

Table 1. List of Co-based FT Catalysts Formulated

CAT. NO.	wt% Co	wt% M	wt% Prom.	Support	Notes	Prepared
Co.001	20%	1.94% Re	1% La ₂ O ₃ , 0.13% K	γ-alumina	U.S. Pat. 4,880,763	P
Co.002	20%	0.4343% Ru	1% La ₂ O ₃	γ-alumina	U.S. Pat. 4,413,064	P
Co.003	20%	0.595% Ru	1% La ₂ O ₃	γ-alumina	U.S. Pat. 4,413,064	P
Co.004	20%	0.4343% Ru	1% La ₂ O ₃	γ-alumina	Reproduce Co.002	P
Co.005	20%	0	0	γ-alumina	Base Catalyst	P
Co.005A	20%	0.494% Ru	0	γ-alumina	Ru added to calcined Co.005 by IW impreg.	P
Co.006	12%	0.7575% Re	0	Titania	U.S. Pat. 4,794,009	P
Co.007	20%	0	0	Titania	Base Catalyst	P
Co.008	20%	0	0	Silica	UK Pat. Appl. GB 2 125 062 A (Kneaded with excess liquid)	P
Co.009	20%	0.595% Ru	0	γ-alumina	Ru-Promoted Catalyst (use Ru Chloride, single-step aqueous IW)	P
Co.010	20%	0	0	γ-alumina	Base Catalyst (non-calcined)	P
Co.010A	20%	0.494% Ru	0	γ-alumina	Ru added to dried Co.010 by IW impreg.	P
Co.011	20%	0	0	Silica	UK Pat. Appl. GB 2 125 062 A (Kneaded)	P
Co.012	20%	0	0	Silica	Base Catalyst (Inc. Wetness)	P
Co.013	20%	0	0	Titania	Base Catalyst like Co.007, but all aqueous	P
Co.014	12%	0.595% Ru	0	Titania	Ru-Promoted Catalyst (aqueous IW co- impregnation)	P
Co.015	20%	0.4343% Ru	1% La ₂ O ₃	γ-Alumina	Similar to Co.002, but all aqueous	P
Co.016	20%	0.4343% Ru	1% La ₂ O ₃	γ-Alumina	Similar to Co.015, but calcined after Co impregnation	P

Table 1. List of Co-based FT Catalysts Formulated (Contd.)

CAT. NO.	wt% Co	wt% M	wt% Prom.	Support	Base	Prepared
Co.017	20%	0.0.5% Ru	1% La ₂ O ₃	γ-Alumina	Similar to Co.003, but all aqueous	P
Co.018	20%	0.0.5% Ru	0	γ-Alumina	Ru-Promoted Catalyst (single-step, aqueous IW)	P
Co.019	20%	0.0.5% Ru	0	Silica	Ru-Promoted Catalyst (single-step, aqueous IW)	P
Co.020	0	0.0.5% Ru	0	γ-Alumina	Ru Base Catalyst	P
Co.020A	20%	0.0.4% Ru	0	γ-Alumina	Co added to dried Co.020 by IW impreg.	P
Co.020B	20%	0.0.4% Ru	0	γ-Alumina	Co added to reduced Co.020 by IW impreg.	P
Co.020C	20%	0.0.4% Ru	0	γ-Alumina	Co added to calcined Co.020 by IW impreg.	P
Co.021	20%	0	0.7% Zr	Silica	U.K. Pat. Appl. GB 2 125 062 A (single-step)	P
Co.022	20%	0	0.7% Zr	Silica	U.K. Pat. Appl. GB 2 125 062 A (multiple-steps)	P
Co.023	20%	0	1.4% Zr	Silica	U.K. Pat. Appl. GB 2 125 062 A (multiple-steps)	P
Co.024	20%	0	8.5% Zr	Silica	Eur. Pat. Appl. 0 167 215 A2 (non-aqueous Zr pre-impregnation)	P
Co.025	20%	0	8.5% Zr	Silica	Similar to Co.024 but aqueous Zr pre-impregnation	P
Co.026	20%	0	0	Silica (Davison Grade 59)	Similar to Co.012 but different grade silica	P
Co.027	20%	0.0.5% Ru	0	Silica (Davison Grade 59)	Similar to Co.019 but different grade silica	P
Co.028	20%	0.0.5% Ru	0.5% K	γ-alumina	Ru- and K-Promoted Catalyst (single-step IW)	P
Co.029	30%	0.0.5% Ru	0.5% K	γ-alumina	Similar to Co.028 but 30% Co	P

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CAT. NO.	wt% Co	wt% M	wt% Prom.	Support	Basic	Prepared
Co.030	20%	(0	0.1% Zr	γ -alumina	Zr-Promoted Catalyst (single-step aqueous IW)	P
Co.031	20%	(0	1.4% Zr	γ -alumina	Zr-Promoted Catalyst (single-step aqueous IW)	P
Co.032	20%	(0	8.5% Zr	γ -alumina	Zr-Promoted Catalyst (aqueous IW co-impregnation)	P
Co.033	20%	(0	8.5% Zr	γ -alumina	multiple-steps, aqueous IW, Co pre-impregnation	P
Co.034	20%	(0	8.5% Zr	γ -alumina	multiple-steps, aqueous IW, Zr pre-impregnation	P
Co.035	20%	(0	8.5% Zr	Silica	Zr-Promoted Catalyst (single-step aqueous, kneaded)	P
Co.036	20%	(0	8.5% Zr	Silica	multiple-steps, aq. Co pre-impreg. by kneading, aqueous IW Zr impreg.	P
Co.037	12%	(0	0	Titania	Similar to Co.013, but TiO ₂ mainly anatase	P
Co.038	12%	0.595% Ru	0	Titania	Similar to Co.014, but TiO ₂ mainly anatase	P
Co.039	12%	(0	0	Titania	Similar to Co.007, but only 12% Co	P
Co.040	12%	(0	0	Titania	Similar to Co.013, but only 12% Co	P
Co.041	20%	0.595% Ru	8.5% Zr	Silica	Similar to Co.025, but Ru-promoted	P
Co.042	0	(0	8.5% Zr	Silica	Blank Zr-promoted SiO ₂	P
Co.043	20%	0.595% Ru	8.5% Zr 0.5% K	Silica	Similar to Co.041, but K-promoted	P
Co.044	20%	(0	15% Zr	Silica	Similar to Co.025, but 15% Zr	P
Co.045	20%	(0	4% Zr	Silica	Similar to Co.025, but 4% Zr	P
Co.046	12%	0.7595% Re	4% SiO ₂	Titania	Similar to Co.006, but SiO ₂ -promoted	-
Co.047	20%	0.595% Ru	0.3% K	γ -alumina	Similar to Co.028, but 0.3% K	P

Table 1. List of f Co-based FT Catalysts Formulated (Contd.)

