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APPENDIX

APPENDIX A

SAMPLE OF CALCULATION

A.1 Calculation of designed metal loading for catalyst preparation.

The sample of calculation shown below is for (0.3 wt%)Pt- (0.3 wt%)Sn-(0.6 wt%)Li/Al_2O_3. The hydrochloric acid is also added to the impregnating solution by 5 wt% of the support. The alumina support weight used for all preparation is 2 grams.

If the weight of alumina support used is X grams. So each 100 grams of the catalyst would compose of

Platinum	0.30	g.
Tin	0.30	g.
Lithium	0.60	g.
Hydrochloric acid	(0.05)(X)	g.
Alumina support	X	g.

Then $0.30 + 0.30 + 0.60 + (0.05)(X) + X = 100$ g.

$X = 94.10$ g.

The platinum compound used for supplying the platinum metal component is chloroplatinic acid ($H_2PtCl_6.6H_2O$), its molecular weight is 517.92, and the platinum content in the compound is 37.67 wt.%.

The tin compound used is stannous chloride dihydrate ($SnCl_2.2H_2O$), its molecular weight is 118.69, and the tin content in the compound is 51.02 wt.%.

The lithium compound used is lithium nitrate ($LiNO_3$), its molecular weight is 68.94, and the lithium content is 10.07 wt.%.

Concentration of hydrochloric acid solution is 37 % volume by volume, its density is 1.19 kilogram per liter.

The calculation procedure of the amount of each ingredients for the required composition of the (0.30 wt.%)Pt-(0.30 wt.%)Sn-(0.60 wt.%)Li/Al_2O_3 catalyst shows below.

For 2 grams of alumina support used :

(1) Platinum required = (0.30/94.10)(2) g.

= 6.376×10^{-3} g.

Chloroplatinic acid required

= (100/37.67)(6.376×10^{-3}) g.

= 0.0169 g.

(2). Tin required = (0.30/94.10)(2) g.

= 6.376×10^{-3} g.

Stannous chloride dihydrate required

= (100/51.02)(6.376×10^{-3}) g.

= 0.0125 g.

(3). Hydrochloric acid solution required

= (2)(0.05) g.

= 0.10 g.

The amount of HCl by volume

= 0.10/(1.19x0.37) ml.

= 0.23 ml.

(4). Lithium required = (0.60/94.10)(2) g.

= 0.0128 g.

Lithium nitrate required

= (100/10.07)(0.0128) g.

= 0.1271 g.

As the pore volume of the alumina support is 1 ml./g., the total volume of impregnation solution that must be used is 2 ml. By the requirement of the incipient impregnate method, the de-ionized water is added to the above solution unit the volume equals to the alumina pore volume. This solution is used as the impregnating solution.

A.2 Calculation of metal active site on catalyst.

Let the weight of catalyst used = w g.

height of CO peak after adsorption = A unit

height of 0.18 ml. standard CO peak = B unit

Amounts of CO adsorped on catalyst = B - A unit

Volume of CO adsorbed on catalyst = [(B - A)/B](0.18) ml.

Volume of gas 1 mole at 30°C = 24.86×10^{3} ml.

Mole of CO adsorbed on catalyst

= $[(B - A)/B][(0.18)/24.86\times10^{3})]$ mole

Molecule of CO adsorbed on catalyst

= $7.24\times10^{-6}[(B-A/B)](6.02\times10^{23})$ molecule

Metal active site = 4.36×10^{18} [(B - A)/B] molecule of CO/g. cat.

A.3 BET surface area calculation.

From BET equation :

$$\frac{x}{v(1-x)} = \frac{1}{v_m C} + \frac{(C-1)(x)}{v_m C} \qquad \text{(A.3.1)}$$

where : x = relative partial pressure of N_2, P/P_o

P_o = saturated vapour pressure of N_2 (or adsorbed gas) at the experimental temperature

