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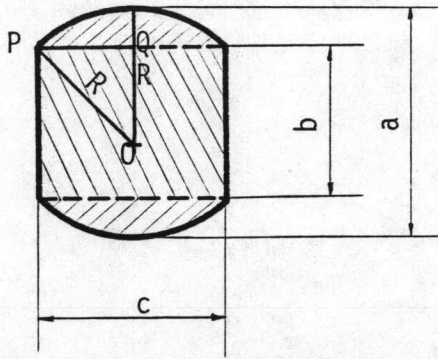
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APPENDIX A

A-1 Calculation of Tableted of Catalyst Volume



consider $\triangle PQR$

$$PO^2 = PQ^2 + OQ^2 \quad (A-1)$$

where

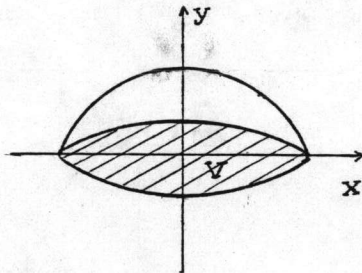
$$PO = R \quad (A-2)$$

$$PQ = \frac{c}{2} \quad (A-3)$$

$$OQ = R - \frac{(a-b)}{2} \quad (A-4)$$

substituted (A-2), (A-3) and (A-4) into (A-1), get

$$\begin{aligned} R^2 &= \left(\frac{c}{2}\right)^2 + \left\{R - \frac{(a-b)}{2}\right\}^2 \\ &= \left(\frac{c}{2}\right)^2 + R^2 - R(a-b) + \frac{(a-b)^2}{2} \\ R &= \frac{1}{(a-b)} \left\{ \left(\frac{c}{2}\right)^2 + \frac{(a-b)^2}{2} \right\} \end{aligned} \quad (A-5)$$



consider a volume V , get that

$$\begin{aligned} V &= \pi \int_0^{\frac{(a-b)}{2}} \left\{ R^2 - (y-R)^2 \right\} dy \\ &= \pi \left\{ R \frac{(a-b)^2}{2} - \frac{1}{3} \left(\frac{a-b}{2}\right)^3 \right\} \end{aligned} \quad (A-6)$$

$$\text{volume of tablet} = \pi \left(\frac{c}{2}\right)^2 b + 2\pi \frac{(a-b)^2}{2} \left[R - \frac{(a-b)}{6} \right] \quad (A-7)$$

A-2 Space Velocity Calculation

1. GHSV (gas hourly space velocity) / or SV (space velocity)

$$\text{GHSV} = \frac{\text{initial flow rate (at STP) (1/hr)}}{\text{vol of catalyst (l)}}$$

where

initial flow rate = flow rate of feed reactant before have the reaction

2. WHSV (weight hourly space velocity)

$$\text{WHSV} = \frac{\text{initial mass flow rate (g/hr)}}{\text{weight of catalyst (g)}}$$

For the experiment of 100% MeOH concentration, we fed liquid methanol at 0°C by using a micro-tube pump and calculated WHSV as following :

$$\text{WHSV} = \frac{\text{SV} \times (\text{vol. of cat.}) \times \text{MeOH density at } 0^{\circ} \text{C}}{\text{cat. wt}}$$

where

$$\begin{aligned} \text{MeOH density}^* \text{ at } 25^{\circ}\text{C} &= 0.7866 \text{ g/ml} \\ \text{at } 0^{\circ} &= 0.8102 \text{ g/ml} \end{aligned}$$

(* data from handbook of chemistry)

For the required WHSV can be achieved by adjust the speed no. of micro-tube pump as following Figure A-1