CAT. NO.	wt% Co	wtwt% M	wt% Prom.	Support	Batch	Prepar- ed
Co.048	20%	0.51.5% Ru	8.5% Zr 0.3% K	Silica	Similar to Co.043, but 0.3% K	P
Co.049	20%	0.51.5% Ru	0.1% K	γ -alumina	Similar to Co.047, but 0.1% K	P
Co.050	20%	0.51.5% Ru	8.5% Zr 0.1% K	Silica	Similar to Co.048, but 0.1% K	P
Co.051	0	0.51.5% Ru	0	Titania (R)		P
Co.052	0	0.51.5% Ru	0	Titania (A)		P
Co.053	20%	0.51.5% Ru	0	γ -alumina	Similar to Co.018 (New Batch)	P
Co.054	20%	0	8.5% Zr 0.3% K	Silica	Similar to Co.043, but without Ru	P
CAL.01 (97E-13E)	20%	0.51.5% Ru	0	γ -alumina	Similar to Co.018 (Calsicat Prep.)	P
CAL.02 (97E-16B)	20%	0.51.5% Ru	0	γ -alumina	Similar to CAL.01 (New Batch)	P
CAL.03 (97E-13F)	20%	0.51.5% Ru	0	γ -alumina	2-step impreg., Similar to CAL.02	P

TABLE 2. DESIRED PROCESS CONDITIONS, ACTIVITY AND SELECTIVITY

PROCESS CONDITIONS	
Feed H ₂ /CO ratio	0.5-2.0
Temperature, °C	230-280
Pressure, bar	10-30
Syngas flow rate, Nm ³ /hr/kg cat.	3-6
ACTIVITY and SELECTIVITY	
Total Hydrocarbon Production, g/Nm ³ syngas used (g/hr/g cat.)	200 (0.6-1.2)
C ₃ + Hydrocarbon Production, % of Total HC production	90

TABLE 3. SLURRY BUBBLE COLUMN STANDARD REACTION CONDITIONS

Period #	Temperature (°C)	Pressure (psi)	H ₂ /CO Ratio	Period Time (hr)
1	240	450	2	48
2	220	450	2	48
3	240	450	2	24
4	240	450	1	48
5	240	600	1	48
6	240	450	2	24

Syngas flow rate: 24Nm³/hr/kg cat.

TABLE 4 - CATALYST SELECTION FOR LOW METHANE SELECTIVITY

Cat. #	Composition ^a	450 psi (H ₂ /CO=2)				600 psi (H ₂ /CO=1)				Attrition Resistance	Pass or Fail (R)
		220°C		240°C		240°C		240°C			
		Rate ^b	%C ₁₊	Rate ^b	%C ₁₊	Rate ^b	%C ₁₊	Rate ^b	%C ₁₊	Particle Size % Change ^c	
Co.005	20Co/A	0.53	99.0	1.34	90.4	0.90	99.0	99.0	10.8	P	
Co.018	20Co0.5Ru/A	0.59	97.2	1.56	88.1	0.84	96.7	96.7	-	F	
Co.028	20Co0.5Ru0.5K/A	0.31	98.1	1.00	92.2	0.67	98.3	98.3	11.1	P	
Co.047	20Co0.5Ru0.3K/A	-	-	1.29	90.7	0.80	96.5	96.5	-	P	
Co.024	20Co8.5Zr/S	0.45	97.9	1.21	89.4	0.80	97.6	97.6	-	F	
Co.041	20Co0.5Zr0.5Ru/S	0.41	98.5	1.16	86.8	0.91	97.0	97.0	17.0	F	
Co.043	20Co8.5Zr0.5Ru0.5K/S	0.20	98.5	0.61	94.4	0.41	97.7	97.7	-	F	
Co.048	20Co8.5Zr0.5Ru0.3K/S	0.28	97.1	0.90	88.4	0.83	96.3	96.3	-	P	

^a numbers = nominal weight loadings of the various metals; A = Alumina; S = Silica

^b rate in g hydrocarbons per g catalyst per hour

^c % change after the entire reaction cycle

^d compared to target set by DOE under given process conditions

Table 5. List of Water-Gas s Shift Catalysts and F-T Catalysts with WGS Function

CAT. NO.	wt% Co	wt% Ni	wt% Prom.	Support	Design	Prepar. Mtd.
WGS.01	0	5.0% Cu	0	γ -alumina	single-step, aqu. IW	P
WGS.02	0	5.0% Cu	10% Zn	γ -alumina	single-step, aqu. IW	P
WGS.03	0	5.0% Cu	4.0% Cr	γ -alumina	single-step, aqu. IW	P
WGS.04	0	0	4.0% Cr	γ -alumina	single-step, aqu. IW	P
WGS.05	0	0	4.0% Mn	γ -alumina	single-step, aqu. IW	P
WGS.06	0	5.0% Cu	4.0% Mn	γ -alumina	single-step, aqu. IW	P
WGS.07	0	4.0% Fe	0	γ -alumina	single-step, aqu. IW	P
WGS.08	0	4.0% Fe	4.0% Cr	γ -alumina	single-step, aqu. IW	P
CoW.01	20%	5.0% Cu	10% Zn	γ -alumina	multiple-steps, aqu. IW, Cu, Zn pre-impr.	P
CoW.02	20%	5.0% Cu	4.0% Cr	γ -alumina	multiple-steps, aqu. IW, Cu, Cr pre-impr.	P
CoW.03	10%	5.0% Cu	4.0% Cr	γ -alumina	similar to CoW.02 (10% Co only)	P
CoW.04	10%	10% Cu	8.0% Cr	γ -alumina	similar to CoW.03; 10% Cu and 8% Cr	P
CoW.05	20%	5.0% Cu	4.0% Cr	γ -alumina	similar to CoW.02 with support calcined at 750°C	P
CoW.06	20%	5.0% Cu	4.0% Cr	Silica	multiple-steps, aqu. IW, Cu, Cr pre-impr.	P

