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## APPENDIX A

### SAMPLE OF CALCULATIONS

#### A-1 Calculation of Si/Metal Atomic Ratio for ZSM-5, Fe-silicate, and Cu-silicate

The calculation is based on weight of Sodium Silicate ( $\text{Na}_2\text{O}\cdot\text{SiO}_2\cdot\text{H}_2\text{O}$ ) in B1 and B2 solutions.

M.W. of Si = 28.0855

M.W. of  $\text{SiO}_2$  = 60.0843

Weight percent of  $\text{SiO}_2$  in Sodium Silicate = 28.5

M.W. of Al = 26.9815

M.W. of  $\text{AlCl}_3$  = 133.3405

Weight percent purity of  $\text{AlCl}_3$  = 97

M.W. of Fe = 55.847

M.W. of  $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$  = 404.00

Weight percent purity of  $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$  = 99

M.W. of Cu = 63.54

M.W. of  $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$  = 241.60

Weight percent purity of  $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$  = 99.5

For example, to prepare ZSM-5 at Si/Al atomic ratio of 50. Using Sodium Silicate 69 g with 45 g of water as B1 solution.

$$\text{mole of Si used} = \frac{\text{wt.(%)}}{100} \cdot (\text{M.W. of Si}) \cdot \frac{(1 \text{ mole})}{(\text{M.W. of } \text{SiO}_2)} \quad (\text{A-1.1})$$

$$\begin{aligned}
 &= 69 \cdot (28.5/100) \cdot (1/60.0843) \\
 &= 0.3273
 \end{aligned}$$

Si/Al atomic ratio = 50

mole of  $\text{AlCl}_3$  required =  $0.3273/50 = 6.5458 \cdot 10^{-3}$  mole

$$\begin{aligned}
 \text{amount of } \text{AlCl}_3 &= 6.5458 \cdot 10^{-3} \cdot 133.34 \cdot (100/97) \\
 &= 0.8998 \text{ g}
 \end{aligned}$$

This is the amount of  $\text{AlCl}_3$  used in A1 and A2 solutions

Si/Fe = 50

mole of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  required =  $0.3273/50 = 6.5458 \cdot 10^{-3}$  mole

$$\begin{aligned}
 \text{amount of } \text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O} &= 6.5458 \cdot 10^{-3} \cdot 404.00 \cdot (100/99) \\
 &= 2.6712 \text{ g}
 \end{aligned}$$

This is the amount of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  used in A1 and A2 solutions.

Si/Cu = 50

mole of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  required =  $0.3273/50 = 6.5458 \cdot 10^{-3}$  mole

$$\begin{aligned}
 \text{amount of } \text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O} &= 6.5458 \cdot 10^{-3} \cdot 241.60 \cdot (100/99.5) \\
 &= 1.5894 \text{ g}
 \end{aligned}$$

This is the amount of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  used in A1 and A2 solutions.

## A-2 Calculation of Metal Ion-exchanged ZSM-5 and Metallosilicate

### Pt ion-exchange

Determine the amount of Pt into catalyst = 0.5 wt.%

The catalyst use =  $x$  g

So that: from the equation

$$\text{Pt}/(x+\text{Pt}) = 0.5/100 \quad (\text{A-2.1})$$

$$100 \cdot \text{Pt} = 0.5 \cdot (x+\text{Pt})$$

$$(100-0.5) \cdot \text{Pt} = 0.5 \cdot x$$

thus  $\text{Pt} = 0.5 \cdot x / (100-0.5)$  g

use  $\text{Pt}(\text{NH}_3)_4\text{Cl}_2\text{H}_2\text{O}$  (M.W. 352.13, 55% Pt)

$$\text{weight of } \text{Pt}(\text{NH}_3)_4\text{Cl}_2\text{H}_2\text{O} = [0.5 \cdot x / (100-0.5)] \cdot [100/55] \text{ g}$$

### Cu ion-exchange

Determine the amount of Cu into catalyst = 0.5 wt.%

the catalyst use =  $x$  g

So that : from the equation

$$\text{Cu}/(x+\text{Cu}) = 0.5/100$$

$$100 \cdot \text{Cu} = 0.5 \cdot (x+\text{Cu})$$

$$(100-0.5) \cdot \text{Cu} = 0.5 \cdot x$$

thus  $\text{Cu} = 0.5 \cdot x / (100-0.5)$  g

use  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (M.W. 241.60, 26.30% Cu, purity 99.5%)

$$\text{weight of Cu(NO}_3)_2 \cdot 3\text{H}_2\text{O} = [0.5 \cdot x / (100 - 0.5)] \cdot [(100/26.30) \cdot (100/99.5)]$$

