APPENDIXES

APPENDIX 1

APPENDIX 1

Metal loading in catalysts investigated.

Catalyst[a]	Metal precursor[b]	Calc. temp. (K)	Co loading[c] (wt %)	Pt, Re, Ir, Pd or Ru loading[c] (wt %)	N loading[d] (wt %)	Cl loading[e] (wt %)
Co/Al_2O_3A	$Co(NO_3)_2 * 6H_2O$	673	8.7	-		
Co/Al_2O_3B	$Co(NO_3)_2 * 6H_2O$	573 648 698	8.5 8.7 8.7	- - -	0.46 0.14	0.0
Co0.1Pt*/Al_2O_3A	$H_2PtCl_6 * 6H_2O$	673	8.7	0.05[f]		0.2
Co1.0Pt*/Al_2O_3A	$H_2PtCl_6 * 6H_2O$	673	8.7	0.6[f]		1.0
Co0.5Pt/Al_2O_3A	$Pt(NH_3)_4(NO_3)_2$	673	8.7	0.5		
Co1.0Pt/Al_2O_3A	$Pt(NH_3)_4(NO_3)_2$	643 673	8.7 8.7	0.9[g] 0.9[g]		0.02
CoPt/Al_2O_3B	$Pt(NH_3)_4(NO_3)_2$	573 648	8.5 8.7	0.9 0.9	0.50 0.17	
Co0.1Re/Al_2O_3A	Re_2O_7	673	8.7	0.1[g]		
Co1.0Re/Al_2O_3A	Re_2O_7	673	8.8	1.2		
CoRe/Al_2O_3B	Re_2O_7	573	8.5	1[g]	0.37	
Co0.1Ir/Al_2O_3A	$H_2IrCl_6 * 6H_2O$	673	8.7	0.1[g]		
Co0.1Pd/Al_2O_3A	$PdCl_2$	673	8.7	0.1[g]		
Co0.1Ru/Al_2O_3A	$RuCl_3$	673	8.7	0.1[g]		
Co_3O_4	$Co(NO_3)_2 * 6H_2O$	648 698				
0.3Pt*/Al_2O_3[c]	$H_2PtCl_6 * 6H_2O$[c]	648	-	0.3		

[a] Designations for the catalysts used in this report.

[b] $Co(NO_3)_2 * 6\ H_2O$ is used in all catalysts in addition to the other precursors mentioned.

[c] Cobalt and Platinum element analyses are carried out at SINTEF, Applied Chemistry and at Analytiche Laboratorien, Malissa und Reuter GmbH, Gummersbach on calcined catalysts. Rhenium element analyses are carried out at Analytiche Laboratorien, Malissa und Reuter GmbH, Gummersbach on calcined catalysts.
Not all the bimetallic catalysts have been analysed for cobalt content, but it is assumed that the sequential impregnated catalysts have the same cobalt content as the monometallic cobalt catalyst used in the preparation.

[d] Nitrogen element analyses are carried out at Mikro Kemi AB, Uppsala on calcined catalysts.

[e] chloride element analyses are carried out at SINTEF, Applied Chemistry on calcined catalysts.

[f] A disagreement between the platinum and the chloride analyses could indicate that these platinum element analyses shows too small platinum loading.

[g] Not analysed, the value is based on amounts used under preparation of the catalyst.

Akzo Chemie Nederland bv
Location Amsterdam-N.

CERTIFICATE OF ANALYSES

Sample : Alumina 000 - 1½ E
Testnumber : 76894

CHEMICAL COMPOSITION :

Loss on ignition (1 hr. °C)	:	1.2	% wb
Pt	:		% db
Re	:		% db
Cl	:	0.04	% db
Fe	:	0.02	% db
Cu	:	50	ppm db
Si	:		ppm db
As	:		ppm db
Na	:	20	ppm db
Mg	:	8	ppm db
S	:	33	ppm db

PHYSICAL PROPERTIES :

Estimated Reactor Density	:	0.57	g/ml
Compacted Bulk Density	:	0.65	g/ml
Surface Area	:	186	m^2/g
Pore Volume N_2	:	0.59	ml/g
Abrasion	:	0.6	%
+ 3.5 mesh (ASTM)	:	0	%
- 14 mesh (ASTM)	:	0.4	%

DIAMETER :

Average	:	1.68	mm
/ 1.60 mm	:		% (number)
/ 1.52 mm	:		% (number)

LENGTH :

Average	:	5.2	mm
/ mm	:		% (number)

SIDE CRUSHING STRENGTH :

Average	:	3.7	lbs/mm
/ 1.6 lbs/mm	:	0	% (number)

[redacted]

[redacted]

Vista Chemical Company

Vista Boehmite Aluminas
- **CATAPAL® Aluminas**
- **DISPAL® Aluminas**
- **DISPAL® Alumina Sols**

Description:
Vista Chemical Company offers two families of high purity boehmite alumina products: CATAPAL® and DISPAL® aluminas. CATAPAL aluminas are available as white, free-flowing, spray-dried powders. DISPAL aluminas are available as white, free-flowing, spray-dried powders or as concentrated colloidal dispersions in water. In all cases, these aluminas consist of small boehmite crystallites, often referred to as pseudoboehmite.