Table 66. Summary of Physical Properties

CATALYST	Composition	BET Surface Area (m ² /g)	Pore Volume (cc/g)	Average Pore Dia. (Å)	Average Part. Size (µm)
Vista-B Al ₂ O ₃	(0-400 meshsh)	299	1.69	269	24
Vista-B Al ₂ O ₃	Calcined 500°C	240	0.49	82	
Vista-B Al ₂ O ₃	Calcined 600°C	206	0.49	95	
Vista-B Al ₂ O ₃	Calcined 600°C	174	0.47	109	
Davison SiO ₂	(0-400 meshsh)	219	0.51	89	121
Degussa P25 TiO ₂	(as received)	47	0.40	335	6
Degussa P25 TiO ₂	Dried 60°C, C.Calc. 350°C/16hrs	46	0.48	419	51
Degussa P25 TiO ₂	Dried 60°C, C.Calc. 650°C/16hrs	12	0.17	573	212
Co.001	20Co/1Re/e/ 1La ₂ O ₃ /0.13KK/A	191	0.31	66	42 40
Co.002	20Co/0.43Ru/ 1La ₂ O ₃ /A	149	0.33	89	74
Co.003	20Co/0.5Ru/ 1La ₂ O ₃ /A	122	0.26	87	77
Co.004	20Co/0.43Ru/ 1La ₂ O ₃ /A				
Co.005	20Co/A	173	0.34	81	65 86
Co.006	12Co/0.75Re/e/T	16	-	-	
Co.007	20Co/T	11	0.10	372	
Co.008	20Co/S	181	1.06	234	
Co.009	20Co/0.5/A				
Co.010	20Co/A				
Co.011	20Co/S	211	1.07	203	107
Co.012	20Co/S	211	-	-	105
Co.013	20Co/T				
Co.014	12Co/0.5Ru/u/T	15	0.12	328	
Co.015	20Co/0.43Ru/ 1La ₂ O ₃ /A	141	-	-	67

Table 6. Summary of Physical Properties (contd.)

CATALYST	Composition	BET Surface Area (m ² /g)	Pore Volume (cc/g)	Average Pore Dia. (Å)	Average Part. Size (µm)
Co.016	20CoB/0.43Ru/ 1La ₂ O ₃ /A	116	-	-	79
Co.017	20Co/0.5Ru/w/ 1La ₂ O ₃ /A	123	-	-	73
Co.018	20Co/0.5Ru/A/A	158	-	-	69
Co.019	20Co/0.5Ru/S/S				110
Co.021	20Co/0.7Zr/S/S	213	1.12	210	
Co.023	20Co/1.4Zr/S/S	213	-	-	
Co.024	20Co/8.5Zr/S/S	215	1.08	202	
Co.025	20Co/8.5Zr/S/S	208	0.97	187	
Co.026	20Co/S(59))	184	-	-	
Co.027	20Co/S(59))	189	-	-	
Co.028	20Co/0.5Ru/0.515K/A	161	0.33	82	
Co.029	30Co/0.5Ru/0.515K/A	140	-	-	
Co.032	20Co/8.5Zr/A/A	155	0.30	77	
Co.034	20Co/8.5Zr/A/A	150	0.31	83	
Co.035	20Co/8.5Zr/S/S	207	1.21	233	
Co.036	20Co/8.5Zr/S/S	209	-	-	
Co.037	12Co/T(A)	38	-	-	
Co.039	12Co/T(R)	13	-	-	
Co.041	20Co/0.5RU/8.515Zr/S	214	-	-	
CAL.01	20Co/0.5Ru/A/A	178	0.34	76	
CAL.02	20Co/0.5Ru/A/A	158	-	-	
CAL.03	20Co/0.5Ru/A/A	158	-	-	

Under "Composition" A = alumina; S = silica; T = titania

Table 7. H₂ Chemisorption and TPR Results

Catalyst	H ₂ Chemisorption ^a				H ₂ TPR	
	Total (μ mol H ₂ /g cat)	Irrevers (μ mol H ₂ /g cat)	Average d_p^b (nm)	% Disp	%Co Red ^c (TPR calc. Cat.)	% Red ^d (stand. red.)
Co.001	174±5	157±±5		10.2		
Co.002	155	130		9.1		
Co.003	165	140		9.6		
Co.004						
Co.005	48	42	20	2.8	89	58
Co.005a	129	110	11	7.6	92	84
Co.006	44	32	19	4	80	
Co.007	33	23	36	2.0	78	78
Co.008						
Co.009	133	109	13	7.8	98	
Co.010						
Co.010a	124	100	12.5	7.3	91	89
Co.011	82	70	15.6	4.8	75	75
Co.012	89	74	15	5.2	80	80
Co.013	21	17	79	1.2	97	
Co.014	38	30	21	3.7	79	
Co.015	146	124	11.7	8.6	94	94
Co.016	163	146	10.5	9.6	96	96
Co.017	202	183	8.5	11.9	97	97
Co.018	185	165	9.2	11	97	94

Table 7. H₂ Chemisorption^a and TPR Results (contd.)

Catalyst	H ₂ Chemisorption ^a				TPR	
	Total (μ mol H ₂ /g cat)	Irrev. (μ mol H ₂ /g cat)	Average d_p^b (nm)	% Disp	%Co Red. ^c (TPR calc. Cat.)	% Red. ^d (stand red.)
Co.018-CI					95	
Co.019	112	92		6.6		
Co.020						
Co.020a	153	1266	10	9.1	88	
Co.020b	134	1133	11	7.9	86	
Co.020c	115	1000	13	6.8	88	
Co.021	74	50		4.3		
Co.022	141	1222		8.3	80	
Co.023	158	1366		9.3	81	
Co.024	87	72		5.1	91	
Co.025	93	77		5.5	75	
Co.026						
Co.027						
Co.028	170	1488		10		
Co.029	175	1555		7		
Co.030						
Co.031	71	51	20	4.2	82	
Co.032	55	39	26	3.2	85	
Co.033	43	32	31	2.5	79	
Co.034	114	91	14	6.7	96	
Co.035	125	1155	11	7.2	82	
Co.036	122	98		7.2		

Table 7. H₂ Chemisorption^a and TPR Results (contd.)