P = equilibrium vapour pressure of N_2

v = volume of gas adsorbed at pressure P, ml. at the NTP/gram of sample

v_m = volume of gas adsorbed in monolayer, ml. at the NTP/gram of sample

C = $\exp(E_1 - E_2/RT)$

where : E_1 = heat of adsorption on the first layer

E_2 = heat of condensation of adsorbed gas on all the layers

assume $C \rightarrow \infty$, then

$$\frac{x}{v(1-x)} = \frac{1}{v_m C} + (x) \qquad (A.3.2)$$

let : v_m = v_m'

v_m' = mean the volume of gas adsorbed to form the N_2 complete monolayer

v = volume of gas adsorbed measured by G.C.

x = P/P_o

$$\frac{P_b V}{273} = \frac{P_t V}{T} \qquad (A.3.3)$$

where : V = constant volume

P_b = pressure at 0°C

P_t = pressure at t°C

T = 273.15 + t, K

P_b = $(273.15/T)\ P_t$ = 1 atm

partial pressure

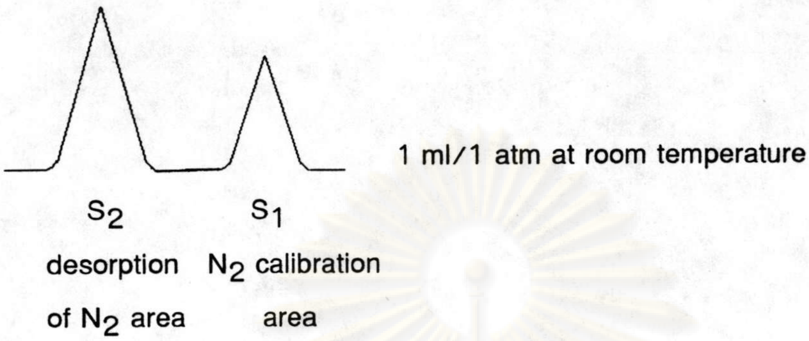
$$P = \frac{[\text{Flow of }(He+N_2) - \text{ Flow of He}] \,.\, P_b}{\text{Flow of }(He+N_2)} \qquad (A.3.4)$$

$$= 0.3 \text{ atm}$$

N_2 saturated vapour pressure, P_o = 1.1 atm = 836 mm. Hg

$$x = P/P_o = P/1.1$$

How to measure v



$$v = \frac{S_2}{S_1} \cdot \frac{1}{w} \cdot \frac{273.15}{T} \quad \text{ml./g of catalyst} \qquad (A.3.5)$$

where : w = weight of sample

$$v_m{}' = \frac{v[1-(\text{flow of He+N}_2 - \text{flow of He})/1.1]}{\text{flow of He+N}_2} \quad \text{ml.NTP/g of cat.}$$

$$S_b = S\ v_m{}' \qquad (A.3.6)$$

where : S = surface area from literature of N_2

= 4.373 m^2/ml. of N_2

so that : S_b = 4.373 $v_m{}'$ m^2/g. of catalyst (A.3.7)

A.4 Electrical Conductivity Measurement.

R = Resistance of catalyst

D = Diameter of pellet

L = Thickness of pellet

$$\rho = \frac{R.A}{L} = \frac{R.\pi.D^2/4}{L} \qquad (A.4.1)$$

$$\text{Electrical Conductivity} = \frac{1}{\rho} \qquad (A.4.2)$$

A.5 Calculation of H/C ratio by Temperature Pregrammed Oxidation (TPO) method.

Temperature Programmed Oxidation gives the data of the amount of oxygen consumed and carbon dioxide produced.

From oxidation reaction :

$$CH_x + (1 + x/4)O_2 \qquad CO_2 + x/2\ H_2O \qquad (A.5.1)$$

$$\text{Where} \quad x = \frac{\text{mole of hydrogen}}{\text{mole of carbon}}$$

From Temperature Programmed Oxidation data

mole of O_2 consumed = total area of consumed x correct. factor 1

moleofCO_2produced total area of CO_2 produced xcorrect. factor 2

$$= [(1 + x/4)/1] \qquad (A.5.2)$$

$$\text{Let} \quad K = \frac{\text{correction factor1}}{\text{correction factor 2}} \qquad (A.5.3)$$

$$1 + x/4 = \frac{\text{total area of } O_2 \text{ consumed}}{\text{total area of } CO_2 \text{ produced}} \times K$$

$$\text{H/C ratio} = 4 \ \text{total area of } O_2 \text{ consumed} \times K - 1 \qquad (A.5.4)$$

A.6 Free Electron (base on Conductivity Unit : $ohm^{-1}cm^{-1}$)

The free electron value could relate to strength of active sites. It was calculated from conductivity.

