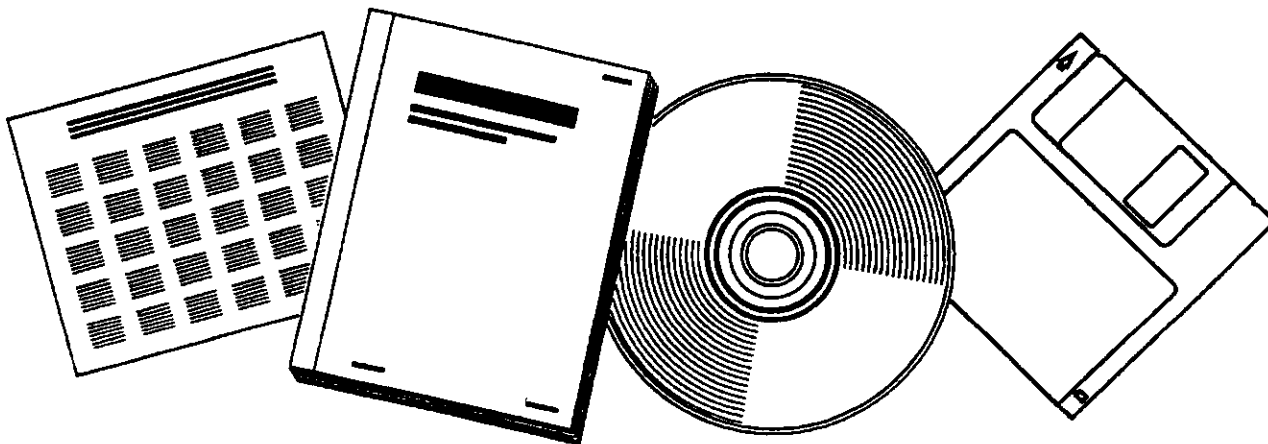NTIS
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TECHNOLOGY DEVELOPMENT FOR COBALT F-T CATALYSTS. TOPICAL REPORT NO.2, COMPARISON OF PATENTED F-T COBALT CATALYSTS

ENERGY INTERNATIONAL, INC.
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FINAL

TECHNOLOGY DEVELOPMENT FOR COBALT F-T CATALYSTS

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TOPICAL REPORT No. 2

COMPARISON OF PATENTED F-T COBALT CATALYSTS

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By

Rachid Oukaci, George Marcelin, and James G. Goodwin,Jr.
University of Pittsburgh
Chemical & Petroleum Engineering Department
Pittsburgh, PA 15261

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ABSTRACT

Based on the information provided in patents assigned to Gulf, Shell, Exxon, and Statoil, a series of catalysts has been prepared consisting of 12-20 wt% cobalt, a second metal promoter (Ru or Re), and an oxide promoter such as lanthana, zirconia, or alkali oxide, the support being alumina, silica, or titania. All catalysts have been extensively characterized by different methods. The catalysts have been evaluated in terms of their activity, selectivity both in a fixed bed reactor and in a slurry bubble column reactor, and the results correlated with their physico-chemical properties.

INTRODUCTION

Recently, there has been renewed interest in the use of Co as a commercial FT catalyst. The considerable commercial interest is evidenced by the large number of patents relating to Co catalysts and FT processes which have been issued. Although a significant amount of activity has taken place in the development of Co catalysts, much of this work has been privately sponsored and thus is maintained as proprietary. Furthermore, comparison of the performance of the various patented catalysts is difficult since they were all tested under different conditions.

Based on the information provided in a selected number of patents assigned to Exxon [1], Gulf [2], Shell [3], and Statoil [4], a series of catalysts has been formulated in order to evaluate all these catalysts under similar reaction conditions. In addition, an investigation of the role of the supports and various promoters on affecting the FT reaction was also undertaken.

EXPERIMENTAL

All catalysts compared in this study had a cobalt loading of 20 wt%, except for the titania-supported catalyst which contained only 12 wt% because of the low support surface area and pore volume. They also consisted of a second metal promoter (Ru or Re), and/or an oxide promoter such as lanthana, zirconia, alkali oxide, the support being alumina (Vista B), silica (Davison 952), or titania (Degussa P25). The catalysts are listed in Table 1 with their composition, the methods of preparation, and the patents on which their formulation was based.

