APPENDIX A

Co Catalyst Formulations

Catalyst Prep #	WGS.09	Date Tech	Jul-13-94	Amount	500.0 g

Compound	Cu	Cr	Al2O3
(%wt)	5	4	

Support	y-Alumina VISTA B	Amount	455.00 g
Particle Size	400 - 0 mesh	Treatmen	500°C / 10 hrs
Metal I	Copper (II) Nitrate	Amount	95.03 g
Metal II	Chromium (III) Nitrate	Amount	153.85 g
Promotor		Amount	
Promotor		Amount	
Promotor		Amount	

PROCEDURE

Preparation X Incipient Wetness Wet Impregnation

Ion Exchange Other

Notes: Incipient wetness: aqueous solution Cu + Cr, ca. 1.2 ml/g

Dry catalyst precursor in an oven 110°C / 16 hrs

Calcination Temperature 500°C Time 24 hrs

Notes:

WGS.09 5 wt% Cu
4 wt% Cr
γ-alumina

Preparation Procedure of Cu-Cr/γ-alumina

Calcine γ-alumina at 500°C for 10 hrs. Use Vista B alumina. Presieve to >38 microns (400-0 mesh).

Impregnate the support with an aqueous solution of $Cu(NO_3)_2.xH_2O$, and $Cr(NO_3)_3.9H_2O$ using appropriate quantities to yield 5 wt% Cu, and 4 wt% Cr and to get incipient wetness (ca. 1.2 ml/g).

Dry the catalyst precursor in an oven for 16 hours at 110°C.

The dried catalyst is then calcined in air by raising its temperature at a heating rate of ca. 1°C/min to 500°C and holding for 24 hours.

Reduction Procedure before Reaction:

Heat the catalyst in inert gas to 120°C at a rate of 1°C/min then start adding hydrogen to give a concentration of 0.5% at the bed inlet. Raise the catalyst bed temperature to 165°C at a rate of ca. 30°C/hr. When the temperature of the bed has reached 165°C increase the hydrogen concentration in the carrier gas to 1.0%. As the reduction proceeds and the temperature rise begins to diminish, the inlet temperature may be raised to 200°C. The inlet hydrogen concentration can then be increased to about 3-5%, provided that the maximum temperature limit of 230°C is not exceeded. When the reduction appears to be complete the inlet temperature should be raised to 230°C and the inlet hydrogen concentration raised to ca. 20%.

Catalyst Handbook 2nd ed. Martyn V. Twigg
J. Catal. 137, 408-422 (1992)

Catalyst Prep #	Co.055	Date Tech	July 12-1994	Amount	200.0 g

Compound	Co	Re	La2O3	Al2O3
(%wt)	20	1	1	

Support	y-Alumina / Vista-B	Amount	156.00 g
Particle Size	400 - 0 mesh	Treatment	500°C / 10 hr
Cobalt	Cobalt Nitrate	Amount	197.29 g
Metal	Perrhenic Acid	Amount	3.67 g
Promotor Promotor Promotor	La-Nitrate / Molycorp C5247	Amount Amount Amount	5.31 g

PROCEDURE

Preparation	X	Incipient Wetness	Wet Impregnation
		Ion Exchange	Other

Notes: Incipient wetness: aqueous solution - ca. 1.2 ml/g support
Dry catalyst precursor in an oven at 115°C / 5 hr

Calcination	Temperature	300°C	Time	2 hr

Notes: 50g of the catalyst precursor are not to be calcined !!

Co.055: **20 wt% Co**
1 wt% Re (molar ratio of Re/Co = 1/63)
1 wt% La_2O_3 [patent uses a mixture of RE oxides (66% La_2O_3, 24% Nd_2O_3, 8.2% Pr_6O_{11}, 0.7% CeO_2 and 1.1% other oxides)(Molycorp 5247)]
γ-alumina

Based heavily on Eri et al., U.S. Pat. No. 4,880,763 (1989).

Preparation Procedure:

Calcine the γ-alumina at 500°C for 10 hrs. Use Vista B alumina. Presieve to 38-63 microns (400-250 mesh).

Impregnate the support with an aqueous solution of Co nitrate [$Co(NO_3)_2 \cdot 6H_2O$], perrhenic acid [$HReO_4$], lanthanum nitrate, and using an appropriate quantity to get incipient wetness (ca. 1.2 ml/g) with the desired loading of Co.

Dry the catalyst precursor in an oven for 5 hrs at 115°C with moderate stirring.

The dried catalyst is then calcined in air by raising its temperature at a heating rate of ca. 1°C/min to 300°C and holding for 2 hrs.

