APPENDIX A

Co o Catalyst Formulations

atalyst rep#	Co.049	Date Tech	Apr-08-94	Amount	200.0 g
Compon (%wt)	ad	CC0 200	Ru K 0.5 0.1		Al2O3

Support y-Alumina VISTAA B	Amount	158.80 g	
Particle Size 400 - 00 mesh	Treatment	500°C / 10 hrs	
			_
Cobalt Cobalt Nitrate	Amount	197.29 g	J
			_
Metal Ruthenium Nitrosysylnitrate	Amount	3.57 g	
			_
Promotor Potassium Nitrate e	Amount	0.52 g	
Premeter	Amount		
Promotor	Amount		_

reparation	X Inc	cipicient Wetness		Wet Impregnation
	Ioı	n Exxchange		Other
s Incipie	ent wetness: aqueou	s sololution - ca. 1.2	ml/g	
Dry ca	atalyst precursor in a	an ooven at 115°C/	5 hrs, mode	erate stirring
, 	<u> </u>			
	Temperature	300°C	Time	2 hrs
leination	MONOROUS I CHILDELALIILE	300 C	x mixc	2 1113
lcination	**************************************			
deination			ን እነ ረ ነጥ ረገል ነ	CINE U
alcination otes	Remove 50g of	f driried catalyst (DC		LCINE !!)

Co.047:

20 wt% Co 0.5 wt% Ru 0.3 wt% K

y-alumina

Ru/K-promoted catalyst

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 ann aqueous solution of Co nitrate $[Co(NO_3)_2 \delta H_2 O]$ an Rn nitrosil nitrate and K nitirate using an appropriate quantity to get incipient wetness (ca. 1.2 ml/g) with these desired loading of Co, Ru, and K.

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

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

Reduction Procedure before RReaction:

Reduce the catalyst in a pure hhydrogen 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

y-alumina

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

Preparation Procedure:

Calcine the γ -alumina at 5600°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 $[Co(NO_3)_2 6H_2O]$ an Ru nitrosil nitrate and K initrate 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 caralcined in air by raising its temperature at a heating rate of ca. 1°C/min to 300°C annd 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.

atalyst *tep#	Co.050	Date Tech :	Apr-08-94	Amount	200.0 g
Compou (%wt)	gd	CCa 2/20	Ru K 0.5 0.1	Zr 8.5	SiO2

Support Silica Davison Grade 952	Amount	141.80 g	
Particle Size 400 - + 0 mesh	Treatment	500°C / 10 hrs	
obalt Cobalt Nitrate	Amount	197.29 g	
Aetal Ruthenium Nitrososylnitrate	Amount	3.57 g	
romotor Potassium Nitratete	Amount	0.52 g	
romotor Zirconium Oxonititrate	Amount	50.92 g	
romotor	Amount		

reparation	X Ir	cipioient Wetness		Wet Impregnation		
· · · · · · · · · · · · · · · · · · ·	Ic	n E£xchange		Other		
tes Incipient	wetness: aqueou	s sololution of Zr				
Dry cata	lyst precursor in	an o oven 115°C / 5 h	rs with stir	ring, calcine 300°C / 2 hrs		
Incipient	wetness: aqueou	is sololution of Co, Ru	, K			
Dry cata	lyst precursor in	an coven 115°C / 5 h	rs with stir	ring, calcine 300°C / 2 hrs		
alcination	Temperature	300°C	Time	2 hrs		
enco ne ncononononon			NOT OU	COTATO AD		
\$500,500,000 ANGES (2,000,000)	Remove 50g of driried catalyst (DO NOT CALCINE !!) Rescreen after calalcination to remove fines					
otes	_					

<u>Co.050</u>: 20 wt% Co 0.5 wt% Ru 8.5 wt% Zr

> 0.1 wt% K SiO₂

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

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

Preparation Procedure:

- # Calcine the SiO₂ at 500°C f for 10 hrs. Presieve to >38 microns (400-0 mesh).
- # Impregnate the support with an aqueous solution of Zr Oxonitrate $[ZrO(NO_3)_2]$ using an appropriate quantity to) get incipient wetness with the desired loading of Zr.
- # Dry the Zr-loaded SiO₂ inn an oven for 5 hrs at 115°C with moderate stirring.
- # Calcine the dried support i in air by raising its temperature at a heating rate of ca. 1°C/min to 300°C and holdding for 2 hrs. [Note: the patent suggests calcination in air at 500°C.]
- Impregnate the Zr-loadeled silica with an aqueous solution of Co nitrate $[Co(NO_3)_2 \cdot 6H_2O]$, Ru nitroosil nitrate $(Ru(NO)(NO_3)_3)$, and K nitrate (KNO_3) using an appropriate quantity to ϱ get incipient wetness with the desired loadings of Co, Ru, and K.
- # Dry the catalyst precursor i in an oven for 5 hrs at 115°C with moderate stirring.
- # Calcine the dried catalyst i in air by raising its temperature at a heating rate of ca. 1°C/min to 300°C and holdding 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 250°C and holding for 100 hrs.

atalyst ep#	Co.()51	Date Tech	Apr-2	.0-94	Amount	10.0	g
(165-040)20000000000000000000000000000000000	pound wt)			Ru 0.5				TiO2
	Particle Size Cobalt		gussa P225 400 - 00 mes Nitrosysylnit	rate	Amount Treatment Amount Amount Amount Amount Amount	9.95 wet / 650°C	2 / 16 hr	
ROCEDI reparatio otes	n Incipient we Dry catalyst	precursor	115°C / / 5 h	nge n of Co and l nrs, calcine 2	50°C / 3 hr			
alcinatio	Dry catalyst	-	eous solution				· · · · · · · · · · · · · · · · · · ·	
otes		r ember aco		250 C	IMAC			

Co.051

0.5 wt% Ru TiO₂ [Rutile]

Preparation Procedure:

Use TiO₂.

Wet TiO₂ to incipient wetnness, then dry in an oven at 60°C with moderate stirring. Calcine the TiO₂ at 650°C for 16 hrs (this should result in a support having ca. 97% rutile).

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

Impregnate the support wivith 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 i in an oven for 5 hrs at 115°C with moderate stirring.

Calcine the dried catalyst i in air by raising its temperature at a heating rate of ca. 1°C/min to 250°C and holdding for 3 hrs.

Rescreen to remove fines. .

Reduction Procedure:

In the original paterent 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 g pure hydrogen at a flow rate of 720 cc/g/hr. The impregnated catalyst is heatted to 100°C at the rate of 1°C/min and then maintained for 1 hr. Next, the catalystst is heated to 200°C at the rate of 1°C/min and held for 2 hrs. The catalyst is theen 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 g of catalyst for 16 hours.

alyst p#	Co	.052	Date Tech	Apr	-20-94	Amount	10.0	g
Comp (%v				Ru 0.5				TiO2
						0.05		
	Support Particle St	*****************************	gussa P225 400 - 00 mes	<u> </u>	Amount Treatment:	9.95 wet / 350°C		
	<i>(</i>)				Amount *			
L	Cobalt							
	Metal	Rutheniun	n Nitrosyylnita	rate	Amount	0.18	g	
	Promotor				Amount			
	Promotor Promotor				Amount Amount			
OCEDU	277. h	v	Turining W	Totalogo		Wet Impreg	agtion	
eparation		X	Incipieænt W Ion Exachan			Other	lauvii	
************************************	_	_	eous solulution : 115°C / / 5 h				ng	
	Incipient v	vetness: aqu	eous solulution	of Co and	Ru, remaini	ng 40%		
 	Dry cataly	st precurso	115°C / / 5 h	rs, calcine	250°C / 3 hr	\$		<u> </u>
lcination		Temperat	ure	_250°C	_ Time	3 hrs		
ntes		_	• • •					
		Prep	. Sheert.	_ see_	Co. 051			

Co.052

0.5 wt% Ru
TiO₂ [Anatase]

Preparation Procedure:

Use TiO₂.

Wet TiO_2 to incipient wetnness, then dry in an oven at 60°C with moderate stirring. Calcine the TiO_2 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 wivith 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 i in an oven for 5 hrs at 115°C with moderate stirring.

Calcine the dried catalyst i in air by raising its temperature at a heating rate of ca. 1°C/min to 250°C and holdding for 3 hrs.

Rescreen to remove fines. .

Reduction Procedure:

In the original paterent 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 g 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 catalystst is heated to 200°C at the rate of 1°C/min and held for 2 hrs. The catalyst is theen 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 g of catalyst for 16 hours.