Chemical Composition (Typical values)

	CATAPAL	DISPAL	
Test	**Powder**	**Powder**	**Sol**
Al_2O_3 content (wt%)	70.7	80	20*
Loss on ignition (wt%)	29.5	20	80
Carbon (wt%)	0.3	0.1	0.1
SiO_2 (wt%)	0.005	0.005	<0.001
Fe_2O_3 (wt%)	0.004	0.004	<0.001
Na_2O (wt%)	0.004	0.004	<0.001
TiO_2 (wt%)	0.14	0.14	0.04
NO^-_3 (wt%)	–	0.01-0.11	0.3
Viscosity (cP @ $100s^{-1}$)	–	–	<50

*Sols of various alumina concentrations are available.

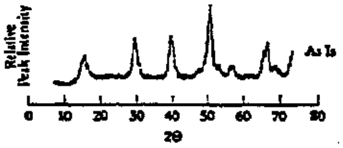
Crystalline composition and size vary as shown in the following table.

Crystalline Properties

		Crystallite Size (Angstroms)	
Product	**$\cdot xH_2O$**	**020 plane**	**021 plane**
CATAPAL A	1.35	26	41
CATAPAL B	1.30	30	43
CATAPAL D	1.25	47	72
DISPAL	1.20	40-110*	110-220*

* Crystallite size can be controlled in ranges indicated.

Figure 1. CATAPAL D alumina X-ray diffraction pattern.



The column designated $\cdot xH_2O$ in the above table represents the amount of water associated with the crystal structure when expressed by the formula $Al_2O_3 \cdot xH_2O$. Crystallite size is expressed in Angstroms as determined by X-ray diffraction analysis.

Properties (typical values)

	CATAPAL A	CATAPAL B	CATAPAL D	DISPAL
Particle size				
% < 45 microns	40	40	40	50
% > 90 microns	18	18	18	20
Average, microns	65	65	65	50
Loose Bulk Density, g/L	753	730	780	800
Surface Area*, m^2/g	273	273	230	110-210

* After calcination to gamma phase at 500°C for one hour. Surface areas for DISPAL aluminas can be controlled in the range indicated.

APPENDIX 2

APPENDIX 2

Gases used in different apparatus

1. TPR and pulse adsorption apparatus

Reduction: H_2 5.0 (99.999 %)
Carrier gases: Ar 6.0 (99.9999 %)
7 wt % H_2 in Ar

Pulse adsorption: H_2 5.0 (99.999 %)
CO 3.7 (99.97 %)
O_2 2.5 (99.5 %)

2. Volumetric chemisorption apparatus

Reduction: H_2 5.0 (99.999 %)
Adsorption: H_2 5.0 (99.999%)
CO 3.7 (99.97 %)
Dead volume: He 4.5 (99.995%)

3. Activity test apparatus

Gas cromatograph: He S4.5 (99.995 %)
H_2 2.7 (99.7 %)
Air kl.2 pkt.A
CO_2 D3.0
Calibration mixture: 35 % CO, 60 % H_2, 3 % N_2, 1 % CH_4, 1 % CO_2
CO hydrogenation: 7,5 % N_2 in CO
H_2 2.7 (99.7%)
He 4.5 (99.995 %)

All gases are delivered by HydroGas.

APPENDIX 3

APPENDIX 3

Example of an adsorption isotherm and the calculation of dispersion from chemisorption of H_2 on Co/Al_2O_3B.

The following equations show the calculation of amount of adsorbed gas by use of hydrogen chemisorption (Adsorption method), and are taken from the ASTM-standard /59/:

15. Calculations for Hydrogen Chemisorption (Adsorption Method)

DOSE I

$$V_{ads}(STP)_1 = \left[V_m \left(\frac{P_{m_1}/T_{m_{A1}}}{P_{e_1}/T_{m_{B1}}} - 1 \right) - V_d \right] \left(\frac{273}{T} \right) \left(\frac{P_{e_1}}{760} \right)$$

DOSE II

$$V_{ads}(STP)_2 = \left[V_m \left(\frac{P_{m_2}/T_{m_{A2}}}{P_{e_2}/T_{m_{B2}}} - 1 \right) + V_d \left(\frac{P_{e_1}/T_{m_{B1}}}{P_{e_2}/T_{m_{B2}}} - 1 \right) \right] \left(\frac{273}{T} \right) \left(\frac{P_{e_2}}{760} \right)$$

DOSE 3

$$V_{ads}(STP)_3 = \left[V_m \left(\frac{P_{m_3}/T_{m_{A3}}}{P_{e_3}/T_{m_{B3}}} - 1 \right) + V_d \left(\frac{P_{e_2}/T_{m_{B2}}}{P_{e_3}/T_{m_{B3}}} - 1 \right) \right] \left(\frac{273}{T} \right) \left(\frac{P_{e_3}}{760} \right)$$

DOSE X

$$V_{ads}(STP)_x = \left[V_m \left(\frac{P_{m_x}/T_{m_{Ax}}}{P_{e_x}/T_{m_{Bx}}} - 1 \right) + V_d \left(\frac{P_{e_{x-1}}/T_{m_{Bx-1}}}{P_{e_x}/T_{m_{Bx}}} - 1 \right) \right] \left(\frac{273}{T} \right) \left(\frac{P_{e_x}}{760} \right)$$

$$V_{ads}(STP)_{cx} = \Sigma\, V_{ads}(STP)_x$$

Calculation of monolayer, U. by extrapolating flat portion of isotherm between 100 and 300 torr to zero pressure.

