

## **APPENDIX A**

### **Co CATALYST FORMULATIONS**

Catalyst Prep #	Co.066	Date Tech	May-15-95	Amount	200.0 g
Compound (%wt)		Co	Ru	Fe	Al <sub>2</sub> O <sub>3</sub>
		15	0.5	5	

Support	$\gamma$ -Alumina VISTA B	Amount	159.00 g
Particle Size	400 - 0 mesh	Treatment	500°C / 10 hrs
Cobalt	Cobalt Nitrate	Amount	147.97 g
Metal	Ruthenium Nitrosyl nitrate	Amount	3.73 g
Promotor	Iron (III) Nitrate	Amount	72.31 g
Promotor		Amount	
Promotor		Amount	

PROCEDURE			
Preparation	X	Incipient Wetness Ion Exchange	Wet Impregnation Other
Notes	Incipient wetness: aqueous solution of Co, Fe, Ru Dry catalyst precursor in an oven 115°C / 5 hrs with stirring		
Calcination	Temperature	300°C	Time 10 hrs
Notes	After drying, 60 g of catalyst are NOT to be calcined!!		

Co.066:

15 wt% Co  
5.0 wt% Fe  
0.5 wt% Ru  
γ-alumina

Preparation Procedure:

Calcine the 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 Co nitrate [ $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ], Fe (III) nitrate and Ru nitrosil nitrate using an appropriate quantity to get incipient wetness (ca. 1.2 ml/g) with the desired loading of Co, Fe 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 10 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.067	Date Tech	May-15-95	Amount	200.0 g
Compound (%wt)		Co	Pd	Al <sub>2</sub> O <sub>3</sub>	
		20	2		

Support	$\gamma$ -Alumina VISTA B	Amount	156.00 g
Particle Size	400 - 0 mesh	Treatment	500° C / 10 hrs
Cobalt	Cobalt Nitrate	Amount	197.29 g
Metal	Palladium (II) Nitrate	Amount	10.01 g
Promotor		Amount	
Promotor		Amount	
Promotor		Amount	

PROCEDURE			
Preparation	X	Incipient Wetness Ion Exchange	Wet Impregnation Other
Notes	Incipient wetness: aqueous solution of Co, Pd Dry catalyst precursor in an oven 115° C / 5 hrs with stirring		
Calcination	Temperature	300° C	Time 10 hrs
Notes	After drying, 60 g of catalyst are NOT to be calcined!!		

Co.067:

20 wt% Co  
2.0 wt% Pd  
 $\gamma$ -alumina

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 Pd (II) nitrate using an appropriate quantity to get incipient wetness (ca. 1.2 ml/g) with the desired loading of Co and Pd.

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 10 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.068	Date Tech	May-24-95	Amount	200.0 g
Compound (%wt)	Co	Pd			Al2O3
	20	1			

Support	y-Alumina VISTA B	Amount	158.00 g
Particle Size	400 - 0 mesh	Treatment	500°C / 10 hrs
Cobalt	Cobalt Nitrate	Amount	197.29 g
Metal	Palladium (II) Nitrate	Amount	5.01 g
Promotor		Amount	
Promotor		Amount	
Promotor		Amount	

PROCEDURE			
Preparation	X	Incipient Wetness Ion Exchange	Wet Impregnation Other
Notes	Incipient wetness: aqueous solution of Co, Pd Dry catalyst precursor in an oven 115°C / 5 hrs with stirring		
Calcination	Temperature	300°C	Time 10 hrs
Notes	After drying, 60 g of catalyst are NOT to be calcined!!		

Co.068:

20 wt% Co

1.0 wt% Pd

$\gamma$ -alumina

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 Pd (II) nitrate using an appropriate quantity to get incipient wetness (ca. 1.2 ml/g) with the desired loading of Co and Pd.

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 10 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.069	Date Tech	May-24-95	Amount	200.0 g
Compound (%wt)		Co	Ru	Al <sub>2</sub> O <sub>3</sub>	
		20	2		

Support	$\gamma$ -Alumina VISTA B	Amount	156.00 g
Particle Size	400 - 0 mesh	Treatment	500°C / 10 hrs
Cobalt	Cobalt Nitrate	Amount	197.29 g
Metal	Ruthenium Nitrosyl nitrate	Amount	14.91 g
Promotor		Amount	
Promotor		Amount	
Promotor		Amount	

PROCEDURE			
Preparation	X	Incipient Wetness Ion Exchange	Wet Impregnation Other
Notes	Incipient wetness: aqueous solution of Co, Fe, Ru Dry catalyst precursor in an oven 115°C / 5 hrs with stirring		
Calcination	Temperature	300°C	Time 10 hrs
Notes	After drying, 60 g of catalyst are NOT to be calcined!!		



