

ZIRCONIA PROMOTION OF FISCHER-TROPSCH COBALT CATALYSTS: BEHAVIOR IN FIXED-BED AND SLURRY BUBBLE COLUMN REACTORS

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ABSTRACT

A series of cobalt-based F-T catalysts supported on alumina and silica were prepared with different loadings of Zr and different sequence of impregnation of Co and Zr. All catalysts were extensively characterized by different methods. The catalysts were evaluated in terms of their activity and selectivity both in fixed bed and slurry bubble column reactors. Addition of ZrO₂ to both Co/SiO₂ and Co/Al₂O₃ catalysts resulted in at least a twofold increase in the catalyst activity for F-T synthesis in the fixed bed reactor. In the slurry bubble column reactor, a similar promotion effect was observed for the SiO₂-supported catalysts, while the addition of Zr to a cobalt/alumina catalyst had a less significant effect.

INTRODUCTION

Cobalt has been one of the most commonly used metals for Fischer-Tropsch catalysts since the 1930's because of its high activity (1). It has received a lot of attention recently (2-8) due to its usefulness in converting CO to liquid hydrocarbons. While many promoters for Fischer-Tropsch (F-T) synthesis, such as the alkali series, have been extensively studied, others such as Zr have not. A number of studies of F-T synthesis over ZrO₂-supported Co (1,9), Ni (9), Ni/Co (9), and Pd (10) have been reported in the literature. The use of ZrO₂ as the support for these different active metals has been found to increase the higher hydrocarbon selectivity. Recently, a number of patents by Shell (11-13) have involved Zr promotion of Co/SiO₂. Addition of up to 15 wt% ZrO₂ promotor was found to increase the overall activity of the Co catalyst without affecting the selectivity for higher hydrocarbons.

A series of cobalt-based F-T catalysts supported on alumina and silica were prepared with different loadings of Zr and different sequence of impregnation of Co and Zr in order to investigate the role of ZrO₂ on affecting the F-T reaction in both fixed bed and slurry bubble column reactors.

EXPERIMENTAL

All catalysts compared in this study consisted of 20 wt% cobalt and different amounts of zirconia (up to 15 wt% Zr), the support being alumina (Vista B) or silica (Davison 952). The supports, calcined at 500°C for 10 hours prior to catalyst preparation, were loaded with Co and/or Zr by either a single or 2-step impregnation method. Aqueous solutions of cobalt nitrate and/or zirconium nitrate were used to prepare all the catalysts except in the case of S[Co/8.5Zr(O)]/SiO₂, where a solution of zirconium tetra-n-propoxide in a mixture of n-propanol, toluene, and acetyl acetone was used to impregnate the Zr in the initial impregnation step. In the case of single step impregnations, the SiO₂-supported catalysts were prepared by kneading (11-13) the aqueous metal precursor solution-support mixture for 3.5 hours. For the sequentially impregnated SiO₂-supported catalysts, kneading was used in the initial step for the addition of Co, followed by use of the incipient wetness method for the impregnation of Zr (11-13). For the other sequentially impregnated SiO₂-catalysts and all the alumina-supported catalysts, the incipient wetness method was used in both steps. After the first impregnation step, the catalyst was dried in an oven for 5 hours at 115°C with occasional stirring. Then, it was calcined in air by raising its temperature to 300°C with a heating rate of 1°C/min and holding for 2 hours. Also, after the second step of impregnation (if used) the catalyst was dried and calcined identically as in the first step. The catalysts are listed in Table 1 with the corresponding preparation methods.

Prior to H₂ chemisorption or reaction, the catalysts were reduced in H₂ at 250°C for the SiO₂-supported catalysts and 350°C for the Al₂O₃-supported catalysts, for 10 hours following a 1°C/min ramp. 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.

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, 0.15 to 0.35 g of prereduced

catalyst were charged into the fixed bed reactor tube and rereduced 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 90 cm³/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 growth probability, α , calculated using the C4 to C16 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, H₂/CO ratio of 2, and 60% N₂ diluent. 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 . After reaching steady-state under these conditions, temperature, pressure, and H₂/CO ratio were varied in turn to study the effect of process conditions. A typical complete run lasted about 10 days. Only the base Co catalysts (non-promoted Co/SiO₂ and Co/Al₂O₃) and the most active catalysts in the fixed bed reactor were tested in the slurry bubble column reactor.

RESULTS AND DISCUSSION

From XRD measurements, it was found that the average diameter of the Co oxide crystallites for all catalysts varied within a narrow range (ca. 20-30 nm), regardless of the amount of Zr present or the support used. In addition, the XRD results suggest that Zr was highly dispersed on Co/SiO₂ since no Zr compound phases were detected.

The TPR results show little difference in the degree of reduction for all the catalysts with the exception of Cl[0.7Zr+Co]/SiO₂ and S[Co/8.5Zr]/Al₂O₃ which exhibited the lowest and the highest reducibility, respectively. The Al₂O₃-supported catalysts had in general higher reducibilities than their silica-supported analogs. It was also found that all the catalysts used in this study were reduced to the maximum degree (defined as % Co reduced during TPR to 900°C) during the standard reduction procedure at 250°C.

