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APPENDIX A

SAMPLE OF CALCULATIONS

1. Preparation of 9%Ce-0.03%Co-0.03%Pd Catalysts with the Incipient Impregnation Method

Reagent : -Cerium [III] nitrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$)

Purity 98% ; Molecular weight = 434.22 g.

Atomic weight of Cerium = 140.12

-Cobalt [II] nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$)

Purity 99% ; Molecular weight = 291.04 g.

Atomic weight of Cobalt = 58.933

-Palladium [II] nitrate ($\text{Pd}(\text{NO}_3)_2$)

Purity 100% ; Molecular weight = 230.43 g.

Atomic weight of Palladium = 106.4

Support : Alumina ($\gamma\text{-Al}_2\text{O}_3$) ; type KNH -3

Pore volume = 1.0 ml./ g.

From Sumitomo Aluminium Smelting Co.,Ltd.

Calculation for prepared 9%Ce-0.03%Co-0.03%Pd / Al_2O_3 (% by weight)

based on : Catalyst 9%Ce-0.03%Co-0.03%Pd/ $\gamma\text{-Al}_2\text{O}_3$ = 100 g.

Hence : each 100 gram. of the catalyst is composed of

Cerium	9	g.
Cobalt	0.03	g.
Palladium	0.03	g.
Aluminium	X	g.

$$\text{Then } 9+0.03+0.03+X = 100 \quad \text{gram.}$$

$$\text{Support (X)} = 90.94 \quad \text{gram.}$$

The alumina support weight used for all preparations is 3 gram.

$$1. \quad \underline{\text{Cerium required}} = 3 \times 9 / 90.94 = 0.2969 \quad \text{g.}$$

Cerium (Ce) was prepared from 25 ml. of solution of Cerium nitrate which was prepared by dissolving 10 g. of Cerium nitrate in de-ionized water.

$$\begin{aligned} \text{Then ; Ce content in stock solution} &= 10 \times 140.12 / (434.22 / 0.98) \\ &= 3.1623 \quad \text{g.} \end{aligned}$$

$$\begin{aligned} \text{Cerium nitrate taken} &= 0.2969 \times 25 / 3.1623 \quad \text{ml.} \\ \text{from stock solution} &= 2.35 \quad \text{ml.} \end{aligned}$$

$$2. \quad \underline{\text{Cobalt required}} = 3 \times 0.03 / 90.94 = 9.8966 \times 10^{-4} \quad \text{g.}$$

Cobalt (Co) was prepared from 25 ml. of solution of Cobalt nitrate which was prepared by dissolving 1 g. of Cobalt nitrate in de-ionized water.

$$\begin{aligned} \text{Then ; Co content in stock solution} &= 1 \times 58.9332 / (291.04 / 0.99) \\ &= 0.2005 \quad \text{g.} \end{aligned}$$

$$\begin{aligned} \text{Cobalt nitrate taken} &= 9.8966 \times 10^{-4} \times 25 / 0.2005 \quad \text{ml.} \\ \text{from stock solution} &= 0.12 \quad \text{ml.} \end{aligned}$$

$$3. \quad \underline{\text{Palladium required}} = 3 \times 0.03 / 90.94 = 9.8966 \times 10^{-4} \quad \text{g.}$$

Palladium nitrate 0.1 g. dissolved in de-ionized water with 0.4 ml. of Hydrochloric acid (concentration of HCl is 37% Volume by Volume)

$$\begin{aligned} \text{Then ; Pd content in stock solution} &= 0.1 \times 106.4 / (291.04) \\ &= 0.046 \text{ g.} \end{aligned}$$

$$\begin{aligned} \text{Palladium nitrate taken} &= 9.8966 \times 10^{-4} \times 25 / 0.046 \text{ ml.} \\ \text{from stock solution} &= 0.54 \text{ ml.} \end{aligned}$$

The incipient impregnation was performed by sequential impregnate method in this research. As the pore volume of the alumina support is 1 ml./g., the total volume of each reagent used, $\text{Ce}(\text{NO}_3)_3$, $\text{Co}(\text{NO}_3)_2$, $\text{Pd}(\text{NO}_3)_2$ is made by adding de-ionized water to increase the volume of the impregnation solution volume by 3 ml. for impregnate in 3 gram of support.

2. Calculation of metal active site on catalyst

$$\text{The weight of catalyst used} = w \text{ g.}$$

$$\text{Area of CO peak after adsorption} = A \text{ unit.}$$

$$\text{Average area of 0.18 cc. standard CO peak} = B \text{ unit.}$$

$$\text{Amounts of CO adsorbed on catalyst} = B-A \text{ unit.}$$

$$\text{Volume of CO adsorbed on catalyst} = [(B-A)/B] \times 0.18 \text{ ml.}$$

$$\text{Volume of gas 1 mole at } 30^\circ\text{C} = 24.86 \times 10^3 \text{ ml.}$$

$$\text{Mole of CO adsorbed on catalyst (mole)} = [(B-A)/B] \times [0.18 / 24.86 \times 10^3]$$

$$1 \text{ mole is } 6.02 \times 10^{23} \text{ molecule}$$

Then, Molecule of CO adsorbed on catalyst

$$= 7.24 \times 10^{-6} [(B-A)/B] \times [6.02 \times 10^{23}] \text{ molecules}$$

$$\text{Metal active site} = 4.36 \times 10^{18} \times [(B-A)/B] \text{ molecules of CO / g. of catalyst.}$$

Example of calculation active site of modified three-way catalyst.