[redacted]

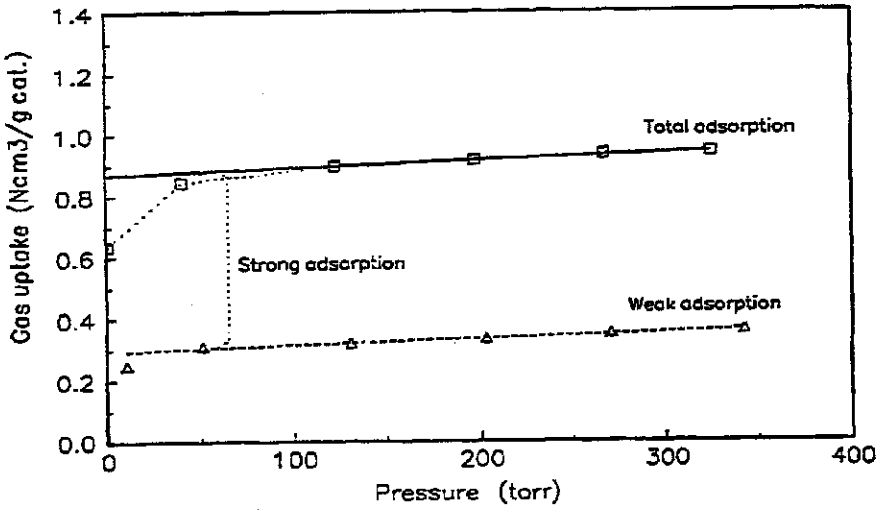


Figure A3-1: Chemisorption of hydrogen. Co/Al_2O_3B, calcined at 573 K.

Calculation of dispersion from the total amount of hydrogen adsorbed:

$$D = \frac{U \cdot A}{V \cdot \nu \cdot W} \cdot 100\%$$

where
U = amount of gas adsorbed [Ncm^3/g cat.]
A = atomic weight, cobalt [g/mol]
V = volume of 1 mol ideal gas at STP (1 atm., 0 °C).
v = stoichiometric factor
W = weight fraction of cobalt

An example:

$$D = \frac{0.88\ (Ncm3/g\ cat.) \cdot 58.93\ (g\ Co/mol)}{22414\ (Ncm3/mol) \cdot 0.5 \cdot 0.085\ (g\ Co/g\ cat.)} \cdot 100\ \% = 5.44\ \%$$

APPENDIX 4

APPENDIX 4

Volumetric chemisorption of H_2 and CO, and dispersion calculated thereof

Table A4-1. **Volumetric chemisorption of H_2 and CO given in [ml adsorbed gas/g catalyst].**

Catalyst	Total H2	Irrev.H2	Total CO	Irrev.CO	$(CO/H_2)_{irrev}$
Co/Al_2O_3B573	0.88	0.66 0.58[a]			
Co/Al_2O_3B648	0.82	0.78			
Co/Al_2O_3A673	0.76	0.54	0.77	0.32	0.59
$Co0.1Pt^*/Al_2O_3A$	0.54	0.26			
$Co1.0Pt^*/Al_2O_3A$	0.63	0.34			
$Co0.5Pt/Al_2O_3A$	1.00	0.63	1.40	0.53	0.84
$Co1.0Pt/Al_2O_3A^b$	1.34	0.86	2.16	1.29	1.32
$Co1.0Pt/Al_2O_3A^c$	1.28	0.79			
$Co1.0Pt/Al_2O_3A^c$	1.42	0.98			
$CoPt/Al_2O_3B^d$	1.26	0.91			
$CoPt/Al_2O_3B^c$	1.36	1.18			
$Co1.0Re/Al_2O_3A$	1.00	0.68	2.01	1.12	1.65
$CoRe/Al_2O_3B$	1.09	0.65			

[a] 103 minutes evacuation time between the two isotherms (normally 20 minutes).

[b] Not calcined between each impregnation

[c] Sequentially impregnated

[d] Coimpregnated

Table A4-2. Dispersion found from totally adsorbed H_2 and CO measured by volumetric chemisorption.

Catalyst	Total H_2 adsorption (ml/g cat.)	Total CO adsorption (ml/g cat.)	Dispersion from H_2 adsorption[d] (%)		Dispersion from CO adsorption (%)		Co loading (%)
			Mod I	Mod II	Mod I	Mod II	
Co/Al_2O_3B573	0.88		5.44				8.5
Co/Al_2O_3B648	0.82		4.96				8.7
Co/Al_2O_3A673	0.76	0.77	4.59		2.33		8.7
Co0.1Pt*/Al_2O_3A	0.54		3.26				8.7
Co1.0Pt*/Al_2O_3A	0.63		3.81				8.7
Co0.5Pt/Al_2O_3A	1.00	1.40	6.04	4.31	4.23	2.49	8.7
Co1.0Pt/Al_2O_3A[a]	1.34	2.16	8.10	4.63	6.53	3.40	8.7
Co1.0Pt/Al_2O_3A[b]	1.28		7.74	4.26			8.7
Co1.0Pt/Al_2O_3A[b]	1.42		8.58	5.46			8.7
CoPt/Al_2O_3B[c]	1.26		7.62	4.14			8.7
CoPt/Al_2O_3B[b]	1.36		8.22	4.75			8.7
Co1.0Re/Al_2O_3A	1.00	2.01	6.04		6.07	1.71	8.7
CoRe/Al_2O_3B	1.09		6.74				8.5

[a] Not calcined between each impregnation

[b] Sequentially impregnated

[c] Coimpregnated

[d] Model I): All the gas molecules or atoms are adsorbed on cobalt.

