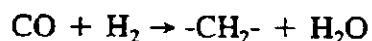


TECHNOLOGY DEVELOPMENT FOR COBALT FISCHER-TROPSCH CATALYST

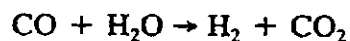
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INTRODUCTION

One of the most promising ways for producing liquid hydrocarbons from coal is via coal gasification to synthesis gas, followed by Fischer-Tropsch (FT) synthesis to convert the syngas to a mixed product consisting primarily of straight chain hydrocarbons. The basic stoichiometry of the FT synthesis may be summarized by:



Syngas from coal tends to have a low H_2/CO ratio and some additional hydrogen must be generated by the water gas shift (WGS) reaction, viz.



Traditionally, iron catalysts have been used for FT synthesis when the syngas is coal-derived, because iron catalysts have the ability to simultaneously carry out the WGS reaction.

Recently, there has been renewed interest in the use of Co as a commercial FT catalyst. Co has a higher specific activity than Fe (1,2); it produces primarily straight chain paraffins; and has shown good lifetimes. The considerable commercial interest is evidenced by the large number of patents relating to catalysts and processes which have been issued to, among others, Gulf, Shell, Exxon, and Statoil (3-6). These recently developed cobalt catalysts share some similarities in that they all consist of four major components:

- (1) the primary FT metal, Co;
- (2) a second metal (Ru, Re, or other noble metal)
- (3) an oxide promoter (lanthana or zirconia, for example); and
- (4) a high surface area refractory oxide support.

Although much activity has taken place in the development of Co catalysts in recent years, much of this work has been privately sponsored and thus is maintained as proprietary. Thus, the time is right for assembling all the current information and developing a family of potentially commercializable catalysts.

There are two main broad objectives of this three-year project: (1) to identify and demonstrate a procedure that will reproducibly produce supported FT cobalt catalysts which meets suitable activity, selectivity, and lifetime criteria and is suitable for use in a slurry bubble column reactor; and (2) to provide design and cost estimates for a facility that can provide cobalt catalyst for testing in a slurry bubble column PDU facility. The activity and selectivity criteria are outlined in Table 1.

EXPERIMENTAL PROGRAM

Catalyst preparation

All catalysts prepared to date have consisted of 20-30 wt% cobalt, a second metal promoter (either Ru or Re) at a level of less than 2 wt%, and an oxide promoter such as lanthana, zirconia, or alkali oxide at a level of less than 5 wt%. All catalysts have been prepared by impregnation on either a silica (Davison 952) or an alumina (Vista B) support. These supports were chosen based on their low sulfur content and microspherical shape. The latter property is important when used in a SBCR as it prevents attrition. Table 2 summarizes the principal catalysts prepared thus far.

After impregnation, the catalysts were dried at 120°C and calcined at temperatures no higher than 350°C. Prior to testing the catalysts were reduced in a flow of hydrogen.

TABLE 1.
PROCESS CONDITIONS AND DESIRED ACTIVITY
AND SELECTIVITY FOR Co CATALYSTS IN A SBCR

Process Conditions

H ₂ /CO in feed	0.7 - 2.0
Temperature, °C	230 - 280
Pressure, bar	10 - 30
Syngas flow rate, Nm ³ /hr/Kg Co	3 - 6

Desired Activity and Selectivity

Total CO + H ₂ used, Nm ³ /hr/Kg Co	2.7 - 5.4
CO + H ₂ conversion, %	90
Hydrocarbon production, g/Nm ³ syngas	
Total	200
C ₃₊	180
C ₃₊ space time yield, Kg/m ³ /day	900 - 1000

TABLE 2.
CATALYSTS WITH LOW METHANE SELECTIVITY
SUMMARY OF INITIAL PREPARATION STRATEGY

Active Metal (Co) Level:	20 - 30%
Second Metal:	Ru, Re, Pt
Second Metal Level:	< 2%
Oxide Promoter:	Rare earths, Alkali oxides, Zirconia
Oxide Level:	< 5%
Supports:	Alumina, Silica, Titania Microspherical shape
Preparation Procedure:	Impregnation (aqueous vs. non-aqueous; simultaneous vs. s e q u e n c i a l) , coprecipitation
Pretreatment:	Varied calcination and reduction procedures

Catalyst characterization

All catalysts have been routinely characterized by BET nitrogen physisorption, particle size distribution, X-ray diffraction, static hydrogen chemisorption, and temperature programmed reduction. Additionally, selected catalysts have also been subjected to ICP elemental analysis for suspected impurities.

