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APPENDIX A

SAMPLE OF CALCULATIONS

A-1 Calculation of Si/Metal Atomic Ratio for Metallosilicates Preparation

The calculations is based on weight of Sodium Silicate ($Na_2O.SiO_2.H_2O$) in G2 and S2 solutions.

Molecular Weight of Si = 28.0855

Molecular Weight of SiO_2 = 60.0843

Weight percent of SiO_2 in Sodium Silicate = 28.5

Using Sodium Silicate 69 g with 45 g of water as a G2 and S2 solution.

$$\text{mole of Si used} = \text{wt.} \times \frac{(\%)}{100} \times \frac{(\text{M.W. of Si})}{(\text{M.W. of } SiO_2)} \times \frac{(1 \text{ mole})}{(\text{M.W. of Si})} \qquad \text{(A-1.1)}$$

$$= 69 \times (28.5/100) \times (1/60.0843)$$

$$= 0.3273 \text{ mole}$$

ZSM-5 Catalyst

For example, to prepare ZSM-5 at Si/Al atomic ratio of 40 by using $AlCl_3$ for aluminium source.

Molecular Weight of Al = 26.9815

Molecular Weight of $AlCl_3$ = 133.3405

Si/Al atomic ratio of 40

mole of $AlCl_3$ required = 0.3273/40 = 8.1825×10^{-3} mole

amount of $AlCl_3$ = $8.1825 \times 10^{-3} \times 133.3405$

= 1.0911 g

Ga-silicate and Ga.Al-silicate Catalyst

For example, to prepare Ga-silicate with Si/Ga atomic ratio of 40 by using $Ga_2(SO_4)_3.nH_2O$ for aluminium source.

Molecular Weight of Ga	=	69.723
Molecular Weight of $Ga_2(SO_4)_3.nH_2O$	=	742.4042

Si/Ga atomic ratio of 40

mole of $Ga_2(SO_4)_3.nH_2O$ required	=	0.3273/40 = 8.1825×10^{-3} mole
amount of $Ga_2(SO_4)_3.nH_2O$	=	$(8.1825 \times 10^{-3} \times 742.4042)/2$
	=	3.0374 g

Zn-silicate and Zn.Al-silicate Catalyst

For example, to prepare Zn-silicate with Si/Ga atomic ratio of 40 by using $ZnSO_4.7H_2O$ for aluminium source.

Molecular Weight of Zn	=	65.39
Molecular Weight of $ZnSO_4.7H_2O$	=	287.54

Si/Zn atomic ratio of 40

mole of $ZnSO_4.7H_2O$ required	=	0.3273/40 = 8.1825×10^{-3} mole
amount of $ZnSO_4.7H_2O$	=	$8.1825 \times 10^{-3} \times 287.54$
	=	2.353 g

This is the amount of $AlCl_3$, $Ga_2(SO_4)_3.nH_2O$ and/or $ZnSO_4.7H_2O$ used in G1 and S1 solutions.

A-2 Calculation of Metal Ion-exchanged ZSM-5 and Metallosilicates

Platinum ion-exchange

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

The catalyst use = X g

So that: from the equation

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

$$100 \times Pt = 0.5 \times (X+Pt)$$

$$(100-0.5) \times Pt = 0.5 \times X$$

thus $$Pt = (0.5 \times X)/(100-0.5) \text{ g}$$

use $Pt(NH_3)_4Cl_2.H_2O$ (Molecular Weight = 352.13, 55 % Pt)