The catalysts were all prepared by either aqueous or non-aqueous impregnation of the supports following the procedures outlined in the corresponding patents [1-4]. In addition, three reference non-promoted catalysts with just cobalt on each of the supports used in the patents were also prepared for comparison purposes. They were subjected to the same pretreatments as their corresponding promoted catalysts.

Prior to testing the catalysts were reduced at 250-350°C, in a flow of hydrogen. They have all been extensively characterized by different methods, including elemental analysis, BET physisorption, particle size distribution, X-ray diffraction, hydrogen chemisorption, temperature programmed reduction. Table 2 summarizes the relevant characterization data.

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The catalysts were evaluated in terms of their activity and selectivity both in a fixed bed reactor and in a slurry bubble column reactor. Typically, 0.1 to 0.3 g of prereduced catalyst were charged into the tubular fixed-bed reactor and rereduced overnight at 250-350°C. The reaction was carried out at 220°C, 1 atm, a H_2/CO ratio of 2.0, and a total flow rate of 50 cm^3/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°C and 240°C in order to calculate an Arrhenius activation energy. Product analysis for C_1-C_{20} 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 growth probability, α, calculated using the C_4-C_{16} data.

For the slurry bubble column 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 slurry bubble column reactor. Approximately 15 g of catalyst a 100 g of liquid medium were used in a run. Typically, the reaction was carried out at 240°C, a total pressure of 450 psi, a H_2/CO ratio of 2, and using 60% N_2 diluent. There are three reasons for the N_2 diluent: (1) it maintains the gas flow and hence the agitation required for uniform slurry bubble column reactor operation through the circumstance of CO/H_2 disappearance from the gas phase due to FT reaction; (2) it aids in experimental data interpretation by serving as an internal standard for the inlet and outlet gas phase analysis; and (3) it enhances the isothermality of the reaction by dampening temperature gradient. Analysis of the gas products, CO, CO_2, and C_1-C_5, 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. After reaching steady-state under these conditions, temperature, pressure, and H_2/CO ratio were varied in turn to study the effect of process conditions. A typical complete run lasted about 10 days.

RESULTS AND DISCUSSION

Table 3 shows selected data obtained from fixed bed reaction which indicate the effects of the noble metal and oxide promotors and of the support on F-T activity and selectivity. The alumina- and silica-supported Co catalysts were found to be more active, by about a factor of 2-7 than the titania-supported catalysts even on a Co basis.

The addition of both noble metal and/or oxide promoters to the supported cobalt catalyst increased its activity by at least a factor of ca. 2 in most cases. On both the TiO_2- and the Al_2O_3-supported catalysts which contained Ru or Re the activity enhancement may be explained by an increased dispersion of the reduced cobalt as shown by the hydrogen chemisorption measurements (see Table 2). The presence of potassium had obviously a negative effect on the activity of ST.01, while its selectivity for higher hydrocarbons was significantly improved. In the case of the SiO_2-supported catalyst, a factor of two in activity was gained by promotion with ZrO_2, although the latter did not seem to affect the dispersion of the cobalt.

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It should be noted that, except for the TiO_2-supported and the K-promoted catalysts neither the support nor the promoters cha τ_{c} d significantly the chracteristics of the reaction products, i.e., no significant change was noted in α or CH_4 selectivity.

Table 4 shows selected data obtained at 240°C, 450 psi, and a H_2/CO ratio of 2, in the slurry bubble column reactor for Co/Al_2O_3 and Co/SiO_2 catalysts. In this case, the support was found to strongly influence the overall hydrocarbon production rate with little effect on α, while the addition of a noble metal promoter seemed to have little effect on the catalytic properties of cobalt. On the other hand, as in the case of the fixed bed testing, the ZrO_2 promoter was found to influence the overall activity of the silica-supported catalyst.

Obviously, diffusion limitations and gas solubilities in the liquid medium in the slurry bubble column reactor may play a role in some of the differences in the results from the two reaction systems. It is also possible that certain promoters or supports may function best in a narrow range of conditions. Clearly, ZrO_2 was the most consistent activity promoter.