Various copper salts used for ion exchange

copper salt	%purity	M.W.	%Cu	weight of copper salt (g)
Cu(NO <sub>3</sub> ) <sub>2</sub> ·3H <sub>2</sub> O	99.5	241.60	26.30	[0.5·x/(100-0.5)]·[(100/26.30)·(100/99.5)]
Cu(CH <sub>3</sub> COO) <sub>2</sub> ·H <sub>2</sub> O	99.0	199.65	31.83	[0.5·x/(100-0.5)]·[(100/31.83)·(100/99)]
CuCl	95	98.993	64.19	[0.5·x/(100-0.5)]·[(100/64.19)·(100/95)]
CuCl <sub>2</sub> ·2H <sub>2</sub> O	97	170.48	37.27	[0.5·x/(100-0.5)]·[(100/37.27)·(100/97)]
CuSO <sub>4</sub> ·5H <sub>2</sub> O	99.5	249.68	25.45	[0.5·x/(100-0.5)]·[(100/25.45)·(100/99.5)]

### A-3 Calculation of Reaction Flow Rate

The catalyst used = 0.5000 g

packed catalyst into quartz reactor (diameter = 0.6 cm)

determine the average high of catalyst bed = x cm

So that, volume of catalyst bed =  $\pi * (0.3)^2 * x$  cc-catalyst

used GHSV(Gas Hourly Space Velocity) = 2,000 h<sup>-1</sup>

GHSV = Volumetric flow rate = 4,000 h<sup>-1</sup>

Volume of Catalyst

Volumetric flow rate = 4,000 · Volume of catalyst

$$\begin{aligned}
 &= 4,000 \cdot \pi (0.3)^2 \cdot x \text{ cc./h} \\
 &= 4,000 \cdot \pi (0.3)^2 \cdot x / 60 \text{ cc./min.}
 \end{aligned}$$

at STP : Volumetric flow rate = Volumetric flow rate = Volume flow rate  $\cdot (273.15+t)$

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273.15

where :  $t$  = room temperature,  $^{\circ}\text{C}$

#### A-4. BET Surface Area Calculation

From BET equation :

$$x / v(1-x) = (1/v_m C) + (C-1) \cdot x / v_m C \quad (\text{A-4.1})$$

where :  $x$  = ratio of partial pressure  $P/P_o$

$P_o$  = saturated vapor pressure of  $\text{N}_2$  (or adsorbed gas)

$P$  = equilibrium vapor pressure of  $\text{N}_2$

$v$  = amount of adsorption to cover the surface, c.c. at the NTP/gm of sample

$C = \exp(E_1 - E_2 / RT)$  (A-4.2)

where :  $E_1$  = heat of adsorption of the first layer

$E_2$  = heat of condensation of adsorbed gas

assume  $C \rightarrow \infty$ , then

$$x / (v * (1-x)) = (1 / v_m C) * x \quad (\text{A-5.3})$$

let :  $v_m = v'_m$

$v_m$  = mean amount of adsorption to form the  $N_2$  complete monolayer

$v$  = amount of adsorption measuring by G.C.