weight of $Pt(NH_3)_4Cl_2.H_2O$ = [0.5 x X/(100-0.5)] x [100/55] g

For other metal ion-exchange

Determine the amount of metal loaded into catalyst = 0.5 wt.%

The catalyst use = X g

So that : from the equation

$$Me/(X+Me) = 0.5/100$$

$$100 \times Me = 0.5 \times (X+Me)$$

$$(100-0.5) \times Me = 0.5 \times X$$

thus weight of metal, Me = 0.5 x X/(100-0.5) g

Various metal salt used for ion-exchange

Metal salt	M.W.	% metal	Weight of metal salt(g)
$Ga_2(SO_4)_3.nH_2O$	737.40	18.78	[0.5 x X/(100-0.5)]x[100/18.78]
$ZnSO_4.7H_2O$	287.54	21.98	[0.5 x X/(100-0.5)]x[100/21.98]
$(NH_4)_6Mo_7O_{24}.4H_2O$	1235.86	54.32	[0.5 x X/(100-0.5)]x[100/54.32]
$Mn(NO_3)_2.4H_2O$	251.01	21.89	[0.5 x X/(100-0.5)]x[100/21.89]
$ZrCl_4$	233.03	39.15	[0.5 x X/(100-0.5)]x[100/39.15]
$Cu(NO_3)_2.3H_2O$	241.60	26.30	[0.5 x X/(100-0.5)]x[100/26.30]
$Ni(NO_3)_2.6H_2O$	290.81	18.47	[0.5 x X/(100-0.5)]x[100/18.47]
VCl_3	157.30	32.40	[0.5 x X/(100-0.5)]x[100/32.40]
$Fe(NO_3)_3.9H_2O$	404.00	13.82	[0.5 x X/(100-0.5)]x[100/13.82]
$Co(NO_3)_2.6H_2O$	291.04	20.24	[0.5 x X/(100-0.5)]x[100/20.24]
$Cr(NO_3)_3.9H_2O$	400.15	12.99	[0.5 x X/(100-0.5)]x[100/12.99]

A-3 NH_3 Temperature Programmed Desorption Calculation

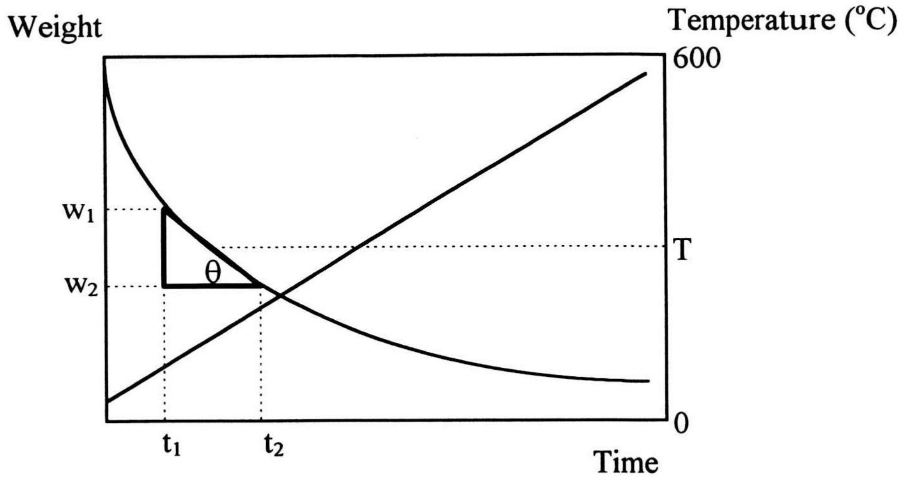


Figure A-3 Plot of weight loss and temperature versus time

Chart speed	=	0.25 cm/min.		
Range	=	10 mg		
w	=	weight of catalyst		
w_w	=	weight of water		
w_d	=	weight of dry catalyst	=	$w - w_w$
dw	=	10 mg x (a /25 cm)		(A-2.1)
dt	=	60 sec x (b /0.25 cm)		(A-2.2)
$\frac{(dw/dt)}{w_d}$	=	$\frac{(10 \text{ mg} \times 0.25 \text{ cm} \times a)/(60 \text{ sec} \times 25 \text{ cm} \times b)}{w_d}$		(A-2.3)

Plot $\frac{(dw/dt)}{w_d}$ versus temperature.

A-4 Calculation of Reaction Flow Rate.