Model II): The noble metal is 100 % dispersed and the amount of hydrogen or CO corresponding to adsorption on noble metal is subtracted from the adsorbed gas amount before calculating the dispersion on cobalt.

For both models: Dispersion is defined as [number of adsorption sites / total cobalt loading] in percent.

APPENDIX 5

APENDIX 5

BET surface and pore size distribution on calcined Co/Al_2O_3A and Co/Al_2O_3

BET-isotherm

91/215

Sample: Co/Al_2O_3A

Date: 1951.04.17

Mass: 0.2384 g

Po: 784 mm Hg

P mm Hg	Va cc(STP)	Po-P	P/Po	$\frac{P}{Va(Po-P)}$
35	11.56	749	0.045	0.00404
58	12.79	726	0.074	0.00625
83	13.78	701	0.106	0.00659
108	14.76	676	0.138	0.01082
134	15.62	650	0.171	0.01320

I = 0.0009

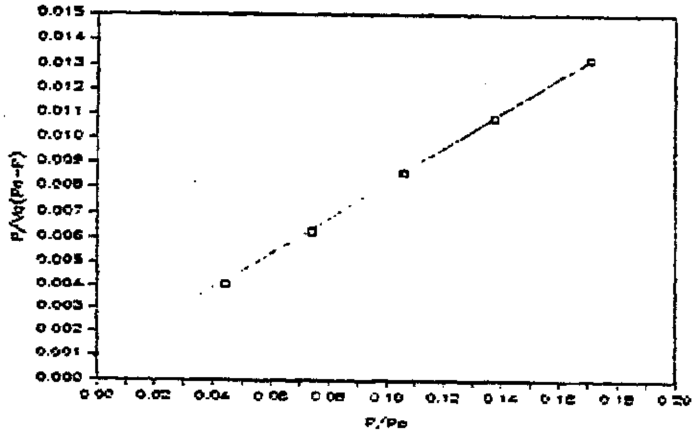
c = 84

s = 0.0723

s+I = 0.0732

Vm = 13.66 cc(STP)

Sg = 176 sqm/g



91/214

BET-isotherm
Sample: Co/Al$_2$O$_3$B
Date: 1991.04.16

Mass: 0.3798 g
Po: 774 mm Hg

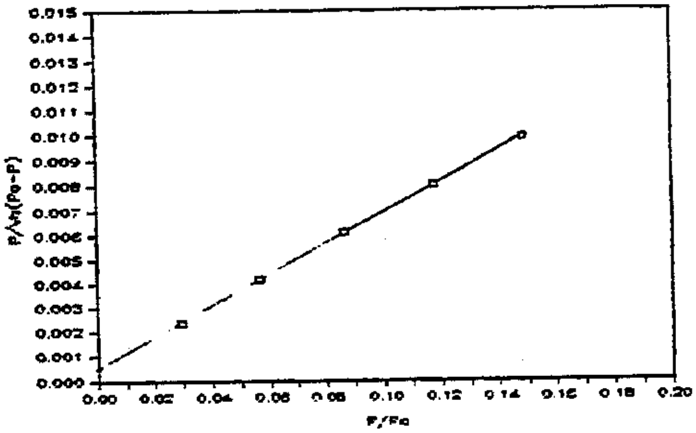
P mm Hg	Va cc(STP)	Po-P	P/Po	$\frac{P}{Va(Po-P)}$
23	12.99	751	0.030	0.00236
44	14.40	730	0.057	0.00419
67	15.56	707	0.087	0.00609
91	16.60	683	0.118	0.00803
115	17.64	659	0.149	0.00989

