

**APPENDIX A**

**Co o Catalyst Formulations**

Catalyst Prep #	Co.049	Date Tech	Apr-08-94	Amount	200.0 g
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Compound (%wt)	Co	Ru	K	Al <sub>2</sub> O <sub>3</sub>
	200	0.5	0.1	

Support	$\gamma$ -Alumina VISTAA B	Amount	158.80 g
Particle Size	400 - 00 mesh	Treatment	500°C / 10 hrs
Cobalt	Cobalt Nitrate	Amount	197.29 g
Metal	Ruthenium Nitrosyl nitrate	Amount	3.57 g
Promotor	Potassium Nitrate e	Amount	0.52 g
Promotor		Amount	
Promotor		Amount	

**PROCEDURE**

Preparation	X	Incipient Wetness Ion Exchange	Wet Impregnation Other
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Notes: Incipient wetness: aqueous solution - ca. 1.2 ml/g  
 Dry catalyst precursor in an oven at 115°C / 5 hrs, moderate stirring

Calcination	Temperature	<u>300°C</u>	Time	<u>2 hrs</u>
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Notes: Remove 50g of dried catalyst (DO NOT CALCINE !!)  
 Rescreen after calcination to remove fines

Co.047:      20 wt% Co  
                  0.5 wt% Ru  
                  0.3 wt% K  
                   $\gamma$ -alumina

Ru/K-promoted catalyst

Preparation Procedure:

Calcine the  $\gamma$ -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 Co nitrate [ $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ] an Ru nitrosil nitrate and K nitrate using an appropriate quantity to get incipient wetness (ca. 1.2 ml/g) with the desired loading of Co, Ru, and K.

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.

Co.049:      20 wt% Co  
                  0.5 wt% Ru  
                  0.1 wt% K  
                   $\gamma$ -alumina

Ru/K-promoted catalyst similar to Co.028.

Preparation Procedure:

Calcine the  $\gamma$ -alumina at 5500°C for 10 hrs. Use Vista B alumina. Presieve to >38 microns (400-0 mesh).

Impregnate the support with an aqueous solution of Co nitrate [ $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ] an Ru nitrosil nitrate and K<sub>2</sub> nitrate using an appropriate quantity to get incipient wetness (ca. 1.2 ml/g) with the desired loading of Co, Ru, and K.

Dry the catalyst precursor i 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 puure hydrogen flow of 3000 cc/g/hr by heating at 1°C/min to 350°C and holding for 100 hrs.

Catalyst Prep #	Co.050	Date	Apr-08-94	Amount	200.0 g
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Compound (%wt)	Co	Ru	K	Zr	SiO2
	200	0.5	0.1	8.5	

Support	Silica Davison Grrade 952	Amount	141.80 g
Particle Size	400 - + 0 mesh	Treatment	500°C / 10 hrs

Cobalt	Cobalt Nitrate	Amount	197.29 g
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Metal	Ruthenium Nitrosylnitrate	Amount	3.57 g
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Promotor	Potassium Nitrate	Amount	0.52 g
Promotor	Zirconium Oxonitrate	Amount	50.92 g
Promotor		Amount	

### PROCEDURE

Preparation	X	Incipient Wetness	Wet Impregnation
		Ion Exchange	Other

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

Calcination	Temperature	300°C	Time	2 hrs
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Notes: Remove 50g of dried catalyst (DO NOT CALCINE !!)  
 Rescreen after calcination to remove fines

Co.050:      20 wt% Co  
                  0.5 wt% Ru  
                  8.5 wt% Zr  
                  0.1 wt% K  
                  SiO<sub>2</sub>

Ru/K/Zr-promoted catalyst similar to Co.043.

# denotes deviations from the patent where indicated by or steps not stated in the patent  
**Bold type** indicates steps listed in the patent.

Preparation Procedure:

- # Calcine the SiO<sub>2</sub> at 500°C for 10 hrs. Presieve to >38 microns (400-0 mesh).
- # Impregnate the support with an aqueous solution of Zr Oxonitrate [ZrO(NO<sub>3</sub>)<sub>2</sub>] using an appropriate quantity to get incipient wetness with the desired loading of Zr.
- # Dry the Zr-loaded SiO<sub>2</sub> 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. [Note: the patent suggests calcination in air at 500°C.]
- # Impregnate the Zr-loaded silica with an aqueous solution of Co nitrate [Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O], Ru nitrosil nitrate (Ru(NO)(NO<sub>3</sub>)<sub>3</sub>), and K nitrate (KNO<sub>3</sub>) using an appropriate quantity to get incipient wetness with the desired loadings of Co, Ru, and K.
- # 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.