The catalyst used = 0.5000 g

packed catalyst into quartz reactor (inside diameter = 0.6 cm)

determine the average high of catalyst bed = H cm. So that,

$$\text{Volume of catalyst} = \pi \times (0.3)^2 \times h \ \text{cc-cat.}$$

used Gas Hourly Space Velocity (GHSV) = 2000 h^{-1}

$$\text{GHSV} = \frac{\text{Volumetric flow rate}^1}{\text{Volume of catalyst}}$$

$$\text{Volumetric flow rate}^1 = 2000 \times \text{Volume of catalyst}$$

$$= 2000 \times \pi \times (0.3)^2 \times H \quad \text{cc/h}$$

$$= (2000 \times \pi \times (0.3)^2 \times H)/60 \quad \text{cc/min.}$$

at STP condition:

$$\text{Volumetric flow rate} = \text{Volumetric flow rate}^1 \times (273.15 + t)/273.15$$

where t = room temperature, °C.

A-5 Calculation of Conversion and Hydrocarbon Distribution of Aromatization Reaction

The LPG (propane, butane, and their mixtures) aromatization activity was evaluated in term of the conversion of LPG into other hydrocarbons.

$$\text{LPG Conversion (\%)} = \frac{([LPG]_{in}-[LPG]_{out}) \times 100}{[LPG]_{in}}$$

For example : H-Ga.Al-silicate (Si/Ga = 155, Si/Al = 40)

Reaction condition : Reaction temperature 600 °C, GHSV = 2000 h^{-1}, feed 20 % propane N_2 balanced, 1 h time on stream.

From Figure A-5.1

VZ-10 (feed)

area of feed propane = 2269572

From Figure A-5.2

VZ-10 (1 h)

area of CH_4, C_1 = 205158

area of C_2 = 65279

area of $C_2^=$ = 152239

area of propane rested = 78996

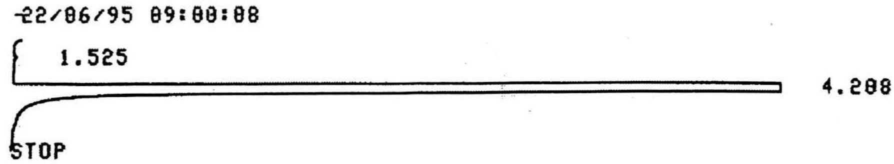
area of $C_3^=$ = 69693

area of C_4 = 932

area of $C_4^=$ = 645

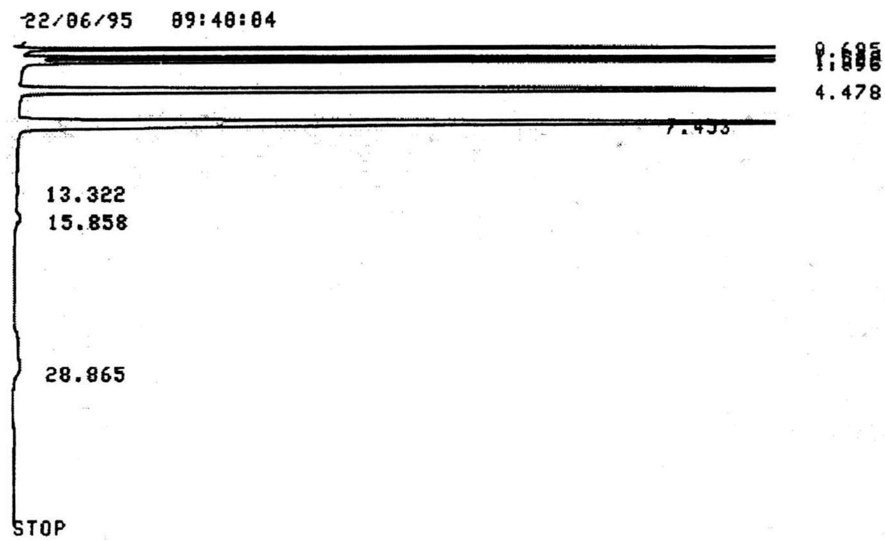
area of C_1-C_4 = 205158+65279+152239+78996+69693+932+645

= 572943



TIME	AREA	MK	IDNO	CONC	NAME
0.067	212			0.0093	
1.525	57			0.0025	
4.208	2269572			99.9882	Propane
TOTAL	2269840			100	

Figure A-5.1 Chromatogram of feed from VZ-10 column



PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	0.058	124			0.0216	
2	0.695	205158			35.7999	Methane
3	1.522	65279	V		11.3912	Ethane
4	1.893	152239	V		26.5657	Ethylene
5	4.478	78996			13.7849	Propane
6	7.453	69693			12.1614	$C_3^=$
7	13.322	231			0.0404	C_4
8	15.858	701			0.1224	
9	28.865	645			0.1126	$C_4^=$
	TOTAL	573067			100	