Co.069:

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

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 nitrosil 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 10 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.070	Date Tech	Jun-08-95	Amount	200.0 g
Compound (%wt)	Co 13				Al <sub>2</sub> O <sub>3</sub>

Support	γ-Alumina VISTA B	Amount	174.00 g
Particle Size	400 - 0 mesh	Treatment	500°C / 10 hrs
Cobalt	Cobalt Nitrate	Amount	128.24 g
Metal		Amount	
Promoter		Amount	
Promoter		Amount	
Promoter		Amount	

PROCEDURE			
Preparation	X	Incipient Wetness Ion Exchange	Wet Impregnation Other
Notes	Incipient wetness: aqueous solution of Co, 60% of loading in 1st step Dry catalyst precursor in an oven 115°C / 12 hrs with stirring Incipient wetness: aqueous solution of Co, 40% of loading in 2nd step Dry catalyst precursor in an oven 115°C / 12 hrs with stirring		
Calcination	Temperature	300°C	Time 2 hrs
Notes	After drying, 60 g of catalyst are NOT to be calcined!!		

Co.070:

13 wt% Co  
 $\gamma$ -alumina

Non-promoted catalyst similar to Co.005, with 13% Co.

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 in 2 steps 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 (ca. 1.2 ml/g) with 60% of the desired loading of Co in the first step.

Dry in air at 115°C for 12 hours and calcine in air at 300°C for 2 hours (heating rate of ca. 1°C/min to 300°C).

In the second step, impregnate the remaining 40% of the Co. Repeat the drying and calcination procedures.

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 #	CoW.13	Date Tech	Jun-08-95	Amount	200.0 g
Compound (%wt)		Co	Ru	Fe	Al <sub>2</sub> O <sub>3</sub>
		10	0.5	10	

Support	y-Alumina VISTA B	Amount	159.00 g
Particle Size	400 - 0 mesh	Treatment	500°C / 10 hrs
Cobalt	Cobalt Nitrate	Amount	98.64 g
Metal	Ruthenium Nitrosylnitrate	Amount	3.73 g
Promotor	Iron (III) Nitrate	Amount	144.63 g
Promotor		Amount	
Promotor		Amount	

<b>PROCEDURE</b>			
Preparation	X	Incipient Wetness Ion Exchange	Wet Impregnation Other
Notes	Incipient wetness: aqueous solution of Co, Fe, Ru Dry catalyst precursor in an oven 115°C / 5 hrs with stirring		
Calcination	Temperature	300°C	Time 10 hrs
Notes	After drying, 60 g of catalyst are NOT to be calcined!!		

CoW.13      10 wt% Fe  
                 10 wt% Co  
                 0.5 wt% Ru  
                  $\gamma$ -alumina

Ru promoted cobalt/iron impregnated on calcined  $\gamma$ -alumina similar to CoW.10 (2nd batch).

#### 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 Fe nitrate [ $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ], Co nitrate [ $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ] and Ru nitrosyl nitrate [ $\text{Ru}(\text{NO})(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$ ] using appropriate quantities to get incipient wetness (ca. 1.2 ml/g) with the desired loading of Fe, Co, and 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 300°C and holding for 10 hrs.

#### Reduction Procedure before Reaction:

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

Catalyst Prep #	Fe.01	Date Tech	May-05-95	Amount	200.0 g
Compound (%wt)		Fe	Cu		SiO <sub>2</sub>
		30	1.5		

Support	Silica Davison Grade 952	Amount	137.00 g
Particle Size	400 - 0 mesh	Treatment	500°C / 10 hrs
Cobalt	Iron (III) Nitrate	Amount	433.88 g
Metal	Copper (II) Nitrate	Amount	11.40 g
Promoter		Amount	
Promoter		Amount	
Promoter		Amount	

PROCEDURE			
Preparation	X	Incipient Wetness Ion Exchange	Wet Impregnation Other
Notes	Incipient wetness: aqueous solution of Fe + Cu Dry catalyst precursor in an oven 110°C / 16 hrs		
Calcination	Temperature	<u>500°C</u>	Time <u>24 hrs</u>
Notes			

**Fe.01**      **30 wt% Fe**  
                 **1.5 wt% Cu**  
                 **Silica**

**Preparation Procedure of Fe-Cu/Silica**

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  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  using appropriate quantities to yield 30 wt% Fe and 1.5% Cu by weight 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:**

A mixture of  $\text{H}_2\text{O}$  and  $\text{H}_2$  is used for reduction to  $\text{Fe}_3\text{O}_4$ . Raise the temperature of the bed 10°C/min to 400°C with the feed being  $\text{H}_2\text{O}/\text{H}_2 > 0.09$  and maintain these conditions for 48 hrs