Catalyst	H ₂ Chemisorption ^a				TPR	
	Total (μ mol H ₂ /g cat)	Irrev. (μ mol H ₂ /g cat)	Average d_p^b (nm)	% Disp	%Co Red ^c (TPR calc Cat.)	% Red ^d (stand red.)
Co.037	21	3	48	2	99	
Co.038	45	35.5	21	4.3	91	
Co.039	19	16.5	40	1.8	72	
Co.040	14	11.1		1.4		
Co.041	70	55.5		4		
Co.042						
Co.043	137	116.6		8		
Co.044						
Co.045						
Co.046						
Co.047						
Co.048						
CAL.01	-	-	58 ^e	4.4 ^e		
CAL.02	-	-	63 ^e	5.1 ^e		
CAL.03	-	-	57 ^e	4.2 ^e		

(a) static H₂ chemisorption at 100°C

(b) Est. assuming $H_{tot}/Co_s = 1$, $5.466 \times 10^{-20} \text{ m}^2/Co_s$, and $d_p = 5/S_{Co}/\rho$

S_{Co} is based on amt. Co reducible during standard reduction

(c) % Co reducible from TPR of calcined catalysts up to 900°C

(d) % Co reduced after standard reduction procedure

(e) Based on CO chemisorption

(f) Catalyst Co.018-Cl is chlorinated.

Table 8. Summary of Fixed Bed Reaction Results

Catalyst	Run	CO Conv (%)	Rate g CH ₂ /g cat/hr	wt% CH ₄	alpha	C3-C5 Ole/Par	CO ₂ (%) (CO)	g/g cat/hr	E act. kcal/mol	Comment
Co.001	4	2.6	0.116	19.6.6	0.76	8.61	0.4	0.061		NSH**
Co.002	4	6.7	0.258	26.1.1	0.64	1.97	0.1	0.012		NS*, calcined
Co.003	1	5.5	0.185	30.8.8	0.57	4.22			28.9	old startup
Co.004	1	4.3	0.291	30.4.4	0.62	2.77	0.1	0.025	25.9	NSH
Co.005	2	3.3	0.087	21.4.4	0.66	3.40	0.1	0.005	25.1	NS
"	2a	2.5	0.066	25.5.9	0.59	4.92	0.1	0.004		CO:H ₂ :Ar = 1:2:2
"	2b	2.4	0.064	26.3.3	0.60	6.22	0.1	0.006		+ H ₂ O (eq. 7.5% CO conv.)
"	3	3.3	0.077	28.4.4	0.62	2.29	0.1	0.013		NSH
"	4	4.0	0.069	30.0.0	0.62	2.16	0.2	0.009		NSH
"	5	3.9	0.171	26.5.8	0.76	2.59	0.1	0.018		NSH, 10 atm
Co.005a	1	3.2	0.227	30.0.0	0.60	3.05	0.1	0.034		NSH
Co.006	1	2.7	0.052	45.0.0	0.49	1.90	0.1	0.006		NSH
Co.007	1	3.2	0.024	49.8.8	0.50	0.72	0.2	0.004		NSH
Co.009	1	4.9	0.346	31.1.1	0.57	1.69	0.1	0.020		NSH
"	2	4.9	0.338	31.1.1	0.58	1.64	0.1	0.026		NSH
Co.010a	1	3.5	0.246	29.5.5	0.62	2.58	0.2	0.040		NSH
"	2	4.1	0.262	30.0.0	0.61	2.31	0.1	0.022		NSH
Co.011	2	2.9	0.094	22.4.4	0.61	4.83	0.3	0.030		NSH
Co.012	1	3.8	0.083	26.3.3	0.64	4.40			22.5	slow CO startup (60 min)
"	2	4.4	0.085	29.1.1	0.64	1.93	0.3	0.018		NSH
"	3	2.1	0.081	28.6.6	0.66	3.57	0.4	0.049		NSH
Co.014	1	1.5	0.028	32.3.3	0.63	4.70	0.1	0.003	26.0	NSH
"	2	2.6	0.034	27.7.7	0.69	10.8	0.1	0.011		NSH
Co.015	1	6.8	0.211	26.7.7	0.60	3.30				slow CO startup (120 min)
Co.016	1	5.2	0.161	33.6.6	0.56	6.85				slow CO startup (30 min)
Co.017	2	4.6	0.139	22.0.0	0.69	3.72	0.1	0.012		NS
"	2a	3.7	0.111	25.9.9	0.64	4.19	0.1	0.011		CO:H ₂ :Ar = 1:2:2
"	2b	3.4	0.102	26.9.9	0.65	4.39	0.1	0.013		+ H ₂ O (eq. 7.5% CO conv.)
Co.018	2	3.4	0.170	27.2.2	0.69	2.24	0.1	0.013		NS
"	2a	2.7	0.133	33.2.2	0.64	2.52	0.1	0.011		CO:H ₂ :Ar = 1:2:2
"	2b	3.0	0.147	33.6.6	0.63	2.41	0.1	0.015		+ H ₂ O (eq. 7.5% CO conv.)
"	3	4.1	0.290	30.0.0	0.62	2.34	0.1	0.022		NSH
"	4	3.6	0.340	25.4.4	0.80	1.92	0.1	0.041		NSH, 10 atm
"	5	7.5	0.470	29.0.0	0.60	1.93	0.3	0.055		NSH, calcined in flow air
"	6	6.5	0.409	24.6.6	0.64	2.42			NSH, calcined in flow air, S2"	
Co.018Cl	1	4.5	0.320	33.5.5	0.57	1.45	0.1	0.018		NSH
Co.019	1	4.4	0.088	15.2.2	0.74	7.61				NS
"	2	2.2	0.085	18.5.9	0.73	8.59	0.3	0.040		NSH

Table 8. Summary of Fixed Bed Reaction Results (cont'd)

