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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/Al₂O₃. 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.

$$\text{Then } 0.30 + 0.30 + 0.60 + (0.05)(X) + X = 100 \quad \text{g.}$$

$$X = 94.10 \quad \text{g.}$$

The platinum compound used for supplying the platinum metal component is chloroplatinic acid (H₂PtCl₆.6H₂O), 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 ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$), 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 :

$$\begin{aligned} (1) \text{ Platinum required} &= (0.30/94.10)(2) && \text{g.} \\ &= 6.376 \times 10^{-3} && \text{g.} \end{aligned}$$

Chloroplatinic acid required

$$\begin{aligned} &= (100/37.67)(6.376 \times 10^{-3}) && \text{g.} \\ &= 0.0169 && \text{g.} \end{aligned}$$

$$\begin{aligned} (2). \text{ Tin required} &= (0.30/94.10)(2) && \text{g.} \\ &= 6.376 \times 10^{-3} && \text{g.} \end{aligned}$$

Stannous chloride dihydrate required

$$\begin{aligned} &= (100/51.02)(6.376 \times 10^{-3}) && \text{g.} \\ &= 0.0125 && \text{g.} \end{aligned}$$

$$\begin{aligned} (3). \text{ Hydrochloric acid solution required} & && \\ &= (2)(0.05) && \text{g.} \end{aligned}$$

$$= 0.10 \quad \text{g.}$$

The amount of HCl by volume

$$= 0.10 / (1.19 \times 0.37) \quad \text{ml.}$$

$$= 0.23 \quad \text{ml.}$$

$$(4). \text{ Lithium required} = (0.60/94.10)(2) \quad \text{g.}$$

$$= 0.0128 \quad \text{g.}$$

Lithium nitrate required

$$= (100/10.07)(0.0128) \quad \text{g.}$$

$$= 0.1271 \quad \text{g.}$$

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.

$$\text{Let the weight of catalyst used} = w \quad \text{g.}$$

$$\text{height of CO peak after adsorption} = A \quad \text{unit}$$

$$\text{height of 0.18 ml. standard CO peak} = B \quad \text{unit}$$

$$\text{Amounts of CO adsorped on catalyst} = B - A \quad \text{unit}$$

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

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

Mole of CO adsorbed on catalyst

$$= [(B - A)/B][(0.18)/24.86 \times 10^3] \quad \text{mole}$$

Molecule of CO adsorbed on catalyst

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

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

A.3 BET surface area calculation.

From BET equation :

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

where : x = relative partial pressure of N_2 , P/P_0

P_0 = 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 other
layers

assume $C \rightarrow \infty$, then

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

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.

$x = P/P_o$

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

where : $V =$ constant volume

$P_b =$ pressure at 0 C

$P_t =$ pressure at t C

$T = 273.15 + t, K$

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

partial pressure

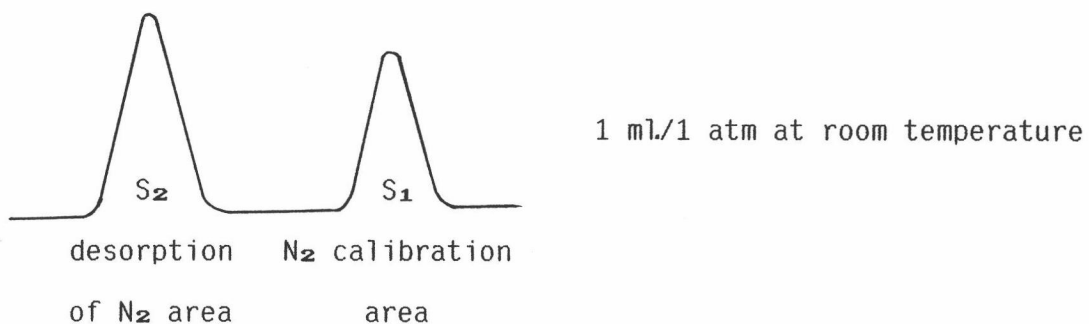
$$P = \frac{[\text{Flow of (He+N}_2\text{)} - \text{Flow of He}] \cdot P_b}{\text{Flow of (He+N}_2\text{)}} \quad (A.3.4)$$

$$= 0.3 \text{ atm}$$

N_2 saturated vapour pressure, $P_o = 1.1 \text{ atm} = 836 \text{ mm. Hg}$

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

How to measure v



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

where : w = weight of sample

$$v_m' = \frac{v[1 - (\text{flow of He} + N_2 - \text{flow of He})/1.1]}{\text{flow of He} + N_2} \quad \text{ml.NTP/g of cat.}$$

$$S_b = S \cdot v_m' \quad (\text{A.3.6})$$

where : S = surface area from literature of N_2
 = 4.373 $\text{m}^2/\text{ml. of } N_2$

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

A.4 Calculation of H/C ratio by Temperature Programmed Oxidation (TPO) method.