Catalyst rep #	Co.051	Date Tech	Apr-20-94	Amount	10.0 g
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Compound (%wt)		Ru		TiO2
		0.5		

Support	Titania Degussa P225	Amount	9.95 g
Particle Size	400 - 00 mesh	Treatment	wet / 650°C / 16 hr
Cobalt		Amount	
Metal	Ruthenium Nitrosylnitrate	Amount	0.18 g
Promotor		Amount	
Promotor		Amount	
Promotor		Amount	

### PROCEDURE

Preparation	X	Incipient Wetness Ion Exchange	Wet Impregnation Other
Notes	Incipient wetness: aqueous solution of Co and Ru, 60% of desired loading Dry catalyst precursor 115°C // 5 hrs, calcine 250°C / 3 hrs Incipient wetness: aqueous solution of Co and Ru, remaining 40% Dry catalyst precursor 115°C // 5 hrs, calcine 250°C / 3 hrs		

Calcination	Temperature	<u>250°C</u>	Time	<u>3 hrs</u>
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Notes

Co.051

0.5 wt% Ru  
TiO<sub>2</sub> [Rutile]

Preparation Procedure:

Use TiO<sub>2</sub>.

Wet TiO<sub>2</sub> to incipient wetness, then dry in an oven at 60°C with moderate stirring. Calcine the TiO<sub>2</sub> at 650°C for 16 hrs (this should result in a support having ca. 97% rutile).

Presieve to >38 microns (400-0 mesh).

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

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 250°C and holding for 3 hrs.

Rescreen to remove fines.

Reduction Procedure:

In the original patent it was just stated that the catalyst should be reduced at 250-450°C for 2-14 hours.

However, to be consistent with other catalysts, use the following procedure. Reduce the catalyst using pure hydrogen at a flow rate of 720 cc/g/hr. The impregnated catalyst is heated to 100°C at the rate of 1°C/min and then maintained for 1 hr. Next, the catalyst is heated to 200°C at the rate of 1°C/min and held for 2 hrs. The catalyst is then heated at 10°C/min until a temperature of 360°C is reached and is then held at that temperature for 16 hrs.

If the catalyst will be exposed to air, cool the catalyst below 200°C, purge with nitrogen, and cool further. Air is bled into the nitrogen stream at ca. 1 cc air in 50 cc nitrogen per min per 5 g of catalyst for 16 hours.



Catalyst prep #	Co.052	Date Tech	Apr-20-94	Amount	10.0 g
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Compound (%wt)		Ru		TiO2
		0.5		

Support	Titania Degussa P225	Amount	9.95 g
Particle Size	400 - 00 mesh	Treatment	wet / 350°C / 16 hr

Cobalt		Amount	
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Metal	Ruthenium Nitrosylnitrate	Amount	0.18 g
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Promotor		Amount	
Promotor		Amount	
Promotor		Amount	

### PROCEDURE

Preparation	X	Incipient Wetness Ion Exchange	Wet Impregnation Other
Notes	Incipient wetness: aqueous solution of Co and Ru, 60% of desired loading Dry catalyst precursor 115°C // 5 hrs, calcine 250°C / 3 hrs Incipient wetness: aqueous solution of Co and Ru, remaining 40% Dry catalyst precursor 115°C // 5 hrs, calcine 250°C / 3 hrs		

Calcination	Temperature	<u>250°C</u>	Time	<u>3 hrs</u>
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Notes  
*Prep. sheet - see Co. 051*

Co.052

0.5 wt% Ru  
TiO<sub>2</sub> [Anatase]

Preparation Procedure:

Use TiO<sub>2</sub>.

Wet TiO<sub>2</sub> to incipient wetness, then dry in an oven at 60°C with moderate stirring. Calcine the TiO<sub>2</sub> at 350°C for 16 hrs (this should result in a support having ca. x% anatase and y% rutile (x > y)).

Presieve to >38 microns (4400-0 mesh).

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

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 250°C and holding for 3 hrs.

Rescreen to remove fines.

Reduction Procedure:

In the original patent it was just stated that the catalyst should be reduced at 250-450°C for 2-14 hours.