$x = P/P_o$

$$P_b * V / 273 = P_t V / T \quad (\text{A-4.4})$$

where :  $V$  = constant volume

$P_b$  = pressure at  $0^\circ\text{C}$

$P_t$  = pressure at  $t^\circ\text{C}$

$T = 273.15 + t, \text{K}$

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

partial pressure

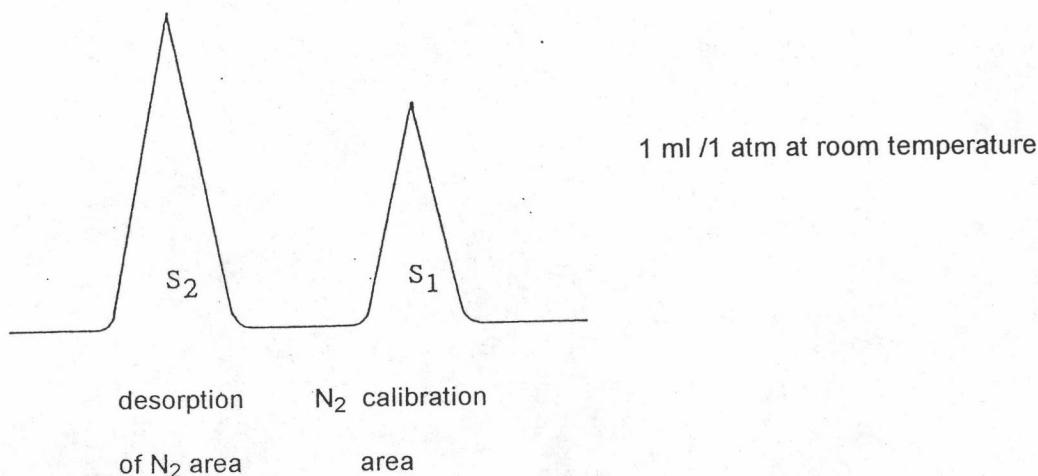
$$P = \frac{(\text{Flow of } (He + N_2) - \text{Flow of He})}{\text{Flow of } (He + N_2) * P_b} \quad (\text{A-4.5})$$

$$= 0.3 \text{ atm}$$

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

$$X = P / P_o = P / 1.1$$

How to measure  $V$



$$V = (S_2 / S_1) \cdot (1 / w) \cdot (273.15 / T) \cdot V \quad \text{c.c. / g of catalyst} \quad (\text{A-4.6})$$

where :  $w$  = weight of sample

$$V'_m = V \cdot [1 - ((\text{flow of He} + \text{N}_2\text{-flow of He}) / 1.1)] \quad (\text{A-4.7})$$


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flow of He +  $N_2$       c.c. NTP /g of catalyst

$$S_b = S \cdot V'_m \quad (\text{A-4.8})$$

where :  $S$  = surface area from literature of  $N_2$

$$= 4.373 \text{ m}^2/\text{c.c. of } N_2$$

so that :  $S_b = 4.373 V'_m \text{ m}^2 / \text{g of catalyst}$

### A-5 TPD calculation

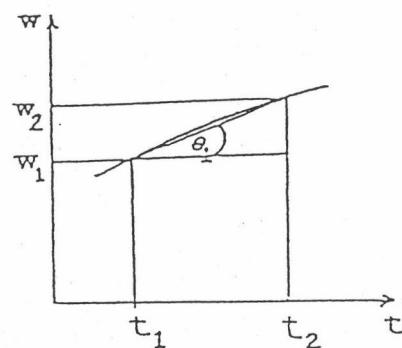


Figure A-5.1 Plot of weight loss vs. time

From figure A-5.1:

$$(dw/dt) = (w_2 - w_1) / (t_2 - t_1) + \tan \theta \quad (\text{A-5.1})$$

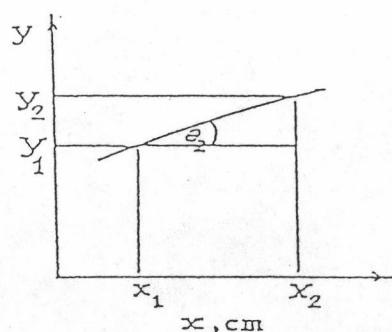


Figure A-5.2 Plot of full scale chart relating weight loss to speed chart which is related to time.

From figure A-5.2 :

The recorder condition was adjust follows :

$$25 \text{ cm} = a \text{ mg}$$

$$y_1 \text{ cm} = (a \cdot y_1)/25 \text{ mg}$$

$$\text{and } y_2 \text{ cm} = (a \cdot y_2)/25 \text{ mg}$$

chart speed                  b cm = 60 sec

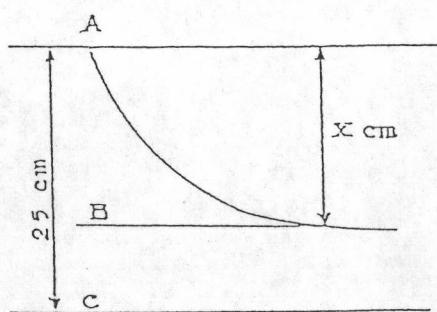
$$x_1 \text{ cm} = (60 \cdot x_1)/b \text{ sec}$$

$$x_2 \text{ cm} = (60 \cdot x_2)/b \text{ sec}$$

$$\frac{dw/dt}{w_0} = \frac{(a/25) \cdot (y_2 - y_1)}{(60/b) \cdot (x_2 - x_1)} = \frac{ab}{(25 \cdot 60)} \tan \theta \quad (\text{A-5.2})$$