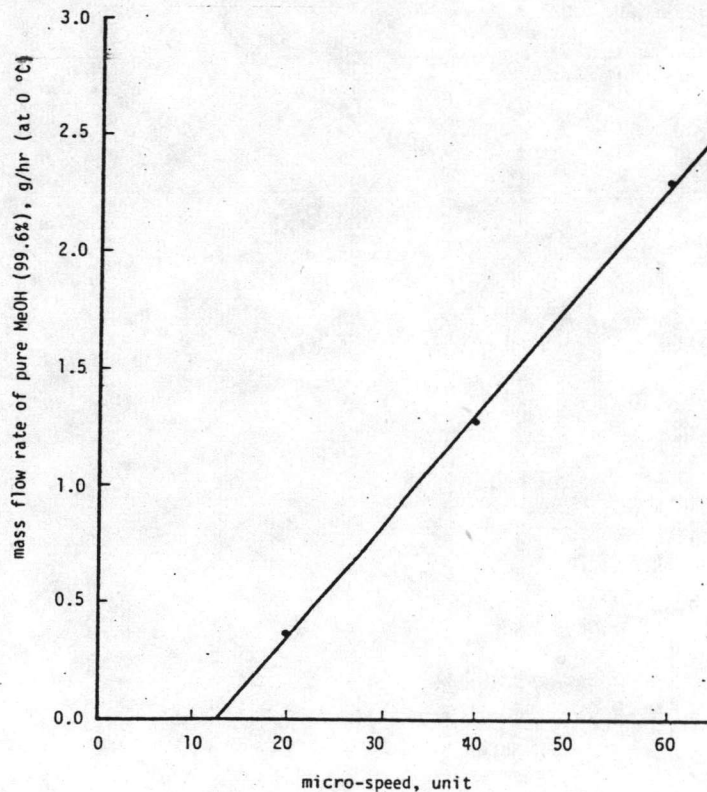


Figure A-1 Calibration curve of micro-speed and mass flow rate of pure MeOH (assay 99.6%) at 0 °C



A-3 Calculation Yield of Product

1. Yield of i product (Y_i)

$$Y_i = \frac{\text{final flow rate (at STP) (1/hr)}}{22.4 (1)} \times \left(\frac{\text{area of } i}{\text{std area of } i} \right) \left(\frac{\text{mole}}{\text{hr}} \right)$$

where

i = considered species

22.4 l is the volume of gas for 1 mole at STP.

2. Space time yield of i product (STY_i)

$$STY_i = \frac{Y_i}{\text{vol. of cat}} \quad \left(\frac{\text{mole/l.hr}}{1} \right)$$

3. Calculation of hydrocarbon distribution of MTG reaction

For hydrocarbons products, we identified the sample by gas chromatography was a FID. The heat detected by the FID detector come from carbon atom, therefore, area of peaks are directly related to the amount of carbon atom of those species.

3.1 Calculation for C-wt% of gasoline fraction range of C_5 to C_{11}

Figure A-2.1 and Table A-1 are the samples of GC analysis peak and data of catalyst H-Si-V (400) in gasoline fraction. The C-wt% of hydrocarbons in gasoline fraction can be calculated as follows:

- 1) Identified the peaks in Figure A-2.1 to Figure A-2.4 as shown under peaks in Figure A-2.1
- 2) Identified retention time of the peaks in Figure A-2.1 to retention time in Table A-1
- 3) Calculated C-wt% of each hydrocarbon by summation the concentration of that retention time interval, for example, C-wt%