Reduction Procedure before Reaction:

Reduce the catalyst in a pure hydrogen flow of 3000 cc/g/hr by heating at 1°C/min to 350°C and holding for 10 hrs.

Catalyst Prep #	Co.056	Date Tech	Jul-12-94	Amount	200.0 g

Compound	Co	La	SiO2
(%wt)	20	8.5	

Support	Silica Davison Grade 952	Amount	143.00 g
Particle Size	400 - 250 mesh	Treatment	500°C / 10 hrs
Cobalt	Cobalt Nitrate	Amount	197.29 g
Metal		Amount	
Promotor	La-Nitrate/Molycorp	Amount	105.91 g
Promotor		Amount	
Promotor		Amount	

PROCEDURE

Preparation X Incipient Wetness Wet Impregnation
Ion Exchange Other

Notes: Incipient wetness: aqueous solution of La
Dry catalyst precursor in an oven 115°C / 5 hrs with stirring/calcine at 300 °C/2hrs
Incipient wetness: aqueous solution of Co with catalyst precursor
Dry catalyst precursor in an oven 115°C / 5 hrs with stirring

Calcination Temperature 300°C Time 2 hrs

Notes: 50g of the catalyst precursor are not to be calcined !!

Co.056: 20 wt% Co
8.5 wt% La
SiO_2

La-promoted SiO_2-supported catalyst comparable to Co.025 where Zr is replaced by La. One-step impregnation of silica with lanthanum nitrate followed by one-step impregnation with cobalt nitrate solution.

Preparation Procedure:

Calcine the SiO_2 at 500°C for 10 hrs. Presieve to >38 microns (400-0 mesh).

Impregnate the support with an aqueous solution of La nitrate using an appropriate quantity to get incipient wetness with the desired loading of La.

Dry the La-loaded SiO_2 in an oven for 5 hrs at 115°C with moderate stirring.

Calcine the dried support in air by raising its temperature at a heating rate of ca. 1°C/min to 300°C and holding for 2 hrs.

Impregnate the La-loaded silica with an aqueous solution of Co nitrate [$Co(NO_3)_2 \cdot 6H_2O$] using an appropriate quantity to get incipient wetness with the desired loading of Co.

Dry the catalyst precursor in an oven for 5 hrs at 115°C with moderate stirring.
Calcine the dried catalyst in air by raising its temperature at a heating rate of ca. 1°C/min to 300°C and holding for 2 hrs.

Reduction Procedure before Reaction:

Reduce the catalyst in a pure hydrogen flow of 3000 cc/g/hr by heating at 1°C/min to **250°C** and holding for 10 hrs.

CoW.07

20 wt% Co
5 wt% Cu
4 wt% Cr
Silica

Cobalt impregnation on calcined Cu-Cr/Silica. Similar to CoW.06, but Cu-Cr/SiO2 calcined at 750°C.

Preparation Procedure

Calcine silica at 500°C for 10 hrs. Use Davisson Grade 952 silica. Presieve to > 38 microns (400-0 mesh).

Impregnate the support with an aqueous solution of $Cu(NO_3)_2.xH_2O$, and $Cr(NO_3)_3.9H_2O$ using appropriate quantity to get incipient wetness (ca. 1.2 ml/g) with the desired loading of Cu and Cr.

Dry the catalyst precursor in an oven for 16 hours at 110°C.

The dried catalyst precursor is then calcined in air by raising its temperature at a heating rate of ca. 1°C/min to 750°C and holding for 24 hours.

Impregnate the $Cu\text{-}Cr/SiO_2$ with an aqueous solution of Co nitrate $[Co(NO_3)_2{\cdot}6H_2O]$ using an appropriate quantity to get incipient wetness with the desired loading of Co.

Dry the catalyst precursor in an oven for 5 hrs at 115°C with moderate stirring.

Calcine the dried catalyst in air by raising its temperature at a heating rate of ca. 1°C/min to 300°C and holding for 10 hrs.

Reduction Procedure before Reaction:

Heat the catalyst in inert gas to 120°C at a rate of 1°C/min then start adding hydrogen to give a concentration of 0.5% at the bed inlet. Raise the catalyst bed temperature to 165°C at a rate of ca. 30°C/hr. When the temperature of the bed has reached 160°C increase the hydrogen concentration in the carrier gas to 1.0%. As the reduction proceeds and the temperature rise begins to diminish, the inlet temperature may be raised to 200°C. The inlet hydrogen concentration can then be increased to about 3-5%, provided that the maximum temperature limit of 230°C is not exceeded. When the reduction appears to be complete the inlet temperature should be raised to 230°C and the inlet hydrogen concentration raised to ca. 20%.