Representative samples of the catalysts have also been evaluated for their attrition resistance.

Fixed bed catalyst testing

A schematic diagram of the fixed-bed reactor system is shown in Figure 1. Typically, 0.1 to 0.3 g of catalyst were charged into the reactor tube and reduced overnight at 300°C. The reaction was carried out at 220°C, 1 atm., H₂/CO ratio of 2.0, and a total flow rate of 50 Scc/min. No inert diluent was used. Sample analyses were taken after approximately 2, 5, 9, and 24 hours on-stream. In some cases the temperature was varied between 210 and 240°C in order to calculate an Arrhenius activation energy.

Product analysis for C₁ to C₂₀ hydrocarbons was performed by on-line gas chromatography. CO conversion rates were calculated based on the GC analysis of the products. Anderson-Schultz-Flory (A-S-F) distributions were plotted and the chain propagation parameter, α , calculated using the C₄ to C₁₆ data.

Slurry bubble column testing

A schematic of the SBCR test unit is shown in Figure 2. For these tests the catalyst was first reduced ex situ in a fluidized bed assembly and then transferred into a glove box for weighing and subsequent transfer into the SBCR. Approximately 15 g of catalyst and 200 g of liquid medium were used in a run. The reaction procedure used for the SBCR testing is shown in Table 3. Analysis of the gas products, CO, CO₂ and C₁ to C₅, was performed hourly. Liquid products were collected at the end of each 24 hour period, blended, and submitted for analysis. A-S-F plots of the liquid products were used to determine α . A typical complete run lasted about 10 days.