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

From oxidation reaction :



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

From Temperature Programmed Oxidation data

$$\frac{\text{mole of O}_2 \text{ consumed}}{\text{mole of CO}_2 \text{ produced}} = \frac{\text{total area of consumed} \times \text{correct. factor 1}}{\text{total area of CO}_2 \text{ produced} \times \text{correct. factor 2}}$$

$$= [(1 + x/4)/1] \quad (\text{A.4.2})$$

$$\text{Let } K = \frac{\text{correction factor 1}}{\text{correction factor 2}} \quad (\text{A.4.3})$$

$$1 + x/4 = \frac{\text{total area of O}_2 \text{ consumed} \times K}{\text{total area of CO}_2 \text{ produced}}$$

$$\text{H/C ratio} = 4 \left[\frac{\text{total area of O}_2 \text{ consumed} \times K - 1}{\text{total area of CO}_2 \text{ Produced}} \right] \quad (\text{A.4.4})$$

A.5 Calculation of amount of metal sites covered by coke deposition and the metal sites covered ratio.

In this study, the 20% propane in nitrogen was used for dehydrogenation reaction at the flow rate of 30 ml./min.

For Pt/Al₂O₃ catalyst, it had the amount of metal sites of 2.7641×10^{18} sites adsorbed by CO molecule/g. cat., the first 5 minutes propane conversion of 0.5675. By the regeneration method, the Δ conversion (500 °C–250 °C) at the 5 minute of time on stream was 0.1249.

The amounts of mole of propane in feed stream

$$\begin{aligned} &= [0.2 \times 30 \times 273 \times 6.02 \times 10^{23}] / [303 \times 22,400] \\ &= 1.4528 \times 10^{20} \quad \text{molecules/min.} \end{aligned}$$

Thus, the amounts of mole of propane reacted

$$\begin{aligned} &= 1.4528 \times 10^{20} \times 0.5675 \\ &= 8.245 \times 10^{19} \quad \text{molecules/min.-g. cat.} \end{aligned}$$

Turn over number

$$\begin{aligned} &= 8.245 \times 10^{19} / 2.7641 \times 10^{18} \\ &= 29.83 \quad \text{molecules/min.-site.} \end{aligned}$$

The amounts of mole of propane reacted at 5 min of time on stream.

$$\begin{aligned} &= 1.4528 \times 10^{20} \times 0.1249 \\ &= 1.8145 \times 10^{19} \quad \text{molecules/min.} \end{aligned}$$

Thus, the amount of metal active sites covered by irreversible coke deposition at the 5 minute of time on stream.

$$\begin{aligned} &= 1.8145 \times 10^{19} / 29.83 \\ &= 6.0828 \times 10^{17} \quad \text{sites/g. cat.} \end{aligned}$$

The percentage coverage

$$\begin{aligned} &= [(6.0828 \times 10^{17})(100)] / 2.7641 \times 10^{18} \\ &= 22.01 \% \end{aligned}$$



APPENDIX B

THE AMOUNTS OF METAL ACTIVE SITES
 CONVERTED TO PLATINUM OXIDE IN REGENERATION METHOD

Table B.1 The amounts of metal active sites converted to platinum oxide in regeneration method.

Catalyst	(1)	(2)	(3) = (2)-(1)
Pt-Sn/Al ₂ O ₃	4.8670×10^{17}	2.1470×10^{17}	2.72×10^{17}

where (1) = amounts of remained metal active site after oxidation by 1% O₂ in He gas mixture at 250 °C for 30 min., sites/g. cat.

(2) = amounts of remained metal active site after oxidation by 1% O₂ in He gas mixture at 500 °C for 30 min., sites/g. cat.

(3) = amounts of metal active site converted to platinum oxide in regeneration method, sites/g.cat.

APPENDIX C

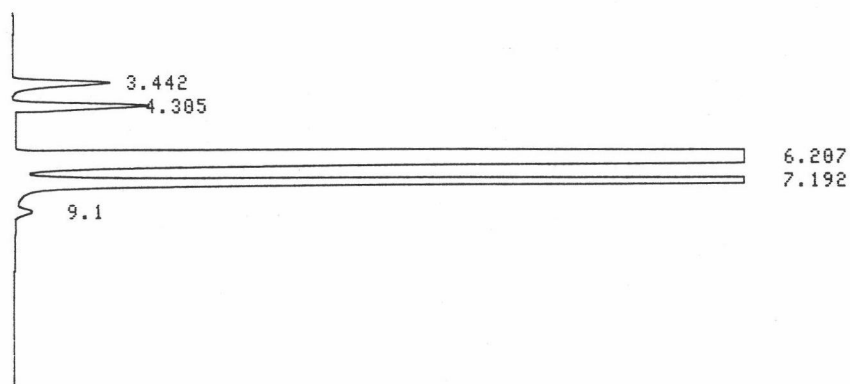
SPECIFICATION OF ALUMINA SUPPORT (Al₂O₃) TYPE KNH-3 FROM SUMITOMO ALUMINIUM SMELTING CO.,LTD.

Table C.1 Specification of alumina support (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/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



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

Mr. Somsak Amornchanthanakorn was born in Bangkok on July 30, 1965. He received his Bachelor of Science Degree in Chemical Technology, from the Faculty of Science, Chulalongkorn University in 1985.