Figure A-5.2 Chromatogram of product from VZ-10 column

From Figure A-5.3

Silicon OV-1 (1h)

determine all of hydrocarbon area into 3 parts

first part are the area of C_1-C_4= 248722

second part are the area of C_5^+ = 879

third part are the area of aromatics = 395623

So that : compared the area from VZ-10 to the area of OV-1

$$\text{area of } C_1 \text{ (OV-1)} = \frac{\text{area of } C_1\text{(VZ-10)} \times \text{area of } C_1\text{-}C_4\text{(OV-1)}}{\text{area of } C_1\text{-}C_4 \text{ (VZ-10)}}$$

= (205158 x 248722)/572943

= 89062

The other were calculated as same as C_1

area of C_2 (OV-1) = 28339

area of $C_2^=$ (OV-1) = 66089

area of C_3 (OV-1) = 34293

area of $C_3^=$ (OV-1) = 30255

area of C_4 (OV-1) = 405

area of $C_4^=$ (OV-1) = 280

Hence : Product distribution (C-wt.%)

C_1 = [area C_1(OV-1) x 100]/[(total area of OV-1) - (area of C_3(OV-1))]

= (89062 x 100)/(732213-34293)

= 12.76 %

C_2 = 4.06 %

$C_2^=$ = 9.47 %

$C_3^=$ = 4.34 %

C_4 = 0.06 %

$C_4^=$ = 0.04 %

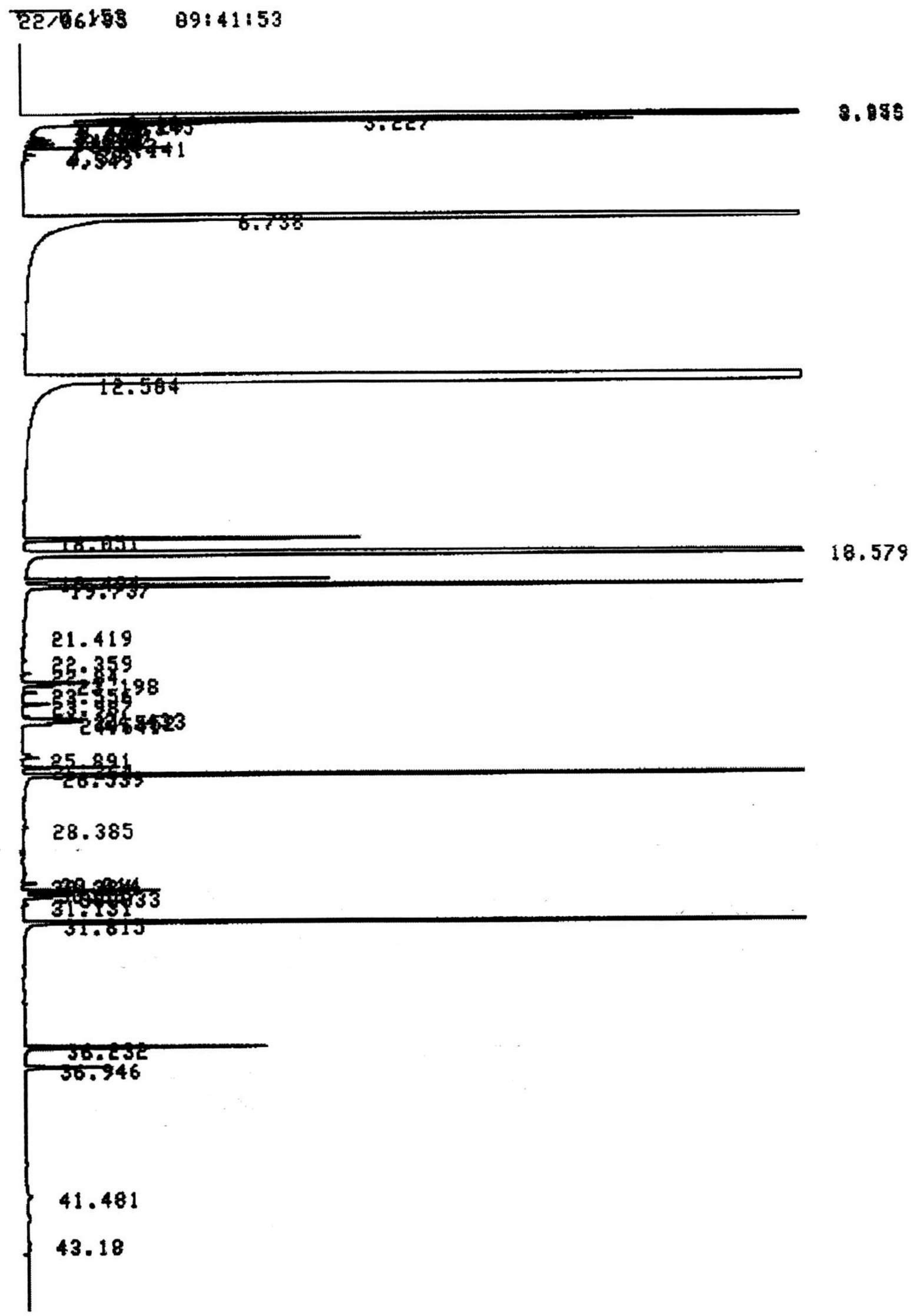


Figure A-5.3 Chromatogram of product from Silicon OV-1 column.

CHROMATOGRAM 1 MEMORIZED

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	0.153	24			0.0033	
2	2.953	185024			25.2684	
3	3.045	59926	V		8.184	
4	3.16	385	V		0.0526	
5	3.227	2088	V		0.2852	C_1-C_4
6	3.29	536	V		0.0733	
7	3.345	763	SV		0.1041	
8	3.497	14	T		0.002	
9	3.607	13	T		0.0018	
10	3.699	13	TV		0.0018	