The sequentially-impregnated Zr/Co on SiO₂ catalysts showed an increase in the amount of total hydrogen chemisorbed compared to that for [Co]/SiO₂. On the other hand, for the sequentially-impregnated Co/Zr on SiO₂ catalysts, the Zr addition did not influence significantly the amount of H₂-chemisorption. The co-impregnated catalyst (Cl[8.5Zr+Co]/SiO₂ had almost twice as much H₂ uptake as either Cl[0.7Zr+Co]/SiO₂ or [Co]/SiO₂. The opposite effect was observed with the Al₂O₃-supported catalysts. The sequentially-impregnated Co/Zr on Al₂O₃ catalyst and the co-impregnated catalyst with low Zr loading (Cl[1.4Zr+Co]/Al₂O₃ had the highest H₂ uptakes.

Table 3 shows selected data obtained from fixed bed reaction which indicate the effect of ZrO₂ promotion on F-T activity and selectivity. While the alumina-supported Co catalysts were found to be in general more active than their silica-supported analogs, Zr promotion of both Co/SiO₂ and Co/Al₂O₃ increased significantly the overall rate of F-T synthesis, compared to the non-promoted catalysts. In addition, the promoting effect of ZrO₂ was more significant on the alumina-supported catalysts, especially the sequentially impregnated catalyst S[Co/8.5Zr]/Al₂O₃. The method of preparation and the amount of promoter used also affected the catalyst activity and selectivity. The sequentially impregnated [Co/Zr] catalysts appeared to be the most active. Addition of Zr beyond 8.5 wt% for the SiO₂-supported catalysts did not seem to have any beneficial effect. The catalysts with the highest Zr loadings (wt% Zr > 1.4) had the highest values of α compared to the non-promoted catalysts, even though the CH₄ selectivity was also slightly higher in several cases. On the other hand, small amounts of Zr promotion (wt% Zr = 0.7 or 1.4) appeared to have a slightly negative effect on the values of α .

Table 4 shows selected data obtained at 240°C, 450 psi, and H₂/CO ratio of 2, in the slurry bubble column reactor for catalysts consisting of Co supported on silica and alumina, respectively. As in the case of the fixed bed testing, the ZrO₂ promoter was found to influence the overall activity of both the silica- and alumina-supported catalysts. However, while the alumina-supported Co catalysts were also found to be in general more active than their silica-supported analogs, the promoting effect of ZrO₂ was not as significant on the

alumina-supported catalysts. Diffusion limitations in the liquid medium in the slurry bubble column reactor may be invoked to explain the discrepancies in the results obtained in the two reaction systems. The overall rate observed for the catalyst S[Co/8.5Zr]/Al₂O₃ was high, but most probably diffusion limited.

In summary, ZrO₂ appears to be an excellent rate promoter for SiO₂- and Al₂O₃-supported Co catalysts. Addition of Zr in both catalysts, probably hinders the formation of Co aluminates and Co silicates, either during the preparation and pretreatment or during the F-T synthesis reaction itself. In addition, high levels of promotion act to increase the selectivity for higher hydrocarbons.

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Table 1: Catalyst Preparation Methods Used

Catalyst ^a	Step # 1 ^b		Step # 2 ^b	
	Method	Solution	Method ^a	Solution
[Co]/SiO ₂	Kneading	aqueous(Co)	N/A	N/A
S[0.7Zr/Co]/SiO ₂	Kneading	aqueous(Co)	Inc. Wet.	aqueous(Zr)
S[1.4Zr/Co]/SiO ₂	Kneading	aqueous(Co)	Inc. Wet.	aqueous(Zr)
S[8.5Zr/Co]/SiO ₂	Kneading	aqueous(Co)	Inc. Wet.	aqueous(Zr)
S[Co/4.0Zr]/SiO ₂	Inc. Wet.	aqueous(Zr)	Inc. Wet.	aqueous(Co)
S[Co/8.5Zr(O)]/SiO ₂	Inc. Wet.	organic(Zr)	Inc. Wet.	aqueous(Co)
S[Co/8.5Zr]/SiO ₂	Inc. Wet.	aqueous(Zr)	Inc. Wet.	aqueous(Co)
S[Co/15.0Zr]/SiO ₂	Inc. Wet.	aqueous(Zr)	Inc. Wet.	aqueous(Co)
CI[0.7Zr + Co]/SiO ₂	Kneading	aqueous(Co + Zr)	N/A	N/A
CI[8.5Zr + Co]/SiO ₂	Kneading	aqueous(Co + Zr)	N/A	N/A
[Co]/Al ₂ O ₃	Inc. Wet.	aqueous(Co)	N/A	N/A
CI[1.4Zr + Co]/Al ₂ O ₃	Inc. Wet.	aqueous(Co + Zr)	N/A	N/A
CI[8.5Zr + Co]/Al ₂ O ₃	Inc. Wet.	aqueous(Co + Zr)	N/A	N/A
S[8.5Zr/Co]/Al ₂ O ₃	Inc. Wet.	aqueous(Co)	Inc. Wet.	aqueous(Zr)
S[Co/8.5Zr]/Al ₂ O ₃	Inc. Wet.	aqueous(Zr)	Inc. Wet.	aqueous(Co)

(a) Nomenclature: S = sequential impregnation, CI = co-impregnation; [A/xxB] = "A" impregnated after "B", [A+xxB] = co-impregnated "A" and "B"; B(O) = organic compound of B used instead nitrate (nonaqueous impregnating solution); xx = wt% Zr.