Catalyst	Run	CO Conv (%)	Rate g CH ₂ /g cat/hr	wt% CH ₄	alpha	C3-C5 Ole/Par	CO ₂ (%) (CO)	g/g cat/hr	E act kcal/mol	Comment
Co.020a	1	4.6	0.343	33.5.5	0.57	1.70	0.1	0.024		NSH
"	2	4.4	0.315	31.2.2	0.59	1.96	0.1	0.028		NSH
Co.020b	1	4.4	0.311	31.7.7	0.58	1.81	0.2	0.051		NSH
Co.020c	1	4.0	0.287	30.4.4	0.60	2.38	0.1	0.017		NSH
Co.021	1	3.4	0.109	27.3.3	0.62	2.78	0.1	0.012	28.2	NSH
"	2	3.6	0.114	28.0.0	0.56	2.69	0.1	0.012		NSH
Co.022	1	3.8	0.121	26.7.7	0.55	2.91	0.1	0.015	30.1	NSH
Co.023	1	3.8	0.123	28.3.3	0.56	3.18	0.2	0.023	29.5	NSH
Co.024	1	5.1	0.165	32.8.8	0.62	2.08	0.5	0.055		NSH
"	2	5.7	0.182	28.7.7	0.62	2.25	0.3	0.035		NSH
Co.025	1	5.0	0.160	23.5.5	0.63	4.13	0.2	0.019	26.9	NSH
Co.026	1	4.4	0.129	26.9.9	0.62	2.65	0.2	0.022		NSH
"	1	22.9	0.170	22.6.6	0.67	0.64	1.5	0.037		NSH, high conv. study
Co.027	1	4.2	0.169	23.0.0	0.65	3.44	0.2	0.026		NSH
"	1	17.8	0.180	19.4.4	0.71	0.96	1.2	0.011		NSH, high conv. study
Co.028	1	3.8	0.146	18.2.2	0.76	7.63	0.2	0.031		NSH
"	2	4.3	0.167	14.7.7	0.80	13.2	0.2	0.030	28.4	NSH
"	3	4.5	0.206	15.5.5	0.79	13.4	0.2	0.037		NSH, re-calc. in flow air
Co.029	1	2.8	0.173	15.3.3	0.79	25.9	0.2	0.026		NSH
Co.031	1	1.9	0.060	26.1.1	0.64	4.65	0.3	0.031		NSH
Co.035	2	4.6	0.147	22.0.0	0.69	4.84	0.2	0.019		NSH
Co.036	2	3.9	0.125	28.9.9	0.67	4.20	0.1	0.013		NSH
Co.037	1	2.7	0.053	32.8.8	0.59	2.82				NSH
Co.038	1	4.5	0.051	25.1.1	0.68	4.63	0.3	0.013	24.2	NSH
Co.039	1	1.1	0.021	57.2.2	0.64	0.84	0.2	0.010	25.6	NSH, cracking in the line
"	2	3.9	0.049	42.4.4	0.48	0.95	0.2	0.009		NSH
Co.040	1	1.9	0.037	45.2.2	0.53	1.79	0.2	0.007		NSH
"	2	2.8	0.033	44.6.6	0.46	1.12	0.2	0.007		NSH
Co.041	1	3.5	0.136	40.7.7	0.69	1.47	0.6	0.079		NSH, cracking in the line
Co.043	1	4.6	0.104	15.3.3	0.78	12.1	0.6	0.048		NSH, 2.5 hr on-stream
"	2	3.7	0.078	16.3.3	0.78	7.75	0.5	0.035	35.1	NSH
Co.047	1	6.4	0.263	21.3.3	0.73	7.20	0.3	0.040	26.6	NSH
Co.048	1	3.5	0.162	16.3.3	0.77	17.1	0.2	0.027	28.0	NSH
Co.049	1	7.1	0.366	23.4.4	0.69	5.63	0.3	0.043		NSH
"	2	6.0	0.388	23.3.3	0.68	5.93	0.3	0.056		NSH, re-calcined in flow air
"	3	6.7	0.409	25.2.2	0.69	4.73	0.3	0.059		NSH, calcined in flow air
"		44.9	0.457	26.5.5	0.67	0.67	3.8	0.131		NSH, calcined in flow air, HCS

Table 8. Summary of Fixed Bed Reaction Results (cont'd)

Catalyst	Run	CO Conv (%)	Rate g-CH ₂ /g-cat/hr	wt% CH ₄	alpha	C3-C5 Ole/Par	CO ₂ (%) (CO)	g/g cat/hr	E act kcal/mol	Comment
Co-052	1	6.8	0.398	28.1 1	0.60	3.07	0.2	0.043		NSH
	1	28.5	0.417	26.8 8	0.64	0.79	1.6	0.081		NSH, high conv. study
	2	6.6	0.433	23.4 4	0.63	2.35	0.2	0.052		NSH, calcined in flow air
	3	7.8	0.453	27.6 6	0.62	1.67	0.1	0.027		NSH
	3	31.5	0.457	25.4 4	0.65	0.52	0.9	0.044		NSH, high conv. study
Co-054	1	1.2	0.041	17.8 8	0.79	16.3	0.2	0.014		NSH
CAL-01	1	4.8	0.181	24.4 4	0.66	5.86	0.3	0.036		NSH, temp. surge (startup)
	2	7.4	0.491	28.7 7	0.61	2.06	0.4	0.083		NSH
	3	2.5	0.164	25.6 5	0.63	4.97	0.2	0.052		NSH, HT, re-reduced
	4	7.3	0.483	35.8 3	0.57	1.21	0.2	0.098		NSH, HT, re-calcined
CAL-02	1	6.1	0.379	27.3 3	0.63	3.04	0.2	0.040		NSH
CAL-03	1	7.3	0.459	29.0 1	0.60	2.59	0.2	0.048		NSH
CoW-01	1	1.2	0.016	30.2 2	0.58	3.78	0.2	0.006		NSH, reduced at 230 °C
	1	0.5	0.007	42.1 1	0.51	0.95	0.1	0.003		NSH, re-reduced at 350 °C
	2	0.2	0.006	40.9 1	0.51	11.3	0.1	0.006		NSH, reduced at 350 °C
CoW-02	1	0.3	0.009	25.6 5	0.60	4.94	0.1	0.008		NSH, reduced at 230 °C

* New startup, if not specified, calcined in UPARC

** New startup, heated inlet, if not specified, calcined in UPARC. In some cases, "re-calcined" means calcination of the calcined catalyst from UPARC for a longer period and "calcined" means calcination of the catalyst precursor.