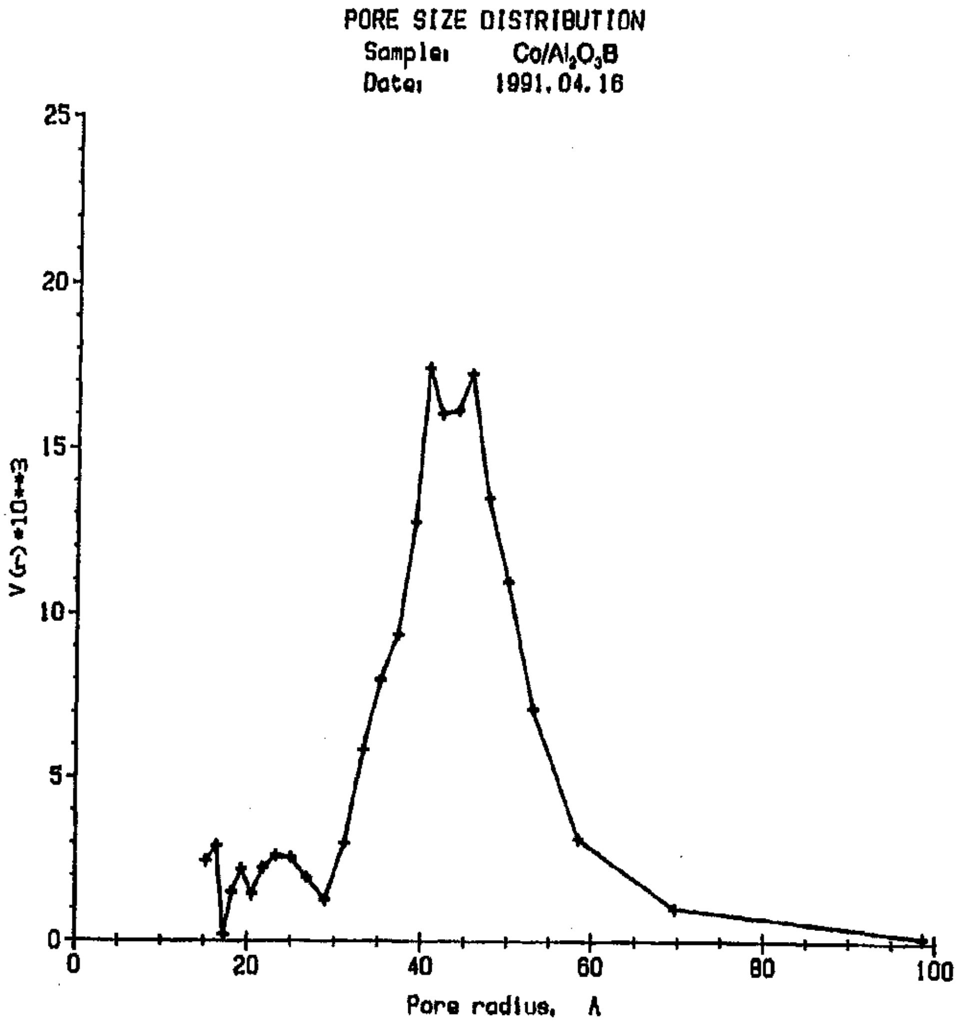
I = 0.0005

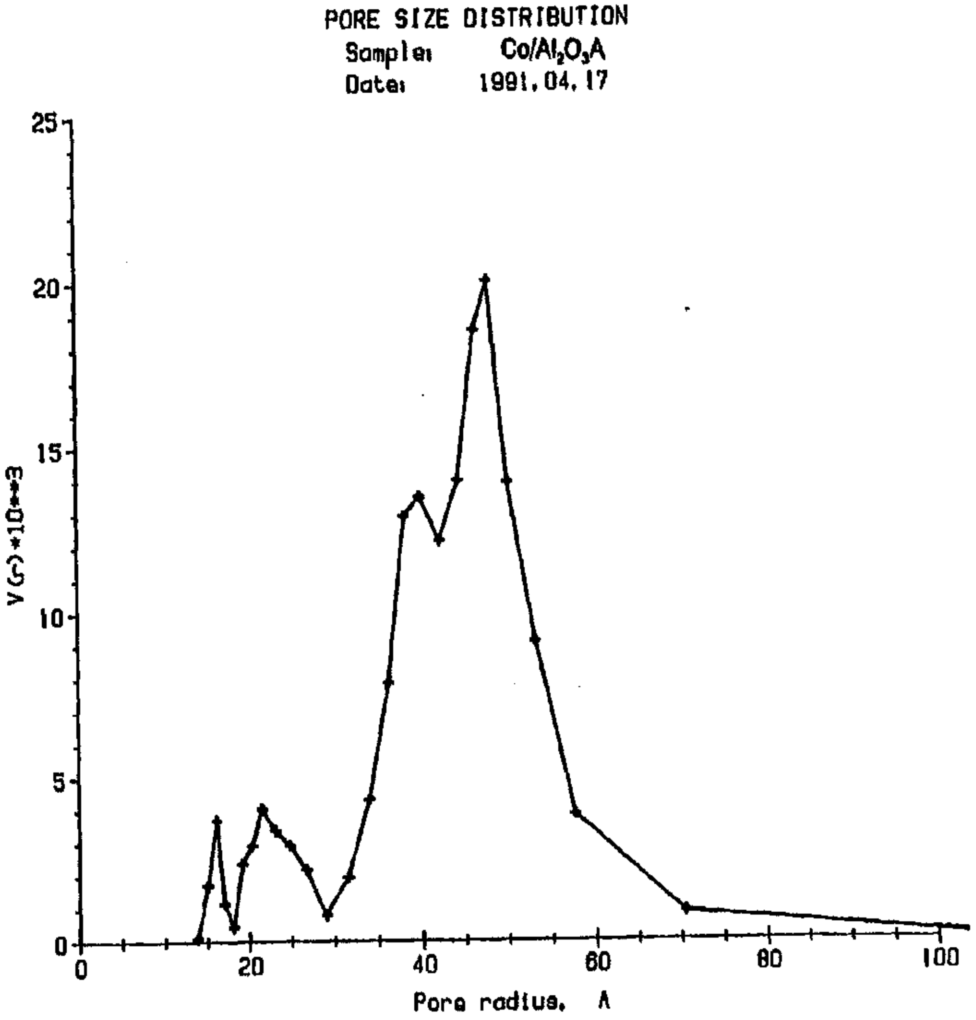