However, to be consistent with other catalysts, use the following procedure. Reduce the catalyst using pure hydrogen at a flow rate of 720 cc/g/hr. The impregnated catalyst is heated to 100°C at the rate of 1°C/min and then maintained for 1 hr. Next, the catalyst is heated to 200°C at the rate of 1°C/min and held for 2 hrs. The catalyst is then heated at 10°C/min until a temperature of 360°C is reached and is then held at that temperature for 16 hrs.

If the catalyst will be exposed to air, cool the catalyst below 200°C, purge with nitrogen, and cool further. Air is bled into the nitrogen stream at ca. 1 cc air in 50 cc nitrogen per min per 5 g of catalyst for 16 hours.

Catalyst Prep #	Co.053	Date Tech	May-02-94	Amount	500.0 g
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Compound (%wt)	Cu	Ru	Al2O3
	20	0.5	

Support	$\gamma$ -Alumina VISTA B	Amount	397.50 g
Particle Size	400 - 0 mesh	Treatment	500°C / 10 hrs

Cobalt	Cobalt Nitrate	Amount	493.22 g
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Metal	Ruthenium Nitrosylnitrate	Amount	8.93 g
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Promotor		Amount	
Promotor		Amount	
Promotor		Amount	

**PROCEDURE**

Preparation	<input checked="" type="checkbox"/> Incipient Wetness	<input type="checkbox"/> Wet Impregnation
	<input type="checkbox"/> Ion Exchange	<input type="checkbox"/> Other

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

Calcination	Temperature	<u>300°C</u>	Time	<u>2 hrs</u>
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Notes: Remove 300g of dried catalyst (DO NOT CALCINE !!)

Co.053:

20 wt% Co  
0.5 wt% Ru  
 $\gamma$ -alumina

Ru-promoted catalyst similar otherwise to Co.018.

Preparation Procedure:

Calcine the  $\gamma$ -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 Co nitrate [ $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ] and Ru nitrosyl nitrate using an appropriate quantity to get incipient wetness (ca. 1.2 ml/g) with the desired loading of Co and Ru.

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.054	Date	May-13-94	Amount	200.0 g
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Compound (%wt)	CCo	K	Zr	SiO2
	220	0.3	8.5	

Support	Silica Davison Grade 952	Amount	142.40 g
Particle Size	400 - - 0 mesh	Treatment	500°C / 10 hrs

Cobalt	Cobalt Nitrate	Amount	197.29 g
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Metal		Amount	
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Promotor	Potassium Nitrate	Amount	1.55 g
Promotor	Zirconium Oxonitrate	Amount	50.92 g
Promotor		Amount	

### PROCEDURE

Preparation	X	Incipient Wetness	Wet Impregnation
		Ion Exchange	Other

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

Calcination	Temperature	300°C	Time	2 hrs
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Notes: Remove 50g of dried catalyst (DO NOT CALCINE !!)

Co.054:      20 wt% Co  
                  8.5 wt% Zr  
                  0.3 wt% K  
                  SiO<sub>2</sub>

K/Zr-promoted catalyst similar to Co.043, but without Ru.

Preparation Procedure:

- # Calcine the SiO<sub>2</sub> at 500°C for 10 hrs. Presieve to >38 microns (400-0 mesh).
- # Impregnate the support with an aqueous solution of Zr Oxonitrate [ZrO(NO<sub>3</sub>)<sub>2</sub>] using an appropriate quantity to get incipient wetness with the desired loading of Zr.
- # Dry the Zr-loaded SiO<sub>2</sub> 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 Zr-loaded silica with an aqueous solution of Co nitrate [Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O], and K nitrate (KNO<sub>3</sub>) using an appropriate quantity to get incipient wetness with the desired loadings of Co and K.
- # 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 110 hrs.