* was done in the second system

- Davison Grade 59 Silica, if not specified, S refers Davison Grade 952 Silica

corrected overheated line on 3/6/1994

Catalyst Co.018Cl is chlorinated

Table 9. Summary of WGS Fixed Bed Reaction Results

Catalyst	Run	CO Conv (%)	Rate gCCO/g cat/hr	R(CO) mmol/g cat/hr	Eact. kcal/mol	Comment
Commercial Cu/ZnO	1	2.8	0.39	14.00	10	
Commercial Cu/Chr	2	14.9	2.49	89.00		
WGS.01	2	2.7	0.476	17.00		
WGS.02	2	3.2	0.597	21.00		
WGS.03	1	4.7	0.79	28.00		
WGS.06	1	1.5	0.24	8.50		
WGS.08	1	0	0	0.00		no activity observed
CoW.01*	1	0	0	0.00		no activity observed
CoW.02*	1	1.8	0.32	10.00		
CoW.03*	1	2.5	0.39	14.00		

Reaction Conditions: 1.5 hours on stream, 171°C, P_{co}=0.096atm, H₂O:CO=1.5, 1 atm
 * 220°C

DATE: 07/07/94

COMPARISON OF CONVERSION AND SELECTIVITY OF
METHANE REDUCTION CATALYSTS AT STARTUP CONDITIONS

Period No.		Temp.	Pres.	H ₂ /CO Ratio									
1		240 CC	450psi	2.0									
Run No	Cat. No	Cat. wt, g	Conv. %	Prod. Rate	Selectivities				Alpha GC	Alpha Liq	Catalyst Promt	Composit. Metal	Suppt
					%CH ₄	%C ₂	%C ₃ +	%CO ₂					
3	SBCR												
5	CO.003	15.1	31.7	1.53	16.7	2.4	79.8	1.16	0.71	--	1.0La	0.5Ru	Al
6	CO.011	15.3	14.3	0.67	7.6	1.6	89.4	1.42	0.78	0.83	0.0	0.0	Si
7	CO.012	15.8	13.9	0.63	6.1	1.5	90.6	1.74	0.80	0.89	0.0	0.0	Si
8	CO.015	15.0	28.3	1.37	12.7	2.0	84.1	1.24	0.76	0.80	1.0La	0.43Ru	Al
9	CO.011	15.0	18.5	0.89	8.8	1.7	88.8	0.77	0.78	0.83	0.0	0.0	Si
11	CO.017	15.0	27.2	1.32	11.2	1.8	85.9	1.14	0.77	0.80	1.0La	0.5Ru	Al
12	CO.018	15.6	33.8	1.56	9.7	2.0	86.6	1.68	0.75	0.85	0.0	0.5Ru	Al
13	CO.016	14.7	26.4	1.31	(1)	1.7	89.3	0.68	0.78	0.81	1.0La	0.43Ru	Al
14	CO.019	15.2	13.9	0.66	(2)	1.7	97.2	0.70	0.80	0.86	0.0	0.5Ru	Si
15	CO.005	14.7	27.1	1.34	7.9	1.6	89.7	0.82	0.79	0.82	0.0	0.0	Al
	CO.002	15.4	30.1	1.42	12.5	2.5	83.9	1.09	0.75	0.80	1.0La	0.43Ru	Al
	CO.025	15.6	26.6	1.24	10.7	2.1	86.4	0.82	0.76	0.82	8.5Zr	0.0	Si
18	CO.004	15.0	33.9	1.64	15.3	2.4	80.9	1.37	0.74	0.79	1.0La	0.43Ru	Al
19	CO.021	15.6	23.2	1.08	9.4	2.0	88.0	0.73	0.77	0.82	0.7Zr	0.0	Si
20	CO.041	15.8	25.3	1.16	11.0	2.1	86.0	0.88	0.76	0.84	8.5Zr	0.5Ru	Si
21	CO.014	15.1	8.5	0.40	8.3	3.5	85.8	2.43	0.74	0.83	0.0	0.5Ru	Ti
22	CO.040	14.5	1.8	0.09	0.0	4.0	94.1	1.89	0.71	0.82	0.0	0.0	Ti
23	CO.047	15.8	28.2	1.29	7.7	1.5	89.3	1.47	0.79	0.84	0.3K	0.5Ru	Al
24	CO.049	15.6	30.6	1.41	10.9	1.8	85.7	1.66	0.76	0.82	0.1K	0.5Ru	Al
25	CO.047	15.6	28.1	1.30	8.8	1.6	88.1	1.50	0.78	0.85	0.3K	0.5Ru	Al
26	CO.031	15.9	30.9	1.41	12.1	1.9	84.9	1.12	0.75	0.83	1.4Zr	0.0	Al
27	CO.029	15.9	28.3	1.27	8.3	1.6	87.9	2.21	0.77	0.84	0.5K	0.5Ru	Al
28	COW.01	15.0	1.1	0.05	0.0	12.	83.9	4.23	0.58	--	5.0Cu	10.0Zn	Al

Note: Catalyst Run 9 screened thru 170 x 400 mesh.

Catalysts For Runs 11 through 28 (except Runs 21 and 22) screened thru 150x 400 mesh.

Catalysts for Runs 21 and 22 screened thru 100 x 400 mesh.

Catalyst No. CO.029 contained 30 wt% cobalt.

C. Problems

- (1) Weak TCD filaments in G.CC. CH₄ peaks smaller than expected.
- (2) Internal valve in G.C. leaked. CH₄ peak undetected.