A = Conductivity of (0.3wt%)Pt-(0.3wt%)Sn-(0.6wt%)M/Al_2O_3

M = Li, Na, K

B = Conductivity of (0.3wt%)Pt-(0.3wt%)Sn/Al_2O_3

C = Conductivity of (0.6wt%)M/Al_2O_3

D = Conductivity of Alumina support.

$$\text{Free electron} = A-(B+C+D) \tag{A.6.1}$$

APPENDIX B

THE AMOUNTS OF COVERED METTAL ACTTIVE SITES BY COKE DEPOSITION

B.1 Calculation of Amount of Metal Active Sites Covered by Coke Deposition

A = Metal active sites of fresh catalyst

B = Metal active sites of spent catalyst

C = Metal active sites of regeneration at 250 °C

% Total coke covered on metal active sites (%TC) $= \frac{A-B}{A} *100$ (B.1.1)

% Irreversible coke covered on metal active sites (%IRC) $= \frac{A-C}{A} *100$ (B.1.2)

% Reversible coke covered on metal active sites (%RC) $= \frac{C-B}{A} *100$ (B.1.3)

B.2 Calculation of % Error from Regeneration Method.

A = Metal active sites of fresh catalyst

B = Metal active sites of regeneration at 500 °C

% error $= \frac{A-B}{A} *100$ (B.2.1)

APPENDIX C

SPECIFICATION OF ALUNINA SUPPORT (Al_2O_3) TYPE KNH-3
FROM SUMITOMO ALUMINIUM SMELTING CO.,LTD.

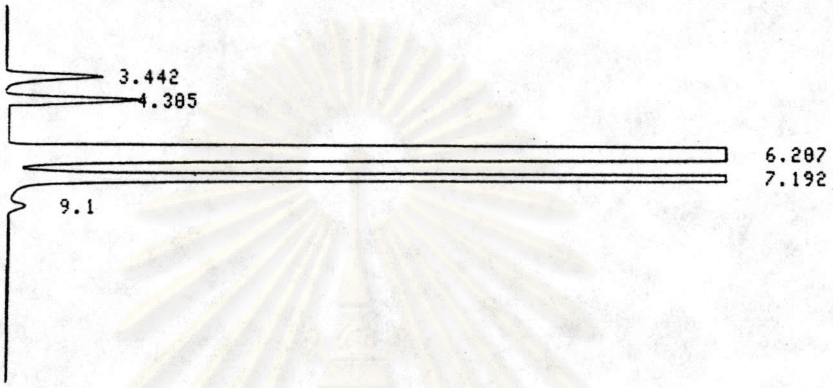
Table C.1 Specification of alumina support (KNH-3).

Chemical Composition (weight percent)	
- Al_2O_3	60-70 %
- SiO_2	30-35 %
- Fe_2O_3	0.3-0.5 %
- TiO_2	0.5-0.7 %
- CaO	0.1-0.2 %
- MgO	0.2-0.4 %
- Na_2O	0.3-0.4 %
- K_2O	0.2-0.3 %
- ZrO_2 + HfO_2	0.03-0.04 %

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

APPENDIX D

SAMPLE OF CHROMATOGRAM



```
CHROMATOPAC      C-R6A                  FILE      7
SAMPLE NO     0                         METHOD     441
REPORT NO      53

PKNO        TIME          AREA    MK    IDNO          CONC               NAME
   1       3.442          2005                       0.0379              Methane
   2       4.305          2910                       0.0551              Ethane-ethylene
   3       6.207       5044382                      95.4707              Propane
   4       7.192        232836     V                 4.4067              Propylene
   5       9.1            1564     V                 0.0296              Butane
                     ---------                   ----------
          TOTAL        5283696                   100
```

Figure D.1 Sample of chromatogram.

VITA

Miss Bualom Jaikaew was born in Ratchaburi, Thailand on October 15, 1967. She received her Bachelor Degree of Science from Department of Chemistry, Faculty of Science, Kasetsart University in 1991