CAT.1 (9%Ce-0.03%Co-0.03%Pd) 0.4 gram. was evaluated.

Area of CO peak after adsorption = 8603 unit.

Average area of 0.18 ml. standard CO peak = 9092 unit

Amount of CO adsorbed on catalyst = (9092-8603) unit.

Volume of CO adsorbed on catalyst = (9092-8603)/9092x0.18
= 9.68×10^{-3} ml.

The adsorption CO condition was carried out at 30°C

Then, Mole of CO adsorbed on catalyst = $(9.68 \times 10^{-3}) / (24.86 \times 10^{-3})$

Molecule of CO adsorbed on catalyst (0.40 g.)

= $(9.68 \times 10^{-3}) / (24.86 \times 10^{-3}) \times 6.02 \times 10^{23} = 2.344 \times 10^{17}$ molecules

Metal active site = $(2.344 \times 10^{17}) / (0.40) = 5.86 \times 10^{17}$ molecules/g. of catalyst

APPENDIX B

Table B-1 Shows Specification of Alumina Support (Al₂O₃) Type

KNH-3

Chemical Composition (weight percent)		
-Al ₂ O ₃	60-70	%
-SiO ₂	30-35	%
-Fe ₂ O ₃	0.3-0.5	%
-TiO ₂	0.5-0.7	%
-CaO	0.1-0.2	%
-MgO	0.2-0.4	%
-Na ₂ O	0.3-0.4	%
-K ₂ O	0.2-0.3	%
-ZrO ₂ + HfO ₂	0.03-0.04	%

Physical Properties	
- Bulk density (g/ml.)	1.3 -1.5
- Apparent Specific Gravity	3.1-3.3
- Packing Density (lb./ft ³)	20-25
- Pore Volume (ml./g)	1.0-1.3
- Surface Area (m ² /g)	340-350

Table B-2 Shows the conditions of calcining the reagent used for preparation modified catalysts.

Name of reagent	Temperature of calcining and holding time (hr.)
1. $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	500 °C : 4 hrs.
2. $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	400 °C : 3 hrs.
3. $\text{Pd}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	500 °C : 2 hrs.
4. $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	300 °C : 1 hrs.
5. $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	500 °C : 4 hrs.
6. $\text{Cd}(\text{Cl}_2) \cdot 2(1/2)\text{H}_2\text{O}$	500 °C : 4 hrs.
7. $\text{Ag}(\text{NO}_3)$	500 °C : 4 hrs.
8. $\text{Ga}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$	500 °C : 4 hrs.
9. $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$	500 °C : 4 hrs.
10. $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	500 °C : 4 hrs.
11. $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	500 °C : 4 hrs.
12. $\text{H}_2\text{PtCl}_6 \cdot \text{H}_2\text{O}$	500 °C : 4 hrs.
13. $\text{Rh}(\text{NO}_3)_3$	500 °C : 4 hrs.

The operating conditions for gas chromatography.

1. A thermal conductivity detector gas chromatograph (model 8ATP) was used to analyze the concentrations of oxygen, nitrogen, carbon monoxide.

OPERATING CONDITIONS ARE AS FOLLOWS :

GC.	: SHIMUDZU-GC-8ATP
Detector	: TCD.
Packed column	: MS-5A
Carrier gas	: Ultra high Purity Helium (99.999%)
Flow rate of Carries gas	: 30 ml./min
Column temperature	: 90 °C
Detector temperature	: 100 °C
Injector temperature	: 100 °C
Current	: 80 mA

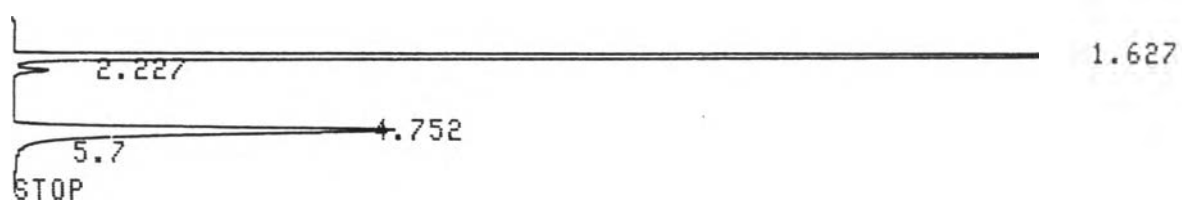
2. For Gas chromatograph model 8AIT was used to analyze the concentration of H₂O , propane, carbon dioxide.

Operating conditions were similar to model 8ATP except :

Column packing	: Porapak - Q
Carrier gas	: High Purity Helium (99.99%)
Flow rate of Carrier gas	: 60 ml./min

The chromatograph from gas analysis are shown in Figure B-1 , B-2 respectively.

Figure B-1 Sample of Chromatogram from GC-8ATP (column MS-5A)



PNKO	TIME	AREA	CONC	NAME
1.	1.627	40954	82.4265	OXYGEN
2.	2.227	386	0.7766	NITROGEN
3.	4.752	8344	16.7969	CARBON MONOXIDE
		-----	-----	
	TOTAL	49674	100	

Figure B-2 Sample of Chromatogram from GC-8AIT (column Porapak Q)

70UT 400 C
START

12/01/95 06:08:12



PNKO	TIME	AREA	CONC	NAME
1.	0.558	8309	56.7033	N ₂ + O ₂
2.	1.018	2397	19.7708	CO ₂
3.	2.595	504	3.4385	H ₂ O
4.	6.192	2943	20.0874	PROPANE
		-----	-----	
	TOTAL	14653	100	

VITA

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