Table 11

DATE: 07/07/94

COMPARISON OF CONVERSION AND SELECTIVITY OF
METHANE REDUCTION CATALYSTS AT STARTUP CONDITIONS

Period No.	Temp.	Pres.	H ₂ /CO Ratio										
1	240 CC	450psi	2.0										
Run No	Cat. wt, g	Conv. %	Prod. Rate	Selectivities				Alpha GC	Alpha Liq	Catalyst Promt	Composit. Metal	Suppt	
				%CH ₄	%C ₂	%C ₃ +	%CO ₂						
4	SBCR												
3	Co.002	15.2	29.4	1.42	17.3	2.3	79.4	1.01	0.73	0.82	1.0La	0.43Ru	Al
4	Co.024	15.4	25.5	1.21	8.6	2.0	89.0	0.43	0.79	0.84	8.5Zr	0.0	Si
5	Co.035	15.4	24.8	1.18	8.5	2.1	89.0	0.47	0.78	0.84	8.5Zr	0.0	Si
6	Co.028	15.4	21.2	1.00	6.1	1.6	91.3	1.01	0.81	0.83	0.5K	0.5Ru	Al
7	Co.043	15.4	13.0	0.61	3.7	1.8	93.4	1.06	0.79	0.85	8.5Zr	0.5Ru	Si
8	Co.006	15.0	2.7	0.13	0.1	0.2	98.0	1.75	0.67	0.85	0.0	0.75Re	Ti
9	Co.048	15.4	19.1	0.90	9.9	1.6	87.4	1.10	0.77	0.88	8.5Zr	0.5Ru	Si
											0.3K		
10	CAL.02	15.9	34.5	1.58	12.9	2.0	83.9	1.23	0.75	0.81	0.0	0.5Ru	Al
11	CAL.03	15.6	29.7	1.39	13.5	2.1	83.4	1.08	0.74	0.86	0.0	0.5Ru	Al
12	Co.053	15.9	34.2	1.56	12.6	2.0	84.2	1.23	0.75	0.83	0.0	0.5Ru	Al
13	Co.054	15.7	10.4	0.48	4.7	1.8	92.3	1.17	0.78	0.86	8.5Zr	0.0	Si
											0.3K		

Note: Catalysts for all runs except Run 8 screened thru 150 x 400 mesh.
Catalyst for Run 8 screened thru 100 x 400 mesh.

.C. Problems

- (1) Weak TCD filaments in G.C.C. CH₄ peaks smaller than expected.
- (2) Internal valve in G.C. leaked. CH₄ peak undetected.

SBCR CATALYST EXTRACTIONS

Catalyst No. (Support)	Run No.	Charge		Recovered (Oxidized) wt, gm	Charge		Recovered		Reduction in Particle Size, %
		(H ₂ Reduced) wt, gm	Particle Size, mvd, microns		Particle Size at 10% microns	Particle Size, mvd, microns	Particle Size at 10% microns		
Co.001 (Al)	1	14.5	42.02	12.63	24.25	41.06	23.62	2.3	
Co.001 (Al)	2	16.5	42.02	15.18	24.25	40.09	22.86	4.6	
Co.005 (Al)	3	19.5	85.66	18.41	30.46	64.53	31.27	24.7	
Co.002 (Al)	4	20.1	73.61	20.4	32.86	71.19	33.50	3.3	
Co.003 (Al)	5	15.1	76.81	14.54	34.40	72.57	34.25	5.5	
Co.011 (Si)	6	15.3	107.09 (1)	16.03	53.19	94.02	40.44	12.2	
Co.012 (Si)	7	15.8	105.22 (1)	14.73	51.33	101.37	44.44	3.7	
Co.015 (Al)	8	15.0	75.63 (1)	15.52	33.15	74.68	32.68	1.3	
Co.015 (Al)	8	15.0	75.63 (1)	15.52	33.15	74.68	32.68	1.3	
Co.011 (Si)	9	15.0	79.88 (2)	15.92	48.31	72.44	36.31	9.3	
Co.016 (Al)	10	15.5	64.60 (2)	15.72	32.16	64.38	32.78	0.3	
Co.017 (Al)	11	15.0	73.14 (3)	15.09	36.29	69.95	35.62	4.4	
Co.018 (Al)	12	15.6	62.89 (3)	16.97	32.56	68.16	34.74	--	
Co.016 (Al)	13	14.7	67.69 (3)	13.30	35.05	64.79	34.20	4.3	
Co.019 (Si)	14	15.2	92.63 (3)	15.00	42.73	84.39	36.52	8.9	
Co.005 (Al)	15	14.7	80.62 (3)	15.30	45.07	71.90	36.79	10.8	
Co.002 (Al)	16	15.4	73.61 (3)	14.98	32.86	67.62	32.67	8.1	
Co.002 (Al)	1 (M4)	15.0	73.61 (3)	11.00	32.86	66.26	35.75	10.0	
Co.025 (Si)	17	15.6	87.19 (3)	14.60	47.35	78.31	36.27	10.2	
Co.004 (Al)	18	15.0	78.12 (3)	15.25	44.15	66.86	33.83	14.4	
Co.021 (Si)	19	15.6	86.18 (3)	16.06	46.54	77.95	35.59	9.55	
Co.041 (Si)	20	15.8	87.48 (3)	17.02	49.26	68.74	26.72	17.0	
Co.021 (Si)	3 (M4)	15.2	73.61 (3)	15.1	24.46	71.38	32.33	3.03	
Co.024 (Al)	4 (M4)	15.4	--	(4)	--	--	--	--	
Co.035 (Si)	5 (M4)	15.4	89.14 (3)	14.08	49.29	74.76	31.67	19.2	
Co.028 (Al)	6 (M4)	15.4	80.83 (3)	15.7	44.81	71.83	36.34	11.1	

(1) Screened through 100x400 mesh screens. (2) Screened through 170x400 mesh screens.
 (3) Screened through 150x400 mesh screens. (4) Did not filter, too waxy

Note: The charge weights are in the hydrogen-reduced state and the recovered weights are in the oxidized state. The particle size is reported as the mean volume diameter (mvd) as measured by a Microtrac particle size analyzer.