REFERENCES

1.   E. Iglesia, S. Soled, and R.A. Fiato, U.S. Patent 4,794,099 (1988)
2.   H. Beuther, C.L. Kibby, T.P. Kobylinski, and R.B. Pannell, U.S. Patent 4,413,064 (1983).
3.   M.F.M. Post and S.T. Sie, European Pat. Appl. 0 167 215 A2 (1986).
4.   S. Erie, J.G. Goodwin, Jr., G. Marcelin, and T. Riis, U.S. Patent 4,880,763 (1989).

TABLE 1. Catalyst formulation

CATALYST	COMPOSITION				Method of Preparation	Patent #
	Co (wt%)	2nd Metal (wt%)	Oxide Promoter (wt%)	Support		
EX.01	12	Re 0.75	-	TiO$_2$	Single-Step Organic Impr./Slurry	U.S. Pat. 4 794 099
Co/TiO$_2$	12	-	-	TiO$_2$	Organic Impr.	-
GU.01	20	Ru 0.43	La$_2$O$_3$ 1.0	Al$_2$O$_3$	Single-Step Organic Impr.	U.S. Pat. 4,413,064
ST.01	20	Ru 0.5	La$_2$O$_3$ 1.0 K 0.13	Al$_2$O$_3$	Single-Step Aqueous Impr./Incipient Wetness	U.S. Pat. 4,880,763
Co/Al$_2$O$_3$	20	-	-	Al$_2$O$_3$	Aqueous Impr.	-
SH.01	20	-	Zr 8.5	SiO$_2$	Two-Steps, Zr Organic Impr., Co Aqueous Impr.	Eur. Pat. Appl. 0 167 215 A2
Co/SiO$_2$	20	-	-	SiO$_2$	Aqueous Impr.	-

TABLE 2. Catalyst characterization results

CATALYST	BET Surface Area (m^2/g cat)	H_2 CHEMISORPTION			H_2 TPR	XRD Co_3O_4
		Total H_2 (μmol/g cat)	d_p^1 (nm)	Co Disp.^{2} (%)	% Red. 25-900°C	d_p (nm)
EX.01	16	44	19	4.3	80	39
Co/TiO$_2$	13	19	40	1.8	72	38
GU.01	149	155	-	9.1	-	-
ST.01	191	168	-	9.9	-	-
Co/Al$_2$O$_3$	173	48	21	2.8	85	20
SH.01	215	93	18.2	5.1	91	31
Co/SiO$_2$	211	89	15	5.0	80	24

(1)   Average particle diameter based on the reduced cobalt.
(2)   Co dispersion based on the total cobalt.

TABLE 3. Fixed bed reaction data

CATALYST	RATE		SELECTIVITY	
	(g CH_2/g cat/hr)	mol CO/mol Co/s x 10^{-4}	CH_4 (wt%)	α
EX.01	0.052	5.1	45.0	0.49
Co/TiO$_2$	0.021	2.0	-	0.64
GU.01	0.258	15.0	26.1	0.64
ST.01	0.116	6.8	19.6	0.76
Co/Al$_2$O$_3$	0.073	4.3	29.2	0.62
SH.01	0.182	11.0	28.7	0.62
Co/SiO$_2$	0.083	4.8	28.9	0.65

P = 1 atm, T = 220°C, H_2/CO = 2, Conversion < 5%, Time-On-Stream = ca. 25 hrs.

TABLE 4. Slurry bubble column reaction data

CATALYST	ACTIVITY		SELECTIVITY	
	% CO Conversion	Rate (g CH_2/g cat/hr)	CH_4 (wt%)	α
EX.01	2.7	0.13	0.1	0.85
Co/TiO$_2$	1.8	0.09	-	-
GU.01	30.1	1.42	12.5	0.80
ST.01	30.9	1.36	11.7	0.87
Co/Al$_2$O$_3$	27.1	1.34	7.9	0.82
SH.01	25.5	1.21	8.6	0.84
Co/SiO$_2$	13.9	0.63	6.1	0.89

Catalyst Weight: ca. 15g; T = 240°C; P = 450 psi; H_2/CO Ratio = 2; Total Flow Rate: ca. 15 L/min, or 3 cm/sec Linear Velocity; Diluent: ca. 60% N_2, Time-On-Stream = ca. 35 hrs.