Catalyst Prep#	Co.053	Datste Teoloh	May-02-94	Amount	500.0 g
Compoun (%wt)	ıd	<u>Co</u> 20	Ru 0.5		Al203

			-
Support y-Alumina VISTTA B	Amount	39 7.50 g	
Particle Size 400) - 0 mesh	Treatment	500°C / 10 hrs	
Cobalt Cobalt Nitrate	Amount	493.22 g	
Metal Ruthenium Nitrosylnitrate	Amount	8.93 g	
Premeter	Amount		
Promotor	Amount		
Promotor	Amount		

PROCEDURE			
Preparation	X Incipipie	ent Wetness	Wet Impregnation
	Ion l Ex	change	Other
Notes Incipient	wetness: aqueous s so	lution - ca. 1.2 ml/g	
Dry catal	yst precursor in ann o	ven at 115°C / 5 hrs.	, moderate stirring
Calcination	Temperature	300°C T	Sime 2 hrs
			<u> </u>
Notes	Remove 300g of f da	ried catalyst (DO NO	OT CALCINE !!)
	_	-	
V.			

Co.053:

20 wt% Co 0.5 wt% Ru y-alumina

Ru-promoted catalyst similar outherwise to Co.018.

Preparation Procedure:

Calcine the γ -alumina atut 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 [Co(NO₃)₂6H₂O] and Ru nitrosil nitrate using g an appropriate quantity to get incipient wetness (ca. 1.2 ml/g) with the desired looading of Co and Ru.

Dry the catalyst precursoor 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 befrfore 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.

Entalyst Prep.#	Co.054	Date : Tech :	May-13-94	Amount	200.0 g
Compour (%wt)	id	220	<u>K</u> 0.3	Zr 8.5	SiO2

Support	Silica Davison Gr/rade 952	Amount	142.40 g	
Particle S	ize 400 0 mesh	Treatment	500°C / 10 hrs	
Cobalt	Cobalt Nitrate	Amount	197.29 g	
Meial		Amount		
				_
Prometer	Potassium Nitratete	Amount	1.55 g	
Promotor	Zirconium Oxonititrate	Amount	50.92 g	
Promotor		Amount		

reparation	X	Incipipient Wetness		Wet Impregnation
		Ion EExchange		Other
otes Incipient w	vetness: aque	ous solution of Zr		
Dry catalys	st precursor	in an coven 115°C / 5 hr	rs with stir	ring, calcine 300°C / 2 hrs
Incipient w	vetness: aque	ous sciolution of Co, Ru,	K	
Dry catalys	st precursor	in an e oven 115°C / 5 hi	rs with stir	ring, calcine 300°C / 2 hrs
	Temperatu	re 300°C	Time	2 hrs
Calcination	Temperatu		_	
Calcination	remperatu		-	

Co.054:

20 wt% Co 8.5 wt% Zr 0.3 wt% K SiO₂

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

Preparation Procedure:

- # Calcine the SiO₂ at 500°C f for 10 hrs. Presieve to >38 microns (400-0 mesh).
- # Impregnate the support with an aqueous solution of Zr Oxonitrate $[ZrO(NO_3)_2]$ using an appropriate quantity to 9 get incipient wetness with the desired loading of Zr.
- # Dry the Zr-loaded SiO₂ inn an oven for 5 hrs at 115°C with moderate stirring.
- # Calcine the dried support i in air by raising its temperature at a heating rate of ca. 1°C/min to 300°C and holdding for 2 hrs.
- # Impregnate the Zr-loadeled silica with an aqueous solution of Co nitrate [Co(NO₃)₂6H₂O], and K nitrate (KNO₃) using an appropriate quantity to get incipient wetness with the c desired loadings of Co and K.
- # Dry the catalyst precursor i in an oven for 5 hrs at 115°C with moderate stirring.
- # Calcine the dried catalyst i in air by raising its temperature at a heating rate of ca. 1°C/min to 300°C and holdding 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 250°C and holding for 100 hrs.