SBCR CATALYST EXTRACTIONS

Catalyst No. (Support)	Run No.	Charge		Charge		Recovered		Recovered		Reduction in Particle Size, %
		(H ₂ Reduced) wt, gm	(Oxidized) wt, gm	Particle Size, mvd, microns	Particle Size at 10% microns	Particle Size, mvd, microns	Particle Size at 10% microns	Particle Size at 10% microns	Reduction in Particle Size, %	
Co.014 (Ti)	21	15.1	15.1	111.70 (1)	32.65	106.66	33.49	4.51		
Co.040 (Ti)	22	14.5	8.5	(5)	(5)	130.40	51.40	--		
Co.047 (Al)	23	15.8	16.95	83.42 (3)	44.41	76.46	39.02	8.34		
Co.049 (Al)	24	15.6	16.54	81.3 (3)	42.39	70.11	35.87	13.8		
Co.047 (Al)	25	15.6	16.69	79.36 (3)	41.72	69.09	36.16	12.94		
Co.031 (Al)	26	15.9	15.37	75.48 (3)	38.34	68.42	35.39	9.35		
Co.029 (Al)	27	15.9	18.28	76.39 (3)	39.56	68.72	36.04	10.04		
Co.043 (Si)	7 (M4)	15.4	15.1	(5)	(5)	85.51	40.20	--		
Co.006 (Ti)	8 (M4)	15.0	9.09	121.38 (1)	52.80	99.31	38.62	18.2		
Co.048 (Si)	9 (M4)	15.4	15.85	82.40 (3)	40.94	70.69	25.53	14.2		
CAL.02 (Al)	10 (M4)	15.9	16.42	74.40 (3)	37.79	65.89	34.14	11.44		
Co.053 (Al)	12 (M4)	15.9	16.95	82.02 (3)	43.10	69.53	35.76	15.23		
Co.054 (Si)	13 (M4)	15.7	17.09	101.17 (3)	57.54	82.37	37.89	18.58		

-
- (1) Screened through 100x400 mesh screens.
 - (3) Screened through 150x400 mesh screens.
 - (5) Insufficient feed sample.

Table 13

CATALYST ATTRITION STUDIESExperimental Procedure

Charge: 20 gm solids
500 ml n-C₇

Apparatus: One liter glass vessel with two internal baffles. Two 2-inch diameter turbine mixers with 6 blades (1/2x3/8 inch paddles).

Procedure: Mixture is stirred for 48 hours and 1000 RPM at room temperature. Particle size distribution is measured by Microtrac.

Results:

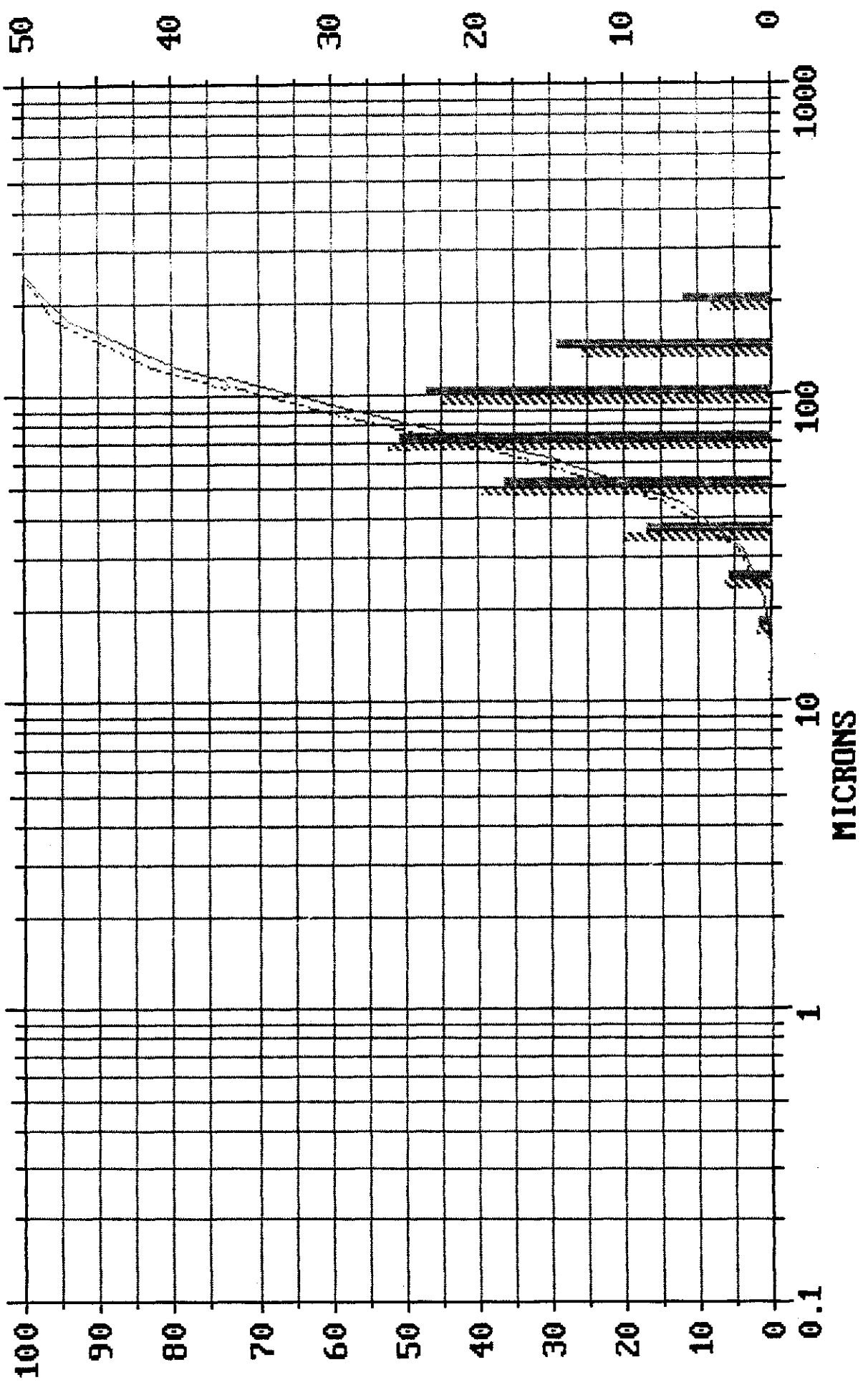
	<u>Solids Charged</u>	<u>Particle Size</u> Charge mvd, mmicrons	<u>Particle Size</u> Product mvd, microns	<u>Change</u> %
1.	Co.005	81.63	74.44	-8.8
2.	Silica 952 calc. @ 500 C	109.89	115.98	+5.4
3.	Titanium Dioxide P25 - as received	9.73	6.06	-37.7
4.	Co.002*	91.07	85.71	-5.9

*Catalyst stirred for 240 hours.

0.00%

catalyst

Figure 1
PARTICLE SIZE DISTRIBUTION OF CHARGED
AND RECOVERED CATALYST NO. Co.002
FROM ATTRITION UNIT



AL. 0.

CAL. 03B

CAL. 03B

Figure 2

DUPLICATE ANALYSIS OF SAME SAMPLE
TO DETERMINE ANALYTICAL PRECISION