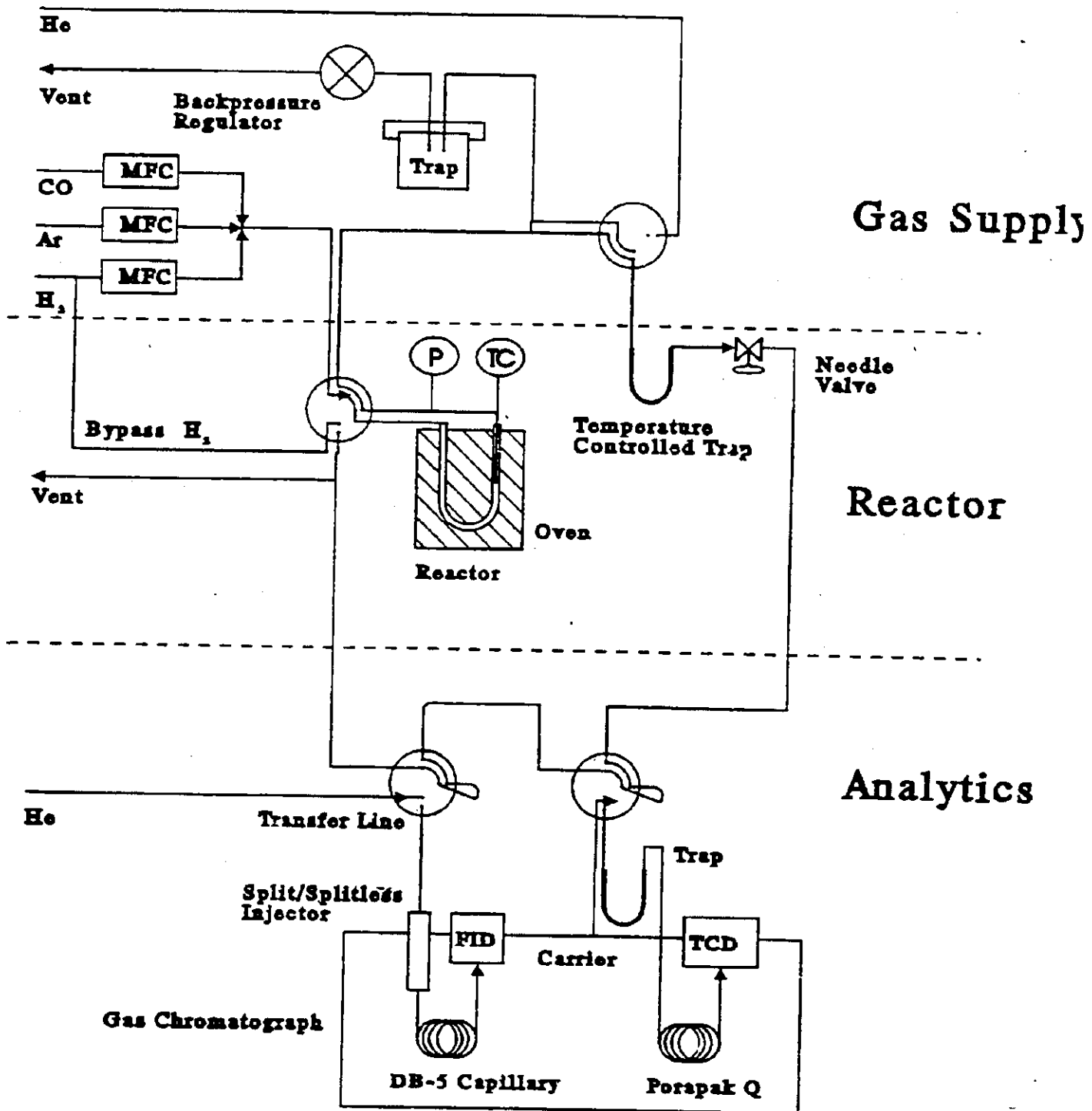


FIGURE 1.
Schematics of the Fixed Bed Reactor System

Slurry Bubble Column Reactor
Catalyst Test Unit

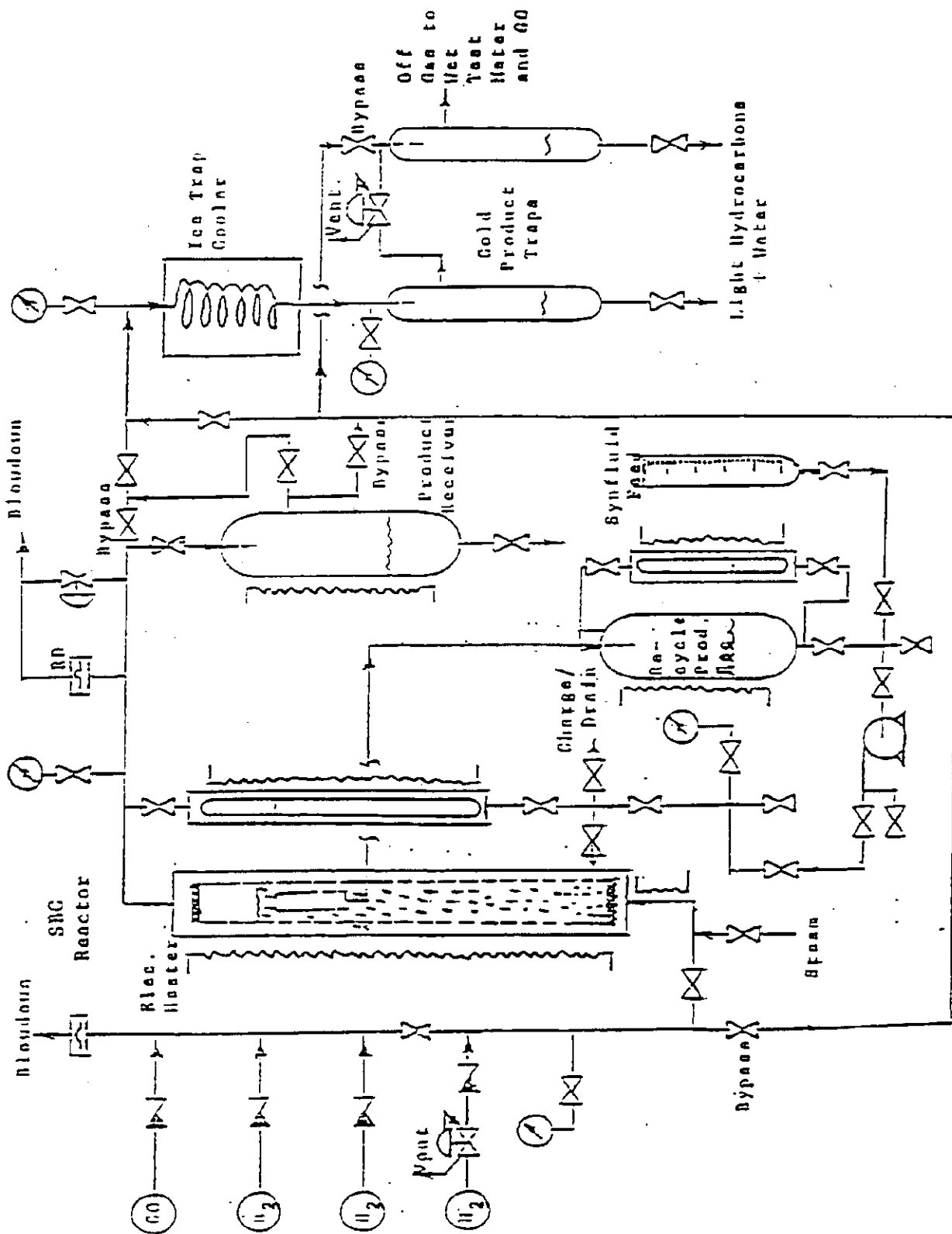


FIGURE 2.