Catalyst Prep#	CoW.01	Datee Techh	Apr-05-94	Amount	200.0 g
Compoun (%wt)	ıd	# €0 : 20	Cu Zn 5 10		Al2O3

Support y-Alumina VISTTA B	Amount	130.00 g
Particle Size 400 0 mesi	h Treatment	500°C / 10 hrs
Metal I Cobalt Nitrate	Amount	197.29 g
Metal II Copper (II) Nitrate	Amount	38.01 g
Metal III. Zinc Nitrate	Smount	90.97 g
Promotor .	Amonut	
Promotor :	Amonue	

PROCEDURE Preparation	X Incipipient Wetness	Wet Impregnation
***********************	Ion F Exchange	Other
20000-20000-000-000-000-000-000-000-000	aqueous s solution Cu + Zn, ca	
Dry catalyst pred	cursor in ann oven 110°C / 16 hrs.	Calcine 500 C 10 hrs.
Incipient wetness	: aqueous s solution Co.	
Incipient wetness		
Incipient wetness Dry catalyst pred	eursor in an a oven 115°C / 5 hrs.	Time 10 hrs
Incipient wetness Dry catalyst prec	s: aqueous s solution Co. cursor in an a oven 115°C / 5 hrs.	Time 10 hrs
Incipient wetness Dry catalyst pred	eursor in an a oven 115°C / 5 hrs. perature 300°C	Time 10 hrs

20 wt% Co 5 wt% Cu 10 wt% Zn γ-alumina

Cobalt impregnation on calcirined Cu-Cr/y-alumina

Preparation Procedure:e

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 $Zn(NO_3)_3$ using appropriate quarantity to get incipient wetness (ca. 1.2 ml/g) with the desired loading of Co.

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

The dried catalyst is thhen 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-1-ZnO/Al₂O₃ with an aqueous solution of Co nitrate [Co(NO₃)₂6H₂O] using an appropriate quantity to get incipient wetness with the desired loading of Co. .

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

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

Reduction Procedure before Reaction:

Heat the catalyst in innert gas to 120°C at a rate of 1°C/min then start adding hydrogen to give a conncentration 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 increases 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 raaised to 200°C. The inlet hydrogen concentration can then be increased to about 3-55%, provided that the maximum temperature limit of 230°C is not exceeded. When t the reduction appears to be complete the inlet temperature should be raised to 2360°C and the inlet hydrogen concentration raised to ca. 20%.

Caralyst Prep#	CoW.02	Datae Teelch	May-02-94	Amount	200.0 g
Compour	nd	Cu 5	Cr Co 4 20		Al2O3

		140.00	Η
Support y-Alumina VISTTA B	Amount	142.00 g	
Particle Size 400) - 0 mesh	Treatment	500°C / 10 hrs	
Metal I Copper (II) Nitrtrate	Amount	38.01 g	
			-
Metal II Chromium (III)) Nitrate	Amount	61.54 g	
			_
Metal III Cobalt Nitrate	Amount	197.29 g	
Promotor	Amount		
Promotor	Amonnt		

Preparation:	X Incipip	ient Wetness		Wet Impregnation
·	Ion 1 F	Exchange		Other
Notes Incipient	wetness: aqueous s s	solution Cu + Zn, c	а. 1.2 п	ո <mark>l</mark> /g
Dry cata	lyst precursor in ann	oven 110°C / 16 hrs	/Calcin	e 500 C 24 hrs.
Incipient	: wetness: aqueous s s	solution Co.		
Dry cata	lyst precursor in ann	oven 115°C / 5 hrs.		

Calcination	Temperature	300°C	Time	10 hrs
				
Notes	Remove 50 g of t d	7 · 1 · / / / / / / / / / / / / / / / / /		

20 wt% Co 5 wt% Cu 4 wt% Cr y-alumina

Cobalt impregnation on calcineed Cu-Cr/γ-alumina

Preparation Procedure

Calcine γ -alumina at 5000°C for 10 hrs. Use Vista B alumina. Presieve to > 38 microns (400-0 mesh).

Impregnate the support with an aqueous solution of $Cu(NO_3)_2xH_2O$, and $Cr(NO_3)_3.9H_2O$ using appropriate quantity to get incipient wetness (ca. 1.2 ml/g) with the desired loading of CCu and Cr.

Dry the catalyst precursoor 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 3 and holding for 24 hours.

Impregnate the $Cu-CCr/Al_2O_3$ with an aqueous solution of Co nitrate $[Co(NO_3)_2 6H_2O]$ using ϵ an appropriate quantity to get incipient wetness with the desired loading of Co.