Catalyst Prep #	CoW.01	Date	Apr-05-94	Amount	200.0 g
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Compound (%wt)	Co	Cu	Zn	Al <sub>2</sub> O <sub>3</sub>
	20	5	10	

Support	γ-Alumina VISTTA B	Amount	130.00 g
Particle Size	400 - 0 mesh	Treatment	500°C / 10 hrs

Metal I	Cobalt Nitrate	Amount	197.29 g
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Metal II	Copper (II) Nitrate	Amount	38.01 g
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Metal III	Zinc Nitrate	Amount	90.97 g
Promoter		Amount	
Promoter		Amount	

**PROCEDURE**

Preparation	X	Incipient Wetness	Wet Impregnation
		Ion Exchange	Other

Notes  
 Incipient wetness: aqueous solution Cu + Zn, ca. 1.2 ml/g  
 Dry catalyst precursor in an oven 110°C / 16 hrs/Calcine 500 C 10 hrs.  
 Incipient wetness: aqueous solution Co.  
 Dry catalyst precursor in an oven 115°C / 5 hrs.

Calcination	Temperature	300°C	Time	10 hrs
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Notes

## CoW.01

20 wt% Co  
5 wt% Cu  
10 wt% Zn  
 $\gamma$ -alumina

Cobalt impregnation on calcined Cu-Cr/ $\gamma$ -alumina

### Preparation Procedure

Calcine  $\gamma$ -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  $\text{Cu}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ , and  $\text{Zn}(\text{NO}_3)_2$  using 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 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 10 hours.

Impregnate the Cu-ZnO/ $\text{Al}_2\text{O}_3$  with an aqueous solution of Co nitrate [ $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ] 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%.



Catalyst Prep #	CoW.02	Date Tech	May-02-94	Amount	200.0 g
Compound (%wt)		Cu	Cr	Co	Al <sub>2</sub> O <sub>3</sub>
		5	4	20	

Support	$\gamma$ -Alumina VISTTA B	Amount	142.00 g
Particle Size	400 - 0 mesh	Treatment	500°C / 10 hrs
Metal I	Copper (II) Nitrate	Amount	38.01 g
Metal II	Chromium (III) Nitrate	Amount	61.54 g
Metal III	Cobalt Nitrate	Amount	197.29 g
Promotor		Amount	
Promotor		Amount	

### PROCEDURE

Preparation	X	Incipient Wetness	Wet Impregnation
		Ion Exchange	Other

Notes: Incipient wetness: aqueous solution Cu + Zn, ca. 1.2 ml/g  
 Dry catalyst precursor in ann oven 110°C / 16 hrs/Calcine 500 C 24 hrs.  
 Incipient wetness: aqueous solution Co.  
 Dry catalyst precursor in ann oven 115°C / 5 hrs.

Calcination	Temperature	300°C	Time	10 hrs
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Notes: Remove 50 g of dried catalyst (DO NOT CALCINE)

## CoW.02

20 wt% Co  
5 wt% Cu  
4 wt% Cr  
 $\gamma$ -alumina

Cobalt impregnation on calcined Cu-Cr/ $\gamma$ -alumina

### Preparation Procedure

Calcine  $\gamma$ -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  $\text{Cu}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ , and  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  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 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.

Impregnate the Cu-Cr/ $\text{Al}_2\text{O}_3$  with an aqueous solution of Co nitrate [ $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ] 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%.

Catalyst Rep #	CoW.03	Date Tech	May-13-94	Amount	200.0 g
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Compound (%wt)	Co	Cu	Cr	Al <sub>2</sub> O <sub>3</sub>
	100	5	4	

Support	$\gamma$ -Alumina VISTAA B	Amount	162.00 g
Particle Size	400 - + 0 mesh	Treatment	500°C / 10 hrs
Metal I	Cobalt Nitrate	Amount	98.64 g
Metal II	Copper (II) Nitrate	Amount	38.01 g
Metal III	Chromium (III) NNitrate	Amount	61.54 g
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/Calcine 500 C 24 hrs.  
 Incipient wetness: aqueous solution Co.  
 Dry catalyst precursor in an oven 115°C / 5 hrs.

Calcination	Temperature	300°C	Time	10 hrs
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Notes: Remove 50 g of dried catalyst (DO NOT CALCINE)

### CoW.03

10 wt% Co  
5 wt% Cu  
4 wt% Cr  
 $\gamma$ -alumina

Cobalt impregnation on calcined (Cu-Cr/ $\gamma$ -alumina similar to CoW.02, but with 10% Co

#### Preparation Procedure

Calcine  $\gamma$ -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  $\text{Cu}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ , and  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  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 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.

Impregnate the Cu-Cr/ $\gamma$ - $\text{Al}_2\text{O}_3$  with an aqueous solution of Co nitrate [ $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ] 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%.

