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TECHNOLOGY DEVELOPMENT FOR COBALT F-T CATALYSTS

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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 H₂/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 objectives of this project are 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.

The objective of Task 1 "Catalyst Development" is to prepare cobalt-based F-T catalysts that show improvement over existing Co catalysts in two areas: low methane selectivity and water-gas shift activity.

The objective of Task 2 "Catalyst Testing" is to determine those catalyst formulations which meet desired specific pre-determined performance characteristics.

The objective of Task 3 is to ensure that the catalyst formulations developed in Task 1 are reproducible and can be scaled up.

The objective of Task 4 is to determine the aging rates of three selected catalysts, one each from Subtasks 1.2, 1.3, and 1.4.

The objective of Task 5 is to prepare a preliminary design and cost estimate for a continuous facility for the preparation of at least 500 pounds/week of the best cobalt catalysts identified in previous tasks.

IV. SUMMARY OF WORK ACCOMPLISHED THIS QUARTER

A computer search of both the open and the patent literature was conducted in order to ascertain the current state of cobalt-based catalyst technology for F-T synthesis. An initial screening of the literature was carried out by examining the abstracts obtained from these searches. The main objective of this initial screening was the selection of the most pertinent publications for this work.

From the initial evaluation of the patent literature a series of benchmark catalysts was established and their formulations were developed. The main chemicals (metal precursors and promoters) and supports required for the catalyst preparation have been ordered and received. Elemental analyses of these chemicals are being carried out in order to determine and confirm the level of impurities.

Laboratories for both the catalyst screening experiments and catalyst characterization have been commissioned. Refurbishment and refitting of the slurry bubble column reactor facility was underway this period.

V. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

A. Task 1: Catalyst Development

Technology Assessment (Subtask 1.1)

A computer search of both the open and the patent literature was conducted in order to ascertain the current state of cobalt-based catalyst technology for F-T synthesis. Two series of literature searches were conducted, one dealing specifically with cobalt catalysts for F-T synthesis and the other focusing on the preparation and/or characterization of supported cobalt catalysts including those not used for F-T synthesis.

The first search used key words such as "cobalt (or Co) catalyst and Fischer-Tropsch, and/or syngas (or synthesis gas) conversion, and/or hydrocarbon synthesis, and/or CO (or carbon monoxide) hydrogenation". This search resulted in 653 references (183 patents and 470 journal articles). The second computer search used key words such as "supported cobalt (or Co) catalysts, and preparation or characterization, not Molybdenum (or Mo), not HDS, not hydrodesulfurization. This search generated 289 references (50 patents and 239 journal articles). The computer searches covered only the literature from 1966 forward to September 1992. Any publication prior to that year and relevant to this work will be obtained through a number of well known review papers and books on F-T synthesis published prior and after 1966.

An initial screening of the literature was carried out by examining the 942 abstracts obtained from these searches. The main objective of this initial screening was the selection of the most pertinent publications for this work. Out of the 230 patent references obtained from the computer search, about 90 were found to be directly related the preparation of cobalt catalysts and their use in FT synthesis. Copies of patents (78 patents) not available within the group have been ordered but not yet received.

Based on a preliminary analysis of the abstracts of the most pertinent patents a distribution among the various patent assignees is given in Table 1. As can be seen in Table 1, most of the patents for Co FT catalysts have been assigned to very few companies, the first four, i.e. Exxon, Shell, Gulf, and Statoil representing the most relevant ones. This preliminary analysis of the patent literature permitted a selection of a number of benchmark catalysts the formulations of which will be based on the patents of these four companies.

A survey of the non-patent literature is in progress: an examination of the 700 abstracts was conducted during this reporting period. Most of the more pertinent publications have been collected. Due to the considerable number of references to be evaluated, it was decided that the best approach in order to render this whole process of literature survey much more useful for catalyst formulation was to establish a database of catalytic properties vs those catalyst parameters which may affect these properties.

The delay in receiving copies of the patents that have been ordered as well as the significant number of publication that have to be analyzed extends the technology assessment task into the next reporting period. However, this should not affect in any way the plans for achieving the contract objectives.

Catalyst Formulation (Subtasks 1.2, 1.3, 1.4)

A list of the main chemicals (metal precursors and promoters) and supports required for the catalyst preparation have been established (Table 2). After contacting various suppliers, a final choice was reached based on various factors such as availability of the required quantities of material, speed of delivery, price, etc. An analysis of these chemicals is being sought in order to determine the concentration of known and possible impurities which may be contained in these chemicals. The elemental analyses to be done on samples of the chemicals are listed in Table 3.

From the preliminary evaluation of the patent literature, a partial series of benchmark catalysts has been established based on patents from Gulf and Statoil listed in Table 1. The compositions and detailed formulations of these benchmark catalysts are given in Table 4 and the appendix, respectively.

B. Task 2: Catalyst Testing

Commissioning of Laboratories

All the necessary modifications were carried out on one of the fixed-bed reactor systems which will be used for the preliminary screening experiments. Reaction and product analysis procedures have been established. A gas chromatograph equipped with both a TCD and a FID will be used for product analysis. A second reactor system will also be modified and made ready to be used if the load on the first reactor system becomes excessive. The data acquisition and analysis system has been improved with the acquisition of a new Spectra-Physics integrator and two 486 computers.