c = 117

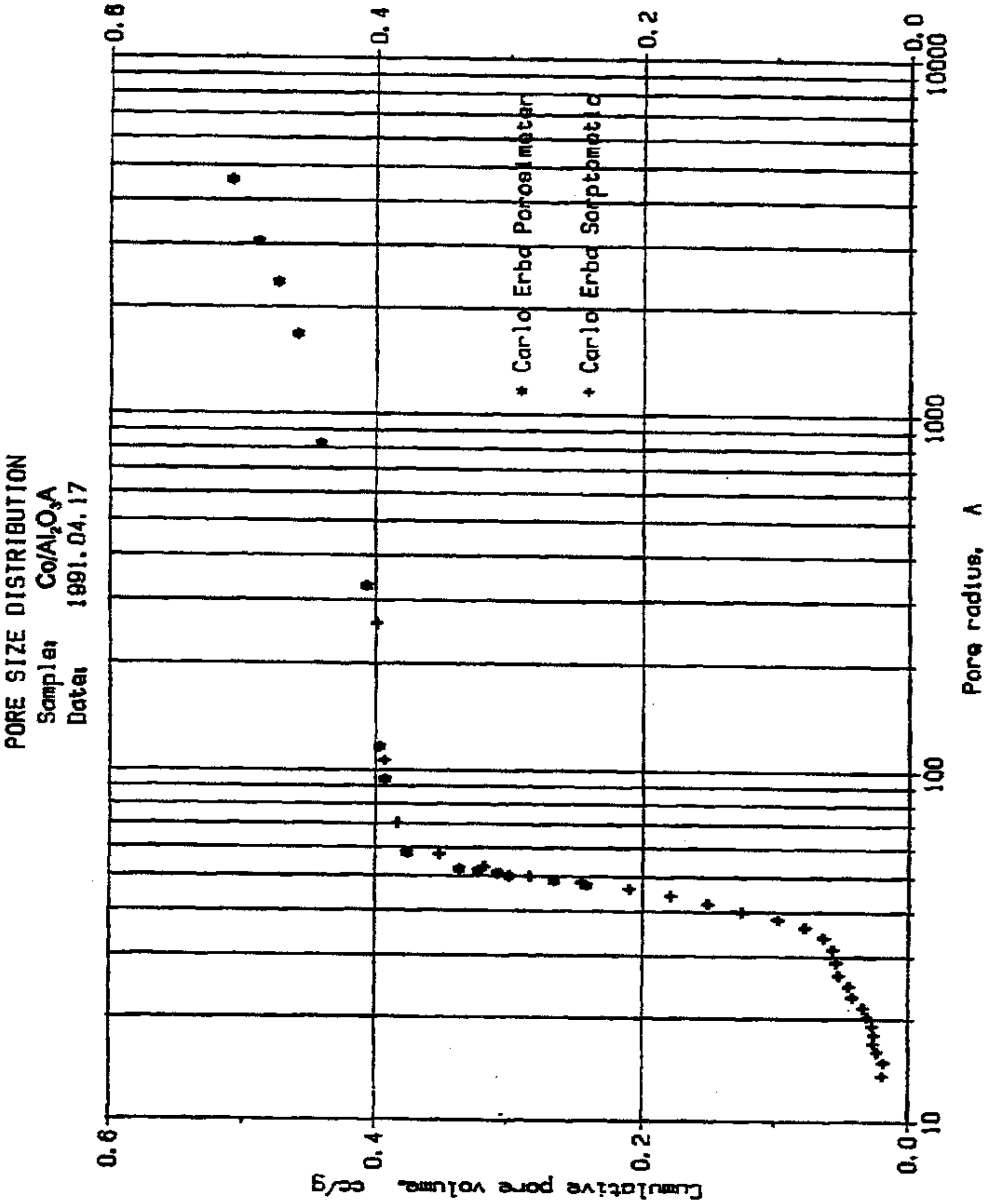
s = 0.0633
s+I = 0.0639
Vm = 15.66 cc(STP)