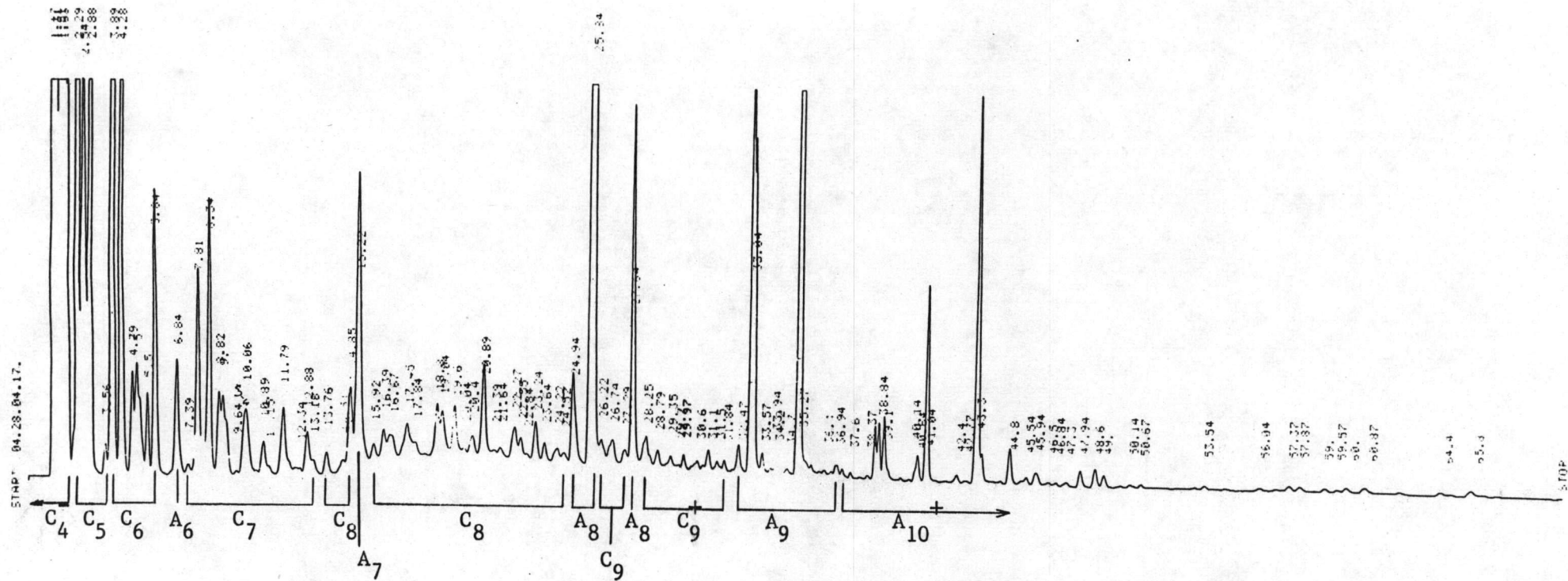


FIGURE A-2.1 GC - Analysis peak of Hydrocarbons (gasoline fraction)

for MTG reaction

Condition: Catalyst - H-Si-V(400), 300 °C, SV = 2000 h⁻¹,
80% N₂, 20% MeOH, 1 h on stream

C-R1A					
SMPL # 00					
FILE # 1					
REPT # 2055					
METHOD 41					
#	NAME	TIME	CONC	MK	AREA
0		1.17	7.3163		45368
0		1.31	10.4572	V	64845
0		1.51	12.856	V	79720
0		1.62	10.0103	V	62074
0		2.24	3.3028	V	55702
0		2.54	2.5671	V	15919
0		2.88	1.4935	V	21663
0		3.56	0.1134		793
0		3.89	5.796	V	35941
0		4.28	2.9373	V	18214
0		4.79	0.3938		2442
0		5	0.7528	V	4668
0		5.5	0.3016	V	1870
0		5.84	1.2414	V	7698
0		6.84	0.5958		3694
0		7.39	0.0321		199
0		7.81	0.9494	V	5887
0		8.34	1.2857	V	7973
0		8.82	0.3416		2118
0		9	0.5444	V	3376
0		9.64	0.0115		71
0		10.06	0.5194	V	3221
0		10.89	0.173		1073
0		11.15	0.0236	V	146
0		11.79	0.4389		2721
0		12.34	0.0317	V	196
0		12.88	0.2299		1426
0		13.18	0.0592	V	367
0		13.76	0.1149		712
0		14.51	0.0685		424
0		14.85	0.4708	V	2975
0		15.21	1.8703	V	11485
0		15.72	0.0000	V	1034
0		16.39	0.2729	V	1444
0		16.67	0.0000	V	1844
0		17.45	0.0872	V	2401
0		17.84	0.1104	V	685
0		18.8	0.3174	V	2092
0		19.04	0.2965	V	1838
0		19.6	0.2796	V	1733
0		20.04	0.0239	V	148
0		20.4	0.1016		630
0		20.89	0.4513		2799
0		21.39	0.0104	V	65
0		21.64	0.0291		181
0		22.27	0.2042		1266
0		22.55	0.1009	V	626
0		22.84	0.0148	V	92
0		23.24	0.1836		1139
0		23.64	0.0736		457
0		24.22	0.0067		538
0		24.52	0.0453	V	281
0		24.84	0.5055		3134
0		25.84	0.6545		41265
0		26.22	0.1441	V	894
0		26.74	0.1776	V	1101
0		27.29	0.0677		420
0		27.64	1.744	V	3644
0		28.25	0.1751		1086
0		28.79	0.0669		415
0		29.35	0.049		304
0		29.7	0.0058		36
0		29.97	0.042		260
0		30.6	0.0503		312
0		31.1	0.091		564
0		31.5	0.0502		187
0		31.84	0.0257		159
0		32.47	0.1233		764
0		33.04	2.3699		15936
0		33.57	0.066	V	409
0		33.94	0.0131		81
0		34.2	0.0664	V	412
0		34.7	0.0157		97
0		35.27	5.3912		53431
0		36.4	0.0097		60
0		36.94	0.0466		289
0		37.6	0.0169		104
0		38.37	0.0107		66
0		38.84	0.154		2195
0		39.1	0.2438	V	1512
0		40.14	0.0056		35
0		40.64	0.1148		712
0		41.04	0.6831		4236
0		42.4	0.0369		229
0		42.77	0.0106		65
0		43.3	1.5825		9813
0		44.8	0.1487		922
0		45.54	0.0444		275
0		45.94	0.0678		420
0		46.5	0.0118		73
0		46.84	0.0079		49
0		47.3	0.0226		140
0		47.94	0.0721		447
0		48.6	0.0742		460
0		49.	0.0477		295
0		50.14	0.0159		99
0		50.67	0.0146		90
0		53.54	0.0154		95
0		56.04	0.0199		123
0		57.37	0.0254		158
0		57.87	0.0239		148
0		59.	0.022		136
0		59.57	0.0092		57
0		60.	0.0237		147
0		60.87	0.0369		229
0		64.4	0.0208		129
0		65.8	0.0375		232
	TOTAL		100		620101