All the systems to be used for catalyst characterization (e.g., chemisorption, TPR/TPD, X-ray diffraction, etc.) are in working order and ready for operation.

Refurbishment and refitting of the laboratory containing the slurry bubble column reactors got underway this period. Procurement of the gas chromatograph and data acquisition system was initiated.

VI. PLANS FOR THE NEXT REPORTING PERIOD

Several tasks are planned for the next reporting period:

(a) As soon as the first series of catalysts (the benchmark catalysts) is received from the catalyst preparation laboratory at U-PARC both the characterization studies and the fixed-bed reaction experiments will be initiated. The following techniques which will be used to characterize systematically all the catalysts produced:

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

(b) The collection of journal articles and patents not already acquired will be continued. The analysis of the literature will be completed and a database of catalytic properties versus those catalyst parameters which may affect these properties will be established.

(c) Based on the information obtained from the literature survey new catalyst formulation will be generated in order to pursue the effect of selectivity promoters.

(d) Refurbishment and refitting of the slurry bubble column reactor units shall be completed next quarter. New reactors and flow meters, gas chromatograph and data acquisition systems should be installed to result in two identical reactors/units with proven capabilities for catalyst testing. Experimentation in the slurry bubble column reactors will get underway with a few "shakedown" runs.

VII. ASSESSMENT OF PROSPECTS FOR FUTURE PROGRESS

Despite the delay for the completion of the first phase of the literature survey, the contract objectives should not be affected. The technical approach which has been proposed remains the same and all the other tasks are proceeding within schedule.

Table 1. Cobalt FT Patent Assignees (1967 - Sept. 1992)

Cobalt FT Patent Assignees	Total No. of Patents	Catalyst Preparation	Process for FT synthesis	Catal. Prep. and Process
Exxon Research and Engineering (USA)	28	6	6	16
Shell Internationale Research Maatschappij B. V. (Neth)	27	6	16	5
Gulf Research and Development Co. (USA)	4	1	1	2
Den Norske Stats Oljeselskap A/S (Norway)	4	2	2	-
British Petroleum Co., PLC (UK)	4	-	-	4
Chevron Research Co. (USA)	3	-	1	2
United States Dept. of Energy (USA)	3	-	-	3
Toyota Central R&D Laboratories, Inc. (Japan)	3	-	-	3
Air Products and Chemicals, Inc. (USA)	2	-	-	2
UOP Inc. (USA)	2	-	-	2
Union Carbide Corp. (USA)	2	-	-	2
Broken Hill Pty. Co. Ltd. (Australia)	2	-	1	1
New Fuel Oil Development Technology Research Assoc. (Japan)	2	-	-	2
Novocherkassk Synthetic Products Plant (U.S.S.R.)	1	-	-	1
Kansi Coke and Chemicals Co., Ltd. (Japan)	1	1	-	-
Mobil Oil Corp. (USA)	1	-	-	1

Table 2. List of Chemicals Ordered for Catalyst Preparation

Chemicals	Purity	Supplier
Cobalt (II) nitrate, $\text{Co}(\text{NO}_3)_2$	ACS Grade	Kodak Chemicals
Ruthenium (III) nitrosyl nitrate, $\text{Ru}(\text{NO})\text{NO}_3 \cdot x\text{H}_2\text{O}$	28% Ru	Alfa, Johnson Matthey
Ru acetylacetonate, $\text{Ru}(\text{AcAc})_3$		"
Perrhenic acid, HReO_4	54-55% Re	"
Dihydrogen hexachloroplatinate $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$	ACS Grade	"
Potassium nitrate, KNO_3	ACS Grade	"
Lanthanum nitrate, $\text{La}(\text{NO}_3)_3$	REacton	"
Zirconium nitrate, $\text{ZrO}(\text{NO}_3)_2$	Puratronic	"
γ -alumina	Vista B	VistaChem

Table 3. Elemental Analyses of Chemicals Used for Catalyst Preparation

Chemicals	Known Impurities	Possible Impurities	Elemental Analyses to be Done
$\text{Co}(\text{NO}_3)_2$	Ni, Cl, SO_4 , Cu, Fe		Ni, Cu, Fe, Cl, P, S
$\text{Ru}(\text{NO})\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$		Cl, Pt	Cl, S, P, Pt, Na
Ru acetylacetonate		Cl, Pt	Cl, Pt, Na
HReO_4		Cl, Mo	Cl, S, P, Na, K, Mo
$\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$	alkali		P, S, Na, K, noble metals, Fe
KNO_3	Cl, I, P, S, Ca, Mg, Pb, Fe, Na		Cl, I, P, S, Ca, Mg, Na, Fe, Pb
$\text{La}(\text{NO}_3)_3$	other RE metals		Ce, other RE metals, Ca, Fe, Cl, P, S
$\text{ZrO}(\text{NO}_3)_2$			Cl, P, S, Na, K, Fe, Ca, other metals?
silica			Cl, P, S, Na, K, Fe
γ -alumina			Cl, P, S, Na, K, Fe
titania			Cl, P, S, Na, K, Fe
zirconia			Cl, P, S, Na, K, Fe

Any constituents listed for the particular chemicals as known impurities should have their concentrations determined.