For TPD curve plot between  $(dw/dt)/w_0$  vs. temperature

where : w = dry weight of catalyst and calculated as follows



we set full chart scale = a mg

at                  A position weight of catalyst = a mg

B position weight of catalyst = ax/25 mg

$$\text{weight loss} = ax/25 \text{ mg} \quad (\text{A-5.3})$$

$$\text{dry wt. of catalyst} = \text{wt. of sample before drying} - \text{wt. loss} \quad (\text{A-5.4})$$

#### A-6 Calculation of NO and C<sub>3</sub>H<sub>8</sub> conversion

The effluent gas was analyzed by gas chromatography, the NO reduction activity was evaluated in terms of the conversion of NO into N<sub>2</sub>.

$$\text{NO Conversion(}\%) = (2[N_2]_{\text{out}} / [\text{NO}]_{\text{in}}) * 100$$

The C<sub>3</sub>H<sub>8</sub> oxidation activity was evaluated in terms of the conversion of C<sub>3</sub>H<sub>8</sub> into CO and CO<sub>2</sub>.

$$\text{C}_3\text{H}_8 \text{ Conversion(}\%) = \frac{([\text{C}_3\text{H}_8]_{\text{in}} - [\text{C}_3\text{H}_8]_{\text{out}}) * 100}{[\text{C}_3\text{H}_8]_{\text{in}}}$$

**APPENDIX B****Physical Properties of Nitric Oxide**

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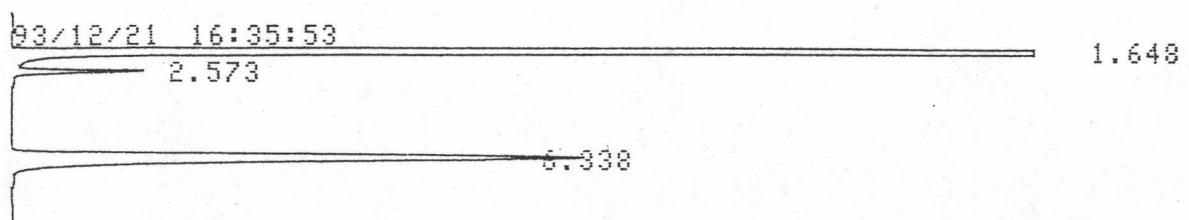
Property	Value
mol. wt.	30.1
m.p., °C	-161
b.p., °C	151.18
heat of fusion, kcal./mole	0.550
heat of vaporization, kcal./mole	3.293
heat of formation, kcal./mole	21.50
density[0 °C, 1 atm], g/L	1.2536
sp. gr., gas, [0 °C, 1 atm], (air = 1)	.93
critical temperature, °C	1.018
critical pressure, atm	64
color	colorless gas, blue liquid and solid

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**Ambient Air Quality Standard of Thailand( 1981)**

Pollutants	average value (mg/m <sup>3</sup> )				methods of measurement
	1 h	8 h	24 h	1 year	
Carbon Monoxide (CO)	50	20	-	-	Non Dispersive Infrared Detection
Nitrogen Dioxide (NO <sub>2</sub> )	0.32	-	-	-	Gas Phase Chemiluminescence
Sulfur Dioxide (SO <sub>2</sub> )	-	- 0.3	1*		Pararosanniline
Suspended Particulate Matter (SPM)	-	-	0.33	0.1*	Gravimetric
Photochemical Oxidant (O <sub>3</sub> )	0.20	-	-	-	Chemiluminescence
Lead (Pb)	-	-	0.01	-	Wet Ashing

Note : \* = Geometric mean

**Sample of Chromatogram**

COLUMN MS-5A

PKNO	TIME	AREA	CONC.	NAME
1	1.648	221521	94.4088	O <sub>2</sub>
2	2.573	1252	0.5336	N <sub>2</sub>
3	6.338	11867	5.0576	CO

21 16:25:27, 2.297 0.533  
F 5.992

## COLUMN PORAPAK-Q

PKNO	TIME	AREA	CONC.	NAME
1	0.533	52711	85.2217	AIR
2	0.98	4111	6.6467	CO <sub>2</sub>
3	2.297	4598	7.4345	H <sub>2</sub> O
4	5.992	431	0.6971	C <sub>3</sub> H <sub>8</sub>

VITA



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