(b) Catalysts dried for 5 hrs at 115 °C and calcined for 2 hrs at 300°C after each step.

Table 2: Catalyst Characterization Results

Catalyst	H ₂ Chemisorption		TPR	XRD
	Total (μmol H ₂ /g cat)	% Co Dispersion	% Reduct. (25-900°C)	Co ₃ O ₄ d _p (nm)
[Co]/SiO ₂	82	4.8	75	27
S[0.7Zr/Co]/SiO ₂	141	8.3	80	28
S[1.4Zr/Co]/SiO ₂	149	8.8	81	27
S[8.5Zr/Co]/SiO ₂	122	7.2	81	29
S[Co/8.5Zr(O)]/SiO ₂	87	5.1	75	31
S[Co/8.5Zr]/SiO ₂	93	5.5	75	27
CI[0.7Zr + Co]/SiO ₂	67	4.0	64	20
CI[8.5Zr + Co]/SiO ₂	125	7.3	77	24
[Co]/Al ₂ O ₃	48	2.8	85	20
CI[1.4Zr + Co]/Al ₂ O ₃	71	4.2	82	19
CI[8.5Zr + Co]/Al ₂ O ₃	55	3.2	85	26
S[8.5Zr/Co]/Al ₂ O ₃	43	2.5	79	24
S[Co/8.5Zr]/Al ₂ O ₃	114	6.7	96	22

Table 3: Fixed Bed Reaction Results

Catalyst	ACTIVITY		SELECTIVITY	
	% CO Conversion	Rate (g CH ₂ /g cat/hr)	CH ₄ (wt%)	α
[Co]/SiO ₂	2.9	0.094	22.4	0.61
S[0.7Zr/Co]/SiO ₂	3.8	0.121	26.7	0.55
S[1.4Zr/Co]/SiO ₂	3.8	0.123	28.3	0.56
S[8.5Zr/Co]/SiO ₂	3.9	0.125	28.9	0.67
S[Co/4.0Zr]/SiO ₂	2.6	0.161	22.2	0.73
S[Co/8.5Zr(O)]/SiO ₂	5.7	0.182	28.7	0.62
S[Co/8.5Zr]/SiO ₂	5.0	0.160	23.5	0.63
S[Co/15.0Zr]/SiO ₂	3.1	0.179	22.7	0.73
Cl[0.7Zr + Co]/SiO ₂	3.6	0.114	28.0	0.56
Cl[8.5Zr + Co]/SiO ₂	4.6	0.147	22.0	0.69
[Co]/Al ₂ O ₃	3.3	0.077	28.4	0.62
Cl[8.5Zr + Co]/Al ₂ O ₃	3.3	0.183	22.0	0.70
S[8.5Zr/Co]/Al ₂ O ₃	1.3	0.73	24.1	0.67
S[Co/8.5Zr]/Al ₂ O ₃	5.0	0.275	24.0	0.67

P = 1 atm, T = 220°C, H₂/CO = 2, Catalyst Weight = 0.15-0.35 g, Total Flow Rate = ca. 90 cm³/min, Time-on-stream = ca. 25 hrs

Table 4: Slurry Bubble Column Reaction Results

Catalyst	ACTIVITY		SELECTIVITY	
	% CO Conversion	Rate (g CH ₂ /g cat/hr)	CH ₄ (wt%)	α
[Co]/SiO ₂	14.3	0.67	7.6	0.83
S[Co/8.5Zr(O)]/SiO ₂	25.5	1.21	8.6	0.84
S[Co/8.5Zr]/SiO ₂	26.6	1.24	10.7	0.82
S[Co/15.0Zr]/SiO ₂	20.9	0.93	6.7	0.83
Cl[0.7Zr + Co]/SiO ₂	23.2	1.08	9.4	0.82
Cl[8.5Zr + Co]/SiO ₂	24.8	1.18	8.5	0.84
[Co]/Al ₂ O ₃	27.1	1.34	7.9	0.82
Cl[1.4Zr + Co]/Al ₂ O ₃	30.9	1.41	12.1	0.83
S[Co/8.5Zr]/Al ₂ O ₃	27.5	1.54	10.4	0.84

Catalyst weight: 13-17g, T = 240°C, P = 450 psi, H₂/CO ratio = 2, Total flow rate = ca. 15 L/min, or 3 cm/sec linear velocity, Diluent: N₂: ca. 60%.