted. The deactivation rate at 240°C was 30.1 gm CO/Kg cat/hr per Kg CO converted; thereby demonstrating that catalyst deactivation is mainly dependent on temperature rather than on total syngas consumed.

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 completed.

(b) The systematic characterization of all the catalysts will be completed 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) The investigation of the effect of temperature on catalyst deactivation will be completed.

(d) An investigation of the effect of certain promoters on the Boudouard reaction and on olefin hydrogenation reactions will be carried out

(e) Additional runs will be made in the SBCR's to test the newly formulated catalysts.

(f) An additional aging run will be made on catalyst obtained from Calsicat.

(g) An iron catalyst supplied by DOE will be tested in the SBCR after an optimization of the conditions simulating the previous LaPorte run with the same catalyst..

(e) The writing of the final report will be started.

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.