EFFECTS OF SUPPORTS AND PROMOTERS ON COBALT F-T CATALYST BEHAVIOR IN FIXED BED VS. SLURRY BUBBLE COLUMN REACTORS

R. Oukaci, J.G. Goodwin, Jr., G. Marcelin, and A. Singleton[1]
Chemical & Petroleum Engineering Department
University of Pittsburgh
Pittsburgh, PA 15261

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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 (F-T) synthesis to convert the syngas to a mixed product consisting mainly of straight chain hydrocarbons. Traditionally, iron catalysts have been used for F-T synthesis when the syngas is coal-derived, because they have the ability to simultaneously carry out the water gas shift reaction.

Recently, there has been renewed interest in the use of Co as a commercial F-T catalyst. Co has a higher specific activity than Fe (1,2); it produces primarily straight chain paraffins; and it has shown good lifetimes. The considerable commercial interest is evidenced by the large number of patents relating to Co catalysts and F-T processes which have been issued. These recently developed cobalt catalysts share some similarities in that they all consist of four major components: (a) the primary F-T metal, Co; (b) a second metal (Ru, Re, or other noble metal); (c) an oxide promoter (lanthana or zirconia, for example); and (d) a high surface area refractory oxide support (3).

Different types of reactor systems are proposed for commercial F-T synthesis. The slurry bubble column reactor has often been suggested as being one of the most appropriate for heat removal from the exothermic F-T synthesis reaction. However, most of the catalyst screening is carried out in fixed bed reactor systems, even for slurry bubble column reactor applications. In addition, there has been hardly any investigations of the effects of supports or promoters carried out in slurry bubble column reactor systems. Because of the different reaction conditions involved in these two systems, i.e., gas phase versus liquid phase, some of the effects observed in one system may not necessarily be found in the other.

A series of catalysts has been formulated in order to investigate the role of the supports and some promoters on affecting the F-T reaction both in a fixed-bed reactor as well as in a slurry bubble column reactor.

EXPERIMENTAL

All catalysts compared in this study consisted of 12-20 wt% cobalt, a second metal promoter (Ru or Re), and/or an oxide promoter such as zirconia, the support being alumina (Vista B), silica (Davison 952), or titania (Degussa P25).

[1] Energy International Corporation, 135 William Pitt Way, Pittsburgh, PA 15238.

These supports were chosen based on their low sulfur content and microspheroidal shape. The latter property is important when used in a slurry bubble column reactor as it prevents attrition.

All catalyst were prepared by impregnation of the supports with the appropriate solution of the nitrates of the various metals. After impregnation, the catalysts were dried at 120°C and calcined at temperatures no higher that 350°C. Prior to testing the catalysts were reduced 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 1 summarizes the relevant characterization data.

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 300°C. The reaction was carried out at 220°C, 1 atm, 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° 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 and 200 g of liquid medium were used in a run. Typically, the reaction was carried out at 240°C, a total pressure of 450 psi, H_2/CO ratio of 2, and using 60% N_2 diluent. 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 2 shows selected data obtained from fixed bed reaction which indicate the effects of noble metal and ZrO_2 promotion 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 two, than their titania- supported analog.

The addition of ruthenium to the γ-alumina supported cobalt catalyst increased its activity by a factor of ca. 6, while it had no effect on the silica-supported catalysts and only a slight enhancing effect on the activity of the TiO_2-supported catalyst. The effect on the Al_2O_3-supported catalyst may be explained by the fact that the presence of Ru increased the reducibility of the Co/Al_2O_3 catalyst while

it did not enhance the reducibility of the SiO_2 and the TiO_2-supported catalysts. In addition, hydrogen chemisorption measurements, shown in Table 1, show that the Ru promoter can increase the dispersion of the reduced Co/Al_2O_3. However, 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 reducibility of the cobalt or its dispersion.

It should be noted that neither the support nor the promoters changed significantly the characteristics of the reaction products, i.e., no significant change was noted in α or CH_4 formation rate. This suggests that the F-T reaction is still being carried out on Co 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 (4-7).

Table 3 shows selected data obtained at 240°C, 450 psi, and 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.

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Table 1. Catalyst Characterization Results.

CATALYST	COMPOSITION		BET Surface Area (m^2/g cat)	H_2 CHEMISORPTION			H_2 TPR % Red. 25-900°C	XRD Co_3O_4 d_p (nm)
	Co (wt%)	Promoter (wt%)		Total H_2 (μmol/g cat)	d_p[1] (nm)	Co Disp.[2] (%)		
Co/Al_2O_3	20	0	173	48	21	2.8	85	20
$RuCo/Al_2O_3$	20	Ru 0.5	158	185	9	11	97	23
Co/SiO_2	20	0	211	89	15	5	80	24
$RuCo/SiO_2$	20	Ru 0.5	-	112	-	7	-	-
$ZrCo/SiO_2$	20	Zr 8.5	208	93	-	5	75	-
$ZrRuCo/SiO_2$	20	Zr 8.5 Ru 0.5	214	70	-	4	-	-
Co/TiO_2	12	0	13	19	40	2	72	38
$ReCo/TiO_2$	12	Re 0.8	16	44	19	4	80	39
$RuCo/TiO_2$	12	Ru 0.5	15	38	21	4	79	45

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

Table 2. 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
Co/Al_2O_3	0.073	4.3	29.2	0.62
$RuCo/Al_2O_3$	0.470	28.0	29.0	0.60
Co/SiO_2	0.083	4.8	28.9	0.65
$RuCo/SiO_2$	0.085	4.9	18.9	0.73
$ZrCo/SiO_2$	0.160	9.4	23.5	0.63
$RuZrCo/SiO_2$	0.136	8.0	-	0.69
Co/TiO_2	0.021	2.0	-	0.64
$ReCo/TiO_2$	0.052	5.1	45.0	0.49
$RuCo/TiO_2$	0.034	3.3	27.7	0.69

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

Table 3. Slurry Bubble Column Reaction Data

CATALYST	RATE (g CH_2/g cat/hr)	SELECTIVITY	
		CH_4 (wt%)	α
Co/Al_2O_3	1.34	7.9	0.82
$RuCo/Al_2O_3$	1.57	9.7	0.85
Co/SiO_2	0.63	6.1	0.89
$RuCo/SiO_2$	0.66	-	0.86
$ZrCo/SiO_2$	1.24	10.7	0.82
$RuZrCo/SiO_2$	1.16	11.0	0.85
Co/TiO_2	0.09	-	-
$ReCo/TiO_2$	0.13	0.1	0.85
$RuCo/TiO_2$	0.40	8.3	0.83

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.