Catalyst Rep #	CoW.04	Date Tech	May-13-94	Amount	200.0 g
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Compound (%wt)	Co	Cu	Cr	Al <sub>2</sub> O <sub>3</sub>
	100	10	8	

Support	$\gamma$ -Alumina VISTAA B	Amount	144.00 g
Particle Size	400 - 60 mesh	Treatment	500°C / 10 hrs

Metal I	Cobalt Nitrate	Amount	98.64 g
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Metal II	Copper (II) Nitrate	Amount	76.02 g
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Metal III	Chromium (III) NNitrate	Amount	123.08 g
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/Calcine 500 C 24 hrs.  
 Incipient wetness: aqueous solution Co.  
 Dry catalyst precursor in an oven 115°C / 5 hrs.

Calcination	Temperature	300°C	Time	10 hrs
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Notes: Remove 50 g of dried catalyst (DO NOT CALCINE)

## CoW.04

10 wt% Co  
10 wt% Cu  
8 wt% Cr  
 $\gamma$ -alumina

Cobalt impregnation on calcined Cu-Cr/ $\gamma$ -alumina similar to CoW.03, but with 10% Cu and 8% Cr.

### Preparation Procedure

Calcine  $\gamma$ -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  $\text{Cu}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ , and  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  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 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.

Impregnate the Cu-Cr/ $\gamma$ - $\text{Al}_2\text{O}_3$  with an aqueous solution of Co nitrate [ $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ] 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%.

Catalyst Prep #	CoW.05	Date	Jun-20-94	Amount	100.0 g
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Compound (% wt)	CCo	Cu	Cr	Al <sub>2</sub> O <sub>3</sub>
	220	5	4	

Support	$\gamma$ -Alumina VISTA A B	Amount	71.00 g
Particle Size	400 - - 0 mesh	Treatment	500°C / 10 hrs

Metal I	Cobalt Nitrate	Amount	98.64 g
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Metal II	Copper (II) Nitrate	Amount	19.01 g
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Metal III	Chromium (III) Nitrate	Amount	30.77 g
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/Calcine 750 °C 24 hrs.  
 Incipient wetness: aqueous solution Co.  
 Dry catalyst precursor in an oven 115°C / 5 hrs.

Calcination	Temperature	300°C	Time	10 hrs
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Notes: Remove 30 g of dried catalyst (DO NOT CALCINE)

## CoW.05

20 wt% Co  
5 wt% Cu  
4 wt% Cr  
 $\gamma$ -alumina

Cobalt impregnation on calcined (Cu-Cr/ $\gamma$ -alumina. Similar to CoW.02, but Cu-Cr/ $\text{Al}_2\text{O}_3$  calcined at 750°C.

### Preparation Procedure

Calcine  $\gamma$ -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  $\text{Cu}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ , and  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  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 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-Cr/ $\text{Al}_2\text{O}_3$  with an aqueous solution of Co nitrate [ $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ] 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%.



Catalyst Prep #	CoW.06	Date	Jun-20-94	Amount	100.0 g
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Compound (%wt)	Co	Cu	Cr	SiO2
	200	5	4	

Support	SiO2	Amount	71.00 g
Particle Size	400 - ( 0 mesh	Treatment	500°C / 10 hrs
Metal I	Cobalt Nitrate	Amount	98.64 g
Metal II	Copper (II) Nitrate	Amount	19.01 g
Metal III	Chromium (III) NNitrate	Amount	30.77 g
Promotor		Amount	
Promotor		Amount	

### PROCEDURE

Preparation	X	Incipient Wetness	Wet Impregnation
		Ion Exchange	Other

Notes: Incipient wetness: aqueous solution Cu + Cr  
 Dry catalyst precursor in an oven 110°C / 16 hrs/Calcine 500 °C 24 hrs.  
 Incipient wetness: aqueous solution Co.  
 Dry catalyst precursor in an oven 115°C / 5 hrs.

Calcination	Temperature	<u>300°C</u>	Time	<u>10 hrs</u>
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Notes: Remove 30 g of dried catalyst (DO NOT CALCINE)

## CoW.06

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

Cobalt impregnation on calcined ( Cu-Cr/Silica

### Preparation Procedure

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

Impregnate the support with an aqueous solution of  $\text{Cu}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ , and  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  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 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.

Impregnate the Cu-Cr/SiO<sub>2</sub> with an aqueous solution of Co nitrate [ $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ] 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%.