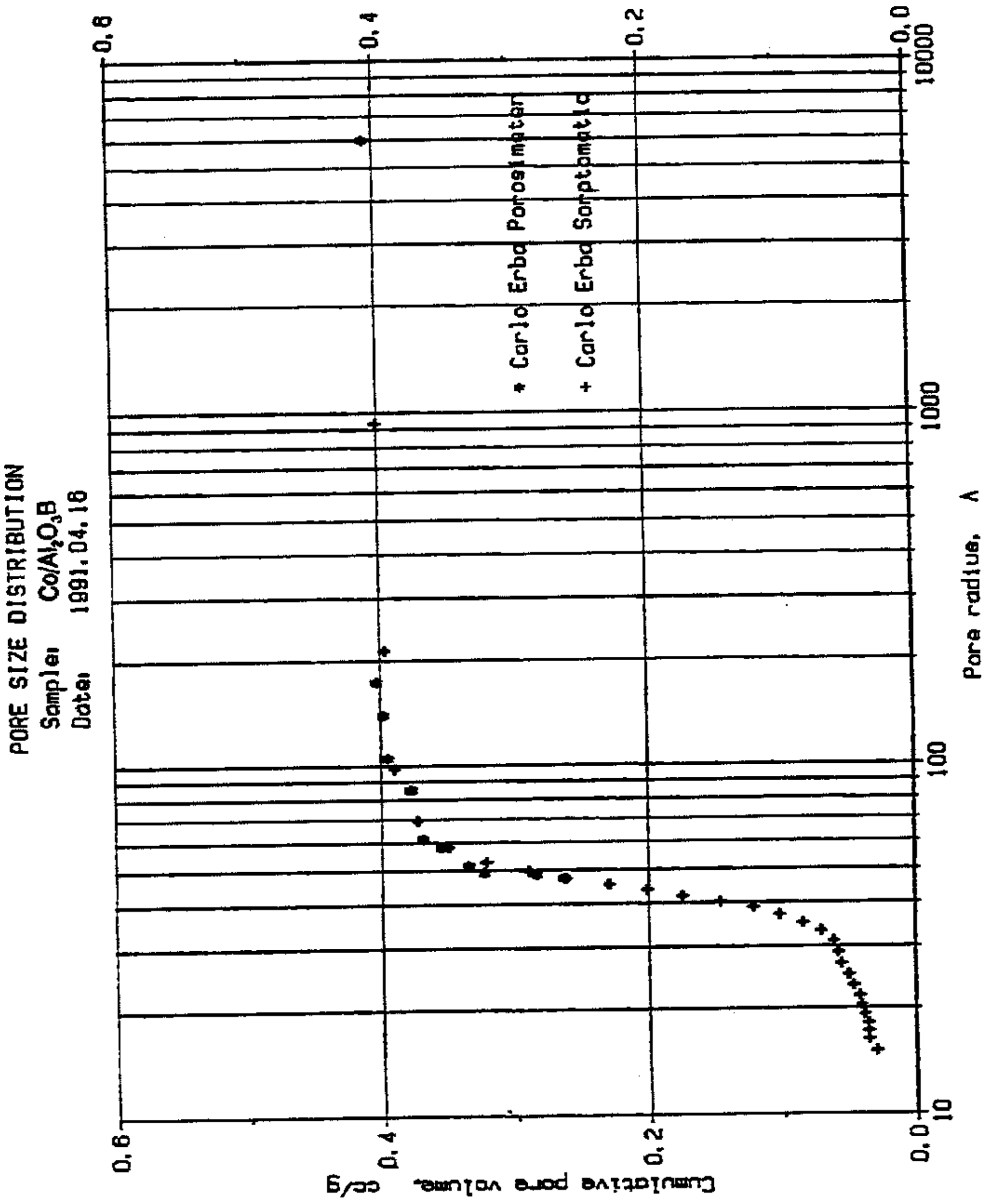
Sg = 179 sqm/g




PORE SIZE DISTRIBUTION
Sample: Co/Al2O3B
Date: 1991.04.16
V (-) *10**3
0
5
10
15
20
25
0
20
40
60
80
100
Pore radius, Å


PORE SIZE DISTRIBUTION
Sample: Co/Al$_2$O$_3$A
Date: 1991.04.17
V(r)*10**3
0
5
10
15
20
25
0
20
40
60
80
100
Pore radius, A


PORE SIZE DISTRIBUTION
Sample: Co/Al$_2$O$_3$A
Date: 1991.04.17
* Carlo Erba Porosimeter
+ Carlo Erba Sorptomatic
Cumulative pore volume, cc/g
0.0
0.2
0.4
0.6
Pore radius, A
10
100
1000
10000


PORE SIZE DISTRIBUTION
Sample: Co/Al$_2$O$_3$B
Date: 1991.04.16
* Carlo Erba Porosimeter
+ Carlo Erba Sorptomatic
0.6
0.4
0.2
0.0
10
100
1000
10000
Pore radius, A
Cumulative pore volume, cc/g

APPENDIX 6

APPENDIX 6

Formulas for calculation of activity and selectivity

The calculations are based on the use of an internal standard, nitrogen, premixed with the carbon monoxide feed gas. Relative response factors, F_x, for CO, CH_4 and CO_2 were determined by analysis of a gas mixture of known composition. They were defined as:

$$F_x = \frac{n_x \cdot A_i \cdot F_i}{n_i \cdot A_x} \tag{A6-1}$$

where
$x = CO, CH_4, CO_2$
i = internal standard (N_2)
n = molar flow [ml/min]
A = peak areal %
F_i = 1.0 (by definition)

Since nitrogen is inert

$$n_{0\,N_2} = n_{1\,N_2} \tag{A6-2}$$

where 0 and 1 represent gas flow in and out of the reactor, respectively.
$n_{0\,N2}$ is found from analysis of the feed gas where $n_{0(CO+N2)}$ is known:

$$\%\,N_2 = \frac{A_{N_2}}{(A_{CO} \cdot F_{CO} + A_{N_2})} \cdot 100\ \% \tag{A6-3}$$

$$n_0\,CO = \frac{n_{0\,(CO+N_2)} \cdot (100 - \%N_2)}{100} \tag{A6-4}$$

$$n_{0\,N_2} = n_{0\,(CO+N_2)} - n_{0\,CO} \tag{A6-5}$$

When $n_{0\,N2}$ is known, the molar flow of CO, CH_4, and CO_2 out of the reactor can be calculated from GC-data by solving Eq. A6-1 for n_x:

$$n_{1\,x} = \frac{A_x \cdot F_x}{A_{N_2} \cdot n_{0\,N_2}} \tag{A6-6}$$

The conversion of CO (η_{CO}) as % of the feed CO can then be calculated:

$$\eta_{CO} = \frac{n_{0\,CO} - n_{1\,CO}}{n_{0\,CO}} \cdot 100\ \% \qquad \text{(A6-7)}$$