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

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

Reduction Procedure befefore Reaction:

Heat the catalyst in ineert gas to 120°C at a rate of 1°C/min then start adding hydrogen to give a conceentration of 0.5% at the bed inlet. Raise the catalyst bed temperature to 165°C at a a rate of ca. 30°C/hr. When the temperature of the bed has reached 160°C increase t 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 there reduction appears to be complete the inlet temperature should be raised to 230°CC and the inlet hydrogen concentration raised to ca. 20%.

atalyst sep#	CoW.03	Date Tech:	May-13-94	Ашонн	200.0 g
Compou (%wt)	ud		Co C o 5 4		Al2O3

Support y-Alumina VISTAA B	Amount	162.00 g	
Particle Size 400 - + 0 mesh	Treatment	500°C / 10 hrs	
Meral 1 Cobalt Nitrate	Amount	98.64 g	
Metal II Copper (II) Nitratate	Amomt	38.01 g	
Metal III Chromium (III) NNitrate	Amount	61.54 g	
Promotor	Amount		
Promotor	Amount		
			—

reparation	X	Incipioient	Wetness		Wet Impregnation
		Ion EExch	ange		Other
otes Incipient w	vetness: aque	eous scsolu	tion Cu + C	, ca. 1.2 m	ıl/g
Dry cataly:	st precursor i	in an cove	n 110°C / 10	hrs/Calcin	e 500 C 24 hrs.
Incipient w	vetness: aque	eous scsolui	tion Co.		
Dry cataly:	st precursor i	in an cove	n 115°C/5	hrs.	
	×o				
alcination	Temperatur	re system	300°C	Time	10 hrs

	Damara 50	a of delaio	d catalyst (De	NOTCAL	CTATEL

10 wt% Co 5 wt% Cu 4 wt% Cr y-alumina

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

Preparation Procedure

Calcine γ -alumina at 500°CC 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 quantity to get incipient wetness (ca. 1.2 ml/g) with the desired loading of Cu a and Cr.

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

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

Impregnate the Cu-Cr/#Al₂O₃ with an aqueous solution of Co nitrate [Co(NO₃)₂·6H₂O] using an 1 appropriate quantity to get incipient wetness with the desired loading of Co.

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

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

Reduction Procedure before Reaction:

Heat the catalyst in inert t 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 rarate of ca. 30°C/hr. When the temperature of the bed has reached 160°C increase thee hydrogen concentration in the carrier gas to 1.0%. As the reduction proceeds annut the temperature rise begins to diminish, the inlet temperature may be raised i to 200°C. The inlet hydrogen concentration can then be increased to about 3-5%, pprovided 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 a and the inlet hydrogen concentration raised to ca. 20%.

ntalyst Tep#	CoW.04	Date Tech	May-13-94	Amount	200.0 g
Compoun (%wt)	d	<u>C</u> Eo	Cu Cr 10 8		Al2O3

Support y-Alumina VISTAA B	Amount	144.00 g	
Particle Size 400 - + 0 mesh	Treatment	500°C / 10 hrs	
Meral I Cobalt Nitrate	Amount	98.64 g	
Metal II Copper (II) Nitratate	Amount	76.02 g	
Metal III Chromium (III) NNitrate	Amount	123.08 g	
Promotor	Amount		
Promotor:	Amount		

reparation	X Incip	oioient Wetness		Wet Impregnation
.v::::::::::::::::::::::::::::::::::	Ion H	EExchange		Other
tes Incipient wet	mess: aqueous s	scolution Cu + Cr	, ca. 1.2 m	l/g
Dry catalyst	precursor in an	o oven 110°C / 16	hrs/Calcine	e 500 C 24 hrs.
Incipient wet	mess: aqueous s	scolution Co.		
Dry catalyst	precursor in an	o oven 115°C / 5	hrs.	
			- '	
alcination T	l'emperature	300°C	Time	10 hrs
_				
ot es F	Remove 50 g of o	idried catalyst (De	O NOT CAL	LCINE)

10 wt% Co 10 wt% Cu 8 wt% Cr γ-alumina

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

Preparation Procedure

Calcine γ -alumina at 500°CC 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 approopriate quantity to get incipient wetness (ca. 1.2 ml/g) with the desired loading of Cu a and Cr.

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

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

Impregnate the $Cu-Cr//Al_2O_3$ with an aqueous solution of Co nitrate $[Co(NO_3)_2 6H_2O]$ using an 1 appropriate quantity to get incipient wetness with the desired loading of Co.