TABLE A-1 Integrated area and c-wt% of Hydrocarbons analysis in Figure A-2.1

of C_6 in Figure A-2.1 is the summation of conc. at interval time of 3.89 to 5.84, ie

$$\begin{aligned} C_6 \text{ (C-wt\%)} &= (5.796+2.9373+0.3938+0.7528+0.3016 \\ &\quad +1.2414) \\ &= 11.4229 \end{aligned}$$

$$\begin{aligned} \text{and } \bar{C}_4 \text{ (C-wt\%)} &= (7.3163+10.4572+12.856+10.0103) \\ &= 40.6398 \end{aligned}$$

(See also appendix D)

3.2 Calculation for C-wt% of C_1 - C_4 hydrocarbons

Figure A-2.2 shown a sample of GC-analysis of C_1 - C_4 hydrocarbons for the catalyst H-Si-V (400) at reaction condition: $SV = 2000 \text{ h}^{-1}$, 300°C , 20% MeOH and 1 h on stream. The C-wt% of C_1 - C_4 hydrocarbons in Figure A-2.2 are calculated as follows:

- 1) Identified the peaks as shown in Figure A-2.2
- 2) Summation the integrating area of C_1 to C_4 hydrocarbons,

i.e.,

$$\begin{aligned} \text{Total (Integrating area)}_{C_1-C_4} &= (7930+4635+144699+77897 \\ &\quad +132868+219785+36318+20156 \\ &\quad +157673+36521) \text{ unit} \\ &= 838482 \text{ unit} \end{aligned}$$

From (3.1), We get that

$$\bar{C}_4 = 40.6398 \quad \text{C-wt\%}$$

Therefore,

Integrating area 838482 units = 40.6398 C-wt%

Then, C₁ through C₄ can be calculated, for example

$$\begin{aligned} \text{CH}_4 &= \frac{40.6398 \times 7930}{838482} \quad \text{C-wt\%} \\ &= 0.3838 \quad \text{C-wt\%} \end{aligned}$$

(see also appendix D)

Integrating Integrating Name

time area

3

218	290	
230	594	
260	7930	— CH ₄
301	287	
385	4635	— C ₂ H ₆
428	144699	— C ₂ H ₄
691	77897	— C ₃ H ₈
949	132868	— C ₃ H ₆
1344	219785] C ₄ H ₁₀
1507	36318	
2180	20156] C ₄ H ₈
2397	157673	
2644	36521	
3225	193450	C ₅ —