11	3.762	71	V		0.0097	
12	3.847	108	V		0.0147	C_5^+
13	3.935	29	V		0.0039	
14	3.992	124	V		0.0169	
15	4.141	399	V		0.0545	
16	4.39	29			0.004	
17	4.549	12			0.0016	
18	6.738	262461			35.8438	**Benzene**
19	12.504	167880			22.927	**Toluene**
20	18.051	1607			0.2195	**EB**
21	18.579	23271			3.1781	**m+p-Xylene**
22	19.494	1365			0.1864	C_5^+
23	19.737	7362	V		1.0054	**o-Xylene**
24	21.419	18			0.0025	
25	22.359	22			0.003	C_5^+
26	22.84	40			0.0055	
27	23.198	431			0.0588	
28	23.556	66	V		0.009	
29	23.987	129			0.0177	
30	24.433	33			0.0045	
31	24.552	303	V		0.0414	
32	24.641	378	V		0.0517	
33	25.891	116			0.0159	
34	26.264	405	V		0.0553	
35	26.539	7428			1.0144	
36	28.385	20			0.0027	A_9^+
37	30.014	32			0.0043	
38	30.304	54	V		0.0074	
39	30.667	590			0.0805	
40	30.833	361	V		0.0493	
41	31.131	39	V		0.0053	
42	31.815	6381			0.8714	
43	36.232	1321			0.1805	
44	36.946	489			0.0667	
45	41.481	51			0.007	
46	43.18	26			0.0035	
	TOTAL	732237			100	

Figure A-5.3 Chromatogram of product from Silicon OV-1 column. (continued)

C_5^+	=	0.13 %
aromatics	=	69.15 %
- benzene	=	37.60 %
- toluene	=	24.06 %
- ethylbenzene	=	0.23 %
- xylene	=	4.40 %
- A_9^+	=	2.86 %

$$\text{Propane conversion} = \frac{[\text{area of feed propane}]-[\text{area of propane rested}]}{[\text{area of feed propane}]}$$

$$= [(2269572-78996) \times 100]/2269572$$

$$= 96.52 \ \%$$

VITA

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