TABLE 3.
SLURRY BUBBLE COLUMN STANDARD REACTION PROCEDURE

T (°C)	P _{H₂} (atm)	P _{CO} (atm)	H ₂ :CO	Total Pressure (psi)*	Time (hr)	Reaction Period	Objective
240	8.0	4.0	2.0	450	*	steady state operation at 240°C	activity with time on stream, check for steady state
240	8.0	4.0	2.0	450	*		
240	8.0	4.0	2.0	450	*		
240	8.0	4.0	2.0	450	*		
220	8.0	4.0	2.0	450	*	reaction at 220°C	compare with fixed bed study
240	8.0	4.0	2.0	450	*		activity check
240	4.0	4.0	1.0	450	*	variation of reactant ratio and pressure	ratio 1:1
240	?	?	1.0	600	*		increase pressure
240	8.0	4.0	2.0	450	*		activity check

* samples at various times

balance in all cases is N₂

RESULTS AND DISCUSSION

Fixed-bed evaluation

Table 4 shows typical data obtained from the fixed-bed reaction tests for three catalysts and shows the effect of noble metal promotion and support on FT activity. The alumina-supported Co catalyst was found to be more active, by about a factor of two, than its silica-supported analog. Additionally, another factor of two in activity was gained by promotion with Ru. It should be noted that neither the support nor the Ru promotion changes the characteristics of the reaction products, i.e., no significant change was noted in α , CH_4 formation rate, amount of oxygenated products, or isomer distribution. This suggests that the FT reaction is still being carried out on the cobalt sites and not on new sites created by the promoter. Similar results were obtained when Re was used as a metal promoter in place of Ru. The results obtained for Ru and Re promotion are similar to those reported in the patent literature (3,4).

Slurry bubble column evaluation

Table 5 shows typical data obtained at 240°C, 450 psig, and H_2/CO ratio of 2, in the SBCR for catalysts consisting of Co supported on alumina and silica, respectively. As in the case of the fixed-bed testing, the support was found to strongly influence the overall hydrocarbon production rate with little effect on the α . At these conditions the C_{6+} hydrocarbon production rate was over 0.8 Kg/Kg catalyst hour. Table 6 summarizes the effect of SBC process conditions on the activity and selectivity of a Co-Ru/ Al_2O_3 catalyst. Small changes in either temperature or H_2/CO ratio resulted in noticeable effects in terms of both activity and selectivity. Particularly interesting is the observed increase in the reaction α (and thus C_{6+} selectivity) from about 0.85 to about 0.88 as the temperature was changed from 240 to 220°C. It should be noted that under the low temperature process conditions, the methane selectivity was below 3 wt%.

An important consideration for catalysts designed for SBC operation is their particle size. The effect of particle size on catalyst performance was evaluated by comparing the SBC behavior of a catalyst in two particle size ranges, 100-400 mesh and 170-400 mesh. Table 7 shows the results of this comparison. Although selectivities remained virtually unchanged, the catalyst with the narrower range of particle size showed about 35% higher overall activity.

**TABLE 4.
FIXED BED REACTION DATA**

Catalyst	Composition		Rate (g CH ₂ / g cat /hr)	CH ₄ (wt%)	C2-C4 (wt%)	C5+ (wt%)	Alpha
	Co wt%	Promoter wt%					
Co.005	20%	-	Al ₂ O ₃	21.4	24.4	54.2	0.66
Co.011	20%	-	SiO ₂	25.8	29.4	44.8	0.62
Co.018	20%	0.5% Ru	Al ₂ O ₃	27.2	22.9	50.0	0.69

Reaction Conditions:

P = 1 atm
T = 220 °C
H₂/CO = 2
Conversion < 5%
Time-on-stream = ca. 25 hrs

TABLE 5.
SLURRY BUBBLE COLUMN REACTION DATA

EFFECT OF SUPPORT

	Co/Al₂O₃	Co/SiO₂
CO Conversion (%)	33.2	18.5
C6+ Rate (kg/kg cat. hr)	0.84	0.56
CH₄ (wt%)	5.6	8.8
C6+ (wt%)	67.8	62.9
alpha	0.80	0.78