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

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

Reduction Procedure before Reaction:

Heat the catalyst in inert t 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 reate of ca. 30°C/hr. When the temperature of the bed has reached 160°C increase these hydrogen concentration in the carrier gas to 1.0%. As the reduction proceeds annul the temperature rise begins to diminish, the inlet temperature may be raised 1 to 200°C. The inlet hydrogen concentration can then be increased to about 3-5%, pprovided that the maximum temperature limit of 230°C is not exceeded. When the r reduction appears to be complete the inlet temperature should be raised to 230°C and the inlet hydrogen concentration raised to ca. 20%.

aralyst Prep#	CoW.05	Date : Fech 1	Jun-20-94	Amount	100.0 g
Compani (%wt)	nd	CCo 220	Cu <u>Cr</u> 5 4		Al2O3

Support y-Alumina VISTAA B	Amount	71.00 g	
Particle Size 400 0 mesh	(Featment)	500°C / 10 hrs	
Control of the Contro			
Meral I Cobalt Nitrate	Amount	98.64 g	
Metal II Copper (II) Nitra ate	Amount	19.01 g	
Metal III Chromium (III) NNitrate	Amount	30.77 g	
Promotor	Amount		
Promotor	Amount		

reparation	X	Incipipient Wetness	Wet Impregnation
		Ion EExchange	Other
lotes Incipient wetr	iess: a	queous sisolution $Cu + Cr$, ca	. 1.2 ml/g
Dry catalyst p	recurs	or in an coven 110°C / 16 hrs/	/Calcine 750 °C 24 hrs.
Incipient wetr	iess: a	queous sisolution Co.	
Dry catalyst p	recurs	or in an coven 115°C / 5 hrs.	

 Calcination
 Temperature
 300°C
 Time
 10 hrs

Notes

Remove 30 g of ddried catalyst (DO NOT CALCINE)

20 wt% Co 5 wt% Cu 4 wt% Cr y-alumina

Cobalt impregnation on calcined (Cu-Cr/ γ -alumina. Similar to CoW.02, but Cu-Cr/Al₂O₃ calcined at 750°C.

Preparation Procedure

Calcine γ -alumina at 500°CC 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 quantity to get incipient wetness (ca. 1.2 ml/g) with the desired loading of Cu a and Cr.

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

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

Impregnate the $Cu-Cr/Al_2O_3$ with an aqueous solution of Co nitrate $[Co(NO_3)_2 \, 6H_2O]$ using an 1 appropriate quantity to get incipient wetness with the desired loading of Co.

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

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

Reduction Procedure before Reaction:

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

arælyst 'rep#	CoW.06	Date Tech	Jun-20-94	Ameunt	100.0 g
Compou (%wt)	nd	СС0 200	Cu Er 5 4		SiO2

Support SiO2	Amount	71.00 g
Particle Size 400 - (0 mesh	Ereatment :	500°C / 10 hrs
Metal I Cobalt Nitrate	Amount	98.64 g
Metal II Copper (II) Nitratite	Amount	19.01 g
Metal III Chromium (III) NNitrate	Amount	30.77 g
Promotor Promotor	Amount Amount	50.77 g

reparation	X Inc	ripicient Wetness		Wet Impregnation
	Io	Exxchange		Other
otes Incipient wetn	iess: aqueou	s sosolution Cu + Cr		
Dry catalyst p	recursor in	n o oven 110°C / 16	hrs/Calcin	e 500 °C 24 hrs.
Incipient wetn	iess: aqueou	s so:olution Co.		
Dry catalyst p	recursor in	ın ooven 115°C / 5 h	rs.	
alcination Te	emperature	300°C	Time	10 hrs
otes Ro	emove 30 g c	f driried catalyst (DO	NOT CAL	LCINE)
\$\$\$6.00 000 \$1000000000000000000000000000000		··		,

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 1 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 2 and Cr.

Dry the catalyst precursor i 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 annd holding for 24 hours.

Impregnate the Cu-Cr/SiO₂ with an aqueous solution of Co nitrate [Co(NO₃)₂·6H₂O] using an appropriate quantitity to get incipient wetness with the desired loading of Co.

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

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

Reduction Procedure before Reaction:

Heat the catalyst in inert t 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 r rate of ca. 30°C/hr. When the temperature of the bed has reached 160°C increase these hydrogen concentration in the carrier gas to 1.0%. As the reduction proceeds annd the temperature rise begins to diminish, the inlet temperature may be raised d to 200°C. The inlet hydrogen concentration can then be increased to about 3-5%, pprovided that the maximum temperature limit of 230°C is not exceeded. When the r reduction appears to be complete the inlet temperature should be raised to 230°C; and the inlet hydrogen concentration raised to ca. 20%.