Additional elements which can be easily screened for should be if that does not increase the cost of analyses significantly.

Other possible impurities which may be present and which might affect results are Li, Ba, Ti, Zr, V, Cr, Mo, W, Mn, Cu, Zn, Hg, B, As, Sb, Bi, Br, and I. If any of these elements can be scanned for at the same time as the others, they should be.

Table 4. Benchmark Catalysts

CAT. NO.	wt% Co	wt% M	wt% Prom.	Support	Basis
Co.001	20%	1% Re	1% La ₂ O ₃ 0.13% K	γ-alumina	U.S. Pat. 4,880,763
Co.002	20%	0.43% Ru	1% La ₂ O ₃	γ-alumina	U.S. Pat. 4,413,064
Co.003	20%	0.5% Ru	1% La ₂ O ₃	γ-alumina	U.S. Pat. 4,413,064
Co.005	20%	0	0	γ-alumina	Base Catalyst

BENCHMARK CATALYST FORMULATIONS

20 wt% Co

1 wt% La_2O_3 [patent uses a mixture of RE oxides (66% La_2O_3 , 24% Nd_2O_3 , 8.2% Pr_6O_{11} , 0.7% CeO_2 and 1.1% other oxides)(Molycorp 5247)]

γ -alumina

Preparation Procedure:

Impregnate the support with an aqueous solution of Co nitrate [$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$], perrenic acid [HReO_4], K nitrate, rare earth nitrate, and using an appropriate quantity to get incipient wetness (ca. 1.2 ml/g) with the desired loading of Co.

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.

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.002: 20 wt% Co
 0.43 wt% Ru (molar ratio of Ru/Co = 1/80)
 1 wt% La₂O₃ (patent suggested 10 wt% La₂O₃ or 2.2 wt% ThO₂)
 -alumina

Based heavily on Beuther et al., U.S. Pat. No. 4,413,064 (1983).

Preparation Procedure:

Calcine the -alumina at 600°C for 2 hrs. Use Vista B alumina. Presieve to 38-63 microns (400-250 mesh).

Impregnate the support with an aqueous solution of Co nitrate [Co(NO₃)₂·6H₂O] using an appropriate quantity to get incipient wetness (ca. 1 ml/g) with the desired loading of Co.

Dry the catalyst precursor for 16 hrs at 120°C.

Impregnate the catalyst precursor with an acetone/ethanol (2:1) solution of lanthanum nitrate hexahydrate and Ru acetylacetonate. The amount of solution may be ca. 2 ml/g.

Remove excess solvent at 0.01 atm and 25-30°C in a rotary evaporator.

Dry at 90°C with moderate stirring. Melting of the nitrate salt and evolution of water occurs at ca. 50-60°C.

Prerreduce 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.

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.

Reduction Procedure before Reaction:

Reduce the catalyst in a pure hydrogen flow of 1000 cc/g/hr by heating to 350°C and holding overnight (for 16 hrs).

Co.003: 20 wt% Co
 0.5 wt% Ru
 1 wt% La₂O₃
 -alumina

Single step non-aqueous

* Based heavily on Beuther et al., U.S. Pat. No. 4,413,064 (1983).

@ modifications for standardization

Preparation Procedure:

@ Use Vista B alumina.

Calcine the -alumina at 750°C for 16 hrs.

@ Presieve to 38-63 microns (400-250 mesh).

Impregnate the support with an acetone solution of Co nitrate [Co(NO₃)₂·6H₂O] (from Kodak), Ru acetylacetonate [Ru(AcAc)₃] (from Alfa), and La nitrate [La(NO₃)₃·H₂O] (from Molycorp C5247) using an appropriate quantity to get incipient wetness (ca. 1 ml/g) with the desired loading of Co. Dissolve first the Ru(AcAc)₃ in the acetone, followed by the La nitrate and then the Co nitrate. Approximately 0.8 cc of acetone will expand to 1 cc upon solution of the salts.

Dry the catalyst precursor in a rotor evaporator at 40°C for at least 30 minutes.

Calcine in air at 300°C for 2 hours.

STOP PREPARATION AT THIS POINT!

Prereduction Procedure:

* Prereduce 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.

* 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.

Reduction Procedure before Reaction:

* Reduce the catalyst in a pure hydrogen flow of 1000 cc/g/hr by heating to 350°C and holding overnight (for 16 hrs).

**Co.005: 20 wt% Co
 γ -alumina**

Non-promoted catalyst similar otherwise to the Re + La-promoted catalyst based on Eri et al., U.S. Pat. No. 4,880,763 (1989).

Preparation Procedure:

Calcine the γ -alumina at 500°C for 10 hrs. Use Vista B alumina. Presieve to 38-63 microns (400-250 mesh).

Impregnate the support 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 (ca. 1.2 ml/g) 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 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.

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