Catalyst weight: ca. 15g

Temperature (°C) = 240

Pressure (psi) = 450

H₂/CO ratio = 2

Total flow rate: ca. 15 L/min, or 3 cm/sec linear velocity

Diluent: N₂: ca. 60%

TABLE 6.
SLURRY BUBBLE COLUMN REACTION DATA
EFFECT OF PROCESS CONDITIONS

Temperature (°C)	240	<u>220</u>	240
Pressure (psi)	450	450	450
H ₂ /CO ratio	2	2	<u>1</u>
CO Conversion (%)	33.8	12.6	12.4
C6+ Rate (kg/kg cat. hr)	0.87	0.52	0.58
CH ₄ (wt%)	9.7	2.8	3.3
C6+ (wt%)	55.4	89.3	66.7
alpha	0.85	0.88	0.86

Catalyst: Co.018, 20% Co/0.5% Ru/ Al₂O₃; weight: ca. 15g
 Total flow rate: ca. 15 L/min, or 3 cm/sec linear velocity
 Diluent: N₂: ca. 60%

TABLE 7.
SLURRY BUBBLE COLUMN REACTION DATA

EFFECT OF PARTICLE SIZE

	100x400 mesh size	170x400 mesh size
CO Conversion (%)	14.3	18.5
C6+ Rate (kg/kg cat. hr)	0.42	0.56
CH₄ (wt%)	7.6	8.8
C6+ (wt%)	62.5	62.9
alpha	0.78	0.78

Catalyst: C0.011, 20% Co/SiO₂; weight: ca. 15g

Temperature (°C) = 240

Pressure (psi) = 450

H₂/CO ratio = 2

Total flow rate: ca. 15 L/min, or 3 cm/sec linear velocity

Diluent: N₂; ca. 60%

Catalysts removed from the SCBR were subjected to XRD and particle size distribution analysis. In all cases the XRD of the used catalyst was similar to that of the fresh catalyst, indicating that little ageing had taken place. No evidence for significant catalyst attrition was found in any of the SBCR runs.

Effect of support and promoters

The role of the supports and promoters on affecting the FT reaction is not yet clear. Hydrogen chemisorption measurements, shown in Table 8, show that metal promoters such as Re and Ru can increase the dispersion of the reduced Co on the support. Zirconia appears to have the same effect of silica-supported catalyst. It is likely that this increased dispersion is reflected on the higher FT activity observed for the promoted catalysts.

SUMMARY

Work for the first year of this project has progressed on schedule. Both fixed-bed and SBCR have been constructed and are operating on a routine basis. A second SBCR unit is expected to be on-line by early 1994. Over 30 catalysts have been formulated, characterized, and tested.

ACKNOWLEDGEMENTS

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TABLE 8.
EFFECT OF SUPPORT AND PROMOTERS ON
REDUCIBILITY AND DISPERSION OF Co CATALYSTS

<u>% Co</u>	<u>% M</u>	<u>% Oxide</u>	<u>Support</u>	<u>% Disp.</u>	<u>% Reduc.</u>
20	0	0	Al ₂ O ₃	2.8	66
20	0.43% Ru	1% La ₂ O ₃	Al ₂ O ₃	9.1	65
20	1% Re	1% La ₂ O ₃ 0.13% K	Al ₂ O ₃	10.2	78
20	0	0	SiO ₂	4.8	69
20	0.5% Ru	0	SiO ₂	6.6	--
20	0	0.7% ZrO ₂	SiO ₂	8.3	--
20	0	1.4% ZrO ₂	SiO ₂	9.3	--

REFERENCES

1. M.A. Vannie, in Catalysis: Science and Technology, vol. 3 (J.R. Anderson and M. Boudart, eds.) Springer-Verlag, Berlin, 1982, pp. 139-198.
2. S.T. Sie, J. Eilers, and J.K. Minderhout, Proc. Int. Cong. Catal., Calgary, 743 (1988).
3. T.P. Kobylinski, C.L. Kibby, R.B. Pannell, and E.L. Eddy, European Pt. Appl. 0 253 924 (1986).
4. S. Eri, J.G. Goodwin, G. Marcelli, and T. Riis, U.S. Patent 4,801,573 (1989).
5. K.P. de Jong, J.H.E. Glazer, and M.F.M. Post, European Pat. Appl. 0 221 598 (1986).
6. C.H. Mauldin, U.S. Pat. 4,568,663 (1986).