The conversion of CO can also be calculated as [mol CO reacted / gram of Co·s]:

$$\text{CO conversion} = \frac{n_{0\,CO} - n_{1\,CO}}{g\ Co \cdot 60 \cdot 22414} \qquad \text{(A6-8)}$$

In some cases, when the temperature was unstabile during the run or the temperature in different runs which should be compared at the same temperature was not equal (± 3 K), the CO conversion was "normalized" by the equation:

$$(\text{CO conversion})_{T_1} = (\text{CO conversion})_{T_0} \cdot \frac{e^{-E_a/RT_1}}{e^{-E_a/RT_0}} \qquad \text{(A6-9)}$$

The CH_4 and CO_2 selectivity can be calculated from TCD data, using the general equation for carbon selectivity:

$$S_x = \frac{n_{1\,x} \cdot N_x}{n_{0\,CO} - n_{1\,CO}} \cdot 100\ \% \qquad \text{(A6-10)}$$

where N_x is the number of C-atoms in product x.

For the hydrocarbon analysis on the FID it was assumed that area% equals carbon% /91/. A link between the TCD and the FID analysis could then be made at CH_4. The selectivity to C_{2+} hydrocarbons could be calculated by:

$$S_x = \frac{A_{x\ FID}}{A_{CH_4\ FID}} \cdot S_{CH_4\ TCD} \qquad \text{(A6-11)}$$

With high quality of the analysis the sum of all S_x should equal the amount of CO consumed (that means: be 100 %).

APPENDIX 7

APPENDIX 7

Product selectivity over the catalysts investigated

Table A7-1. **Product selectivity over Co/Al_2O_3A at different temperatures measured after 200 - 300 minutes. P = 7 bara, H_2/CO = 2.**

Reaction temperature (K)	C_1	C_2-C_4	C_5-C_{10}	C_{11+}
489	13.5	14.3	32.3	39.9
506	13.7	15.7	33.0	37.6
508	15.9	14.6	38.0	31.5
513	17.3	18.1	35.3	29.3
515	17.7	17.9	36.5	27.9
523	24.6	21.0	36.6	17.8
529	25.6	24.7	36.8	12.9

These data are shown in Figure 4-33.

Table A7-2. **Product selectivity over Co/Al_2O_3A at different H_2/CO ratios measured after 200 - 300 minutes. P = 7 and 9 bara, H_2/CO = 2.**

$P_{H2} : P_{CO}$	Reaction temperature (K)	C_1	C_2-C_4	C_5-C_{10}	C_{11+}
4.5 : 4.5	510	11.9	13.6	34.2	40.3
2.3 : 2.3	514	13.4	16.2	39.8	30.6
4.7 : 2.3	508	15.9	14.6	38.0	31.5
4.7 : 2.3	513	17.3	18.1	35.3	29.3
4.7 : 2.3	515	17.7	17.9	36.5	27.9
6.7 : 2.3	509	21.2	19.4	31.5	27.9
4.7 : 1.2	513	28.1	24.5	33.2	14.2
4.7 : 1.2	513	32.9	27.7	29.4	10.0

Some of these data are shown in Figure 4-34.

Table A7-3. **Product selectivity over Co0.1Pt*/Al$_2$O$_3$A at different temperatures measured after 200 - 300 minutes. P = 7 bara, H$_2$/CO = 2.**

Reaction temperature (K)	C_1	C_2-C_4	C_5-C_{10}	C_{11+}
486	13.2	10.0	32.4	44.2
490	12.6	11.0	33.0	43.5
506	14.0	14.5	31.9	39.6
508	17.9	14.9	38.2	28.9
523	24.9	20.9	38.2	16.0

Some of these data are shown in Figure 4-35.

Table A7-4. **Product selectivity over Co1.0Pt*/Al$_2$O$_3$A at different temperatures measured after 200 - 300 minutes. P = 7 bara, H$_2$/CO = 2.**

Reaction temperature (K)	C_1	C_2-C_4	C_5-C_{10}	C_{11+}
506	13.5	17.4	32.5	36.5
509	14.5	17.0	30.3	38.1

Some of these data are shown in Figure 4-35.

Table A7-5. **Product selectivity over Co/Al$_2$O$_3$A at H$_2$/CO ratios = 2 and 3, measured after 200 - 300 minutes. T = 473 K, P = 1 bara, GHSV = 5000 and 7000, respectively.**

H$_2$/CO	C_1	C_2-C_4	C_{5+}
2.0	10	14	76
3.1	15	19	66

These data are shown in Figure 4-40.

Table A7-6. Product selectivity over Co/Al_2O_3A and Co1.0Pt/Al_2O_3A, measured after 200 - 300 minutes. T = 473 K, P = 1 bara, H_2/CO = 3, GHSV = 7000.

Catalyst	C_1	C_2-C_4	C_5-C_{10}
Co/Al_2O_3A	15	19	66
Co1.0Pt/Al_2O_3A	15	21	64

These data are shown in Figure 4-41.