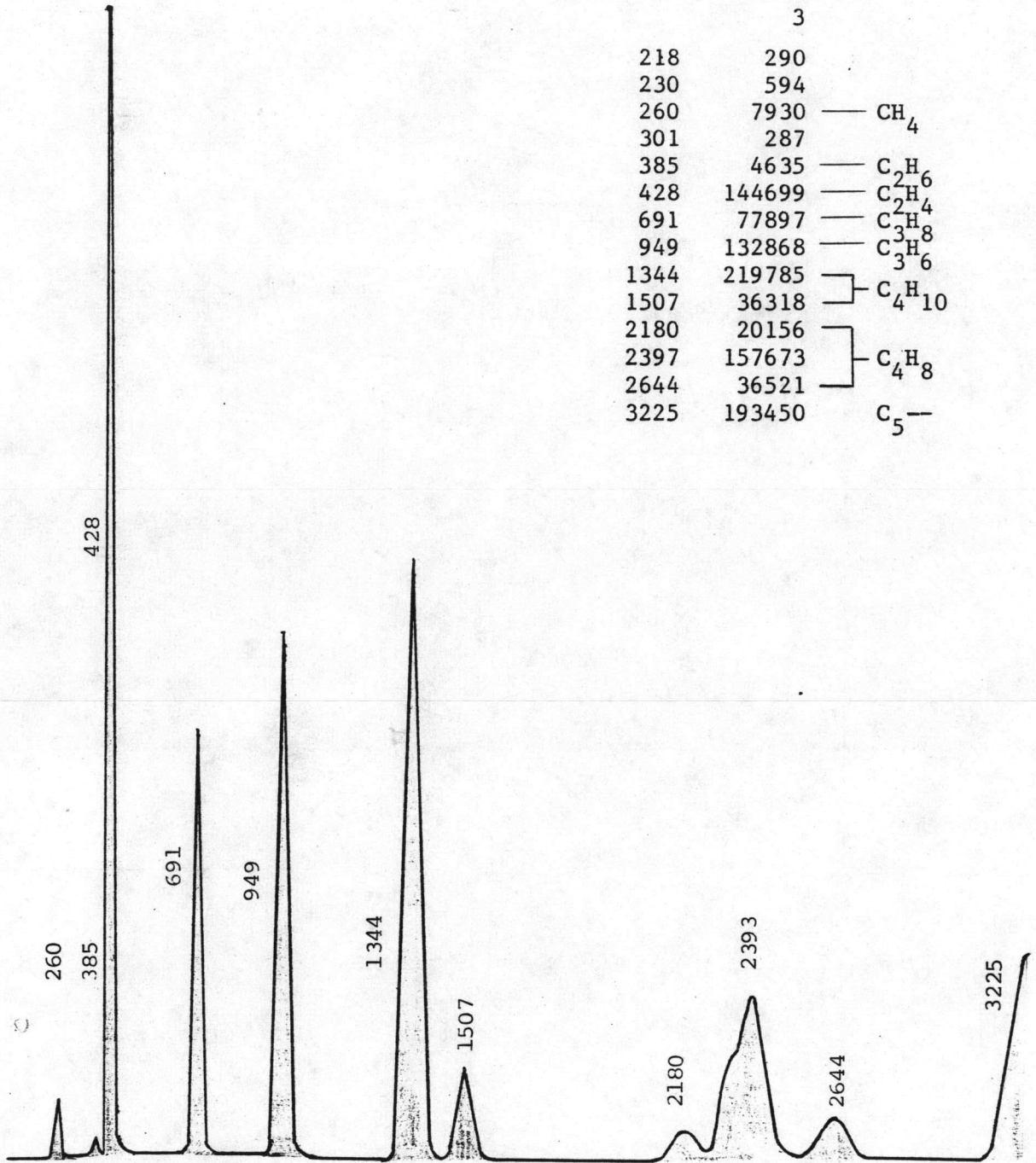


FIGURE A-2.2 GC-Analysis peak of C₁-C₄ hydrocarbons

Regular gasoline の 組成分析 (I)

Sample 0.2 μ l

8-2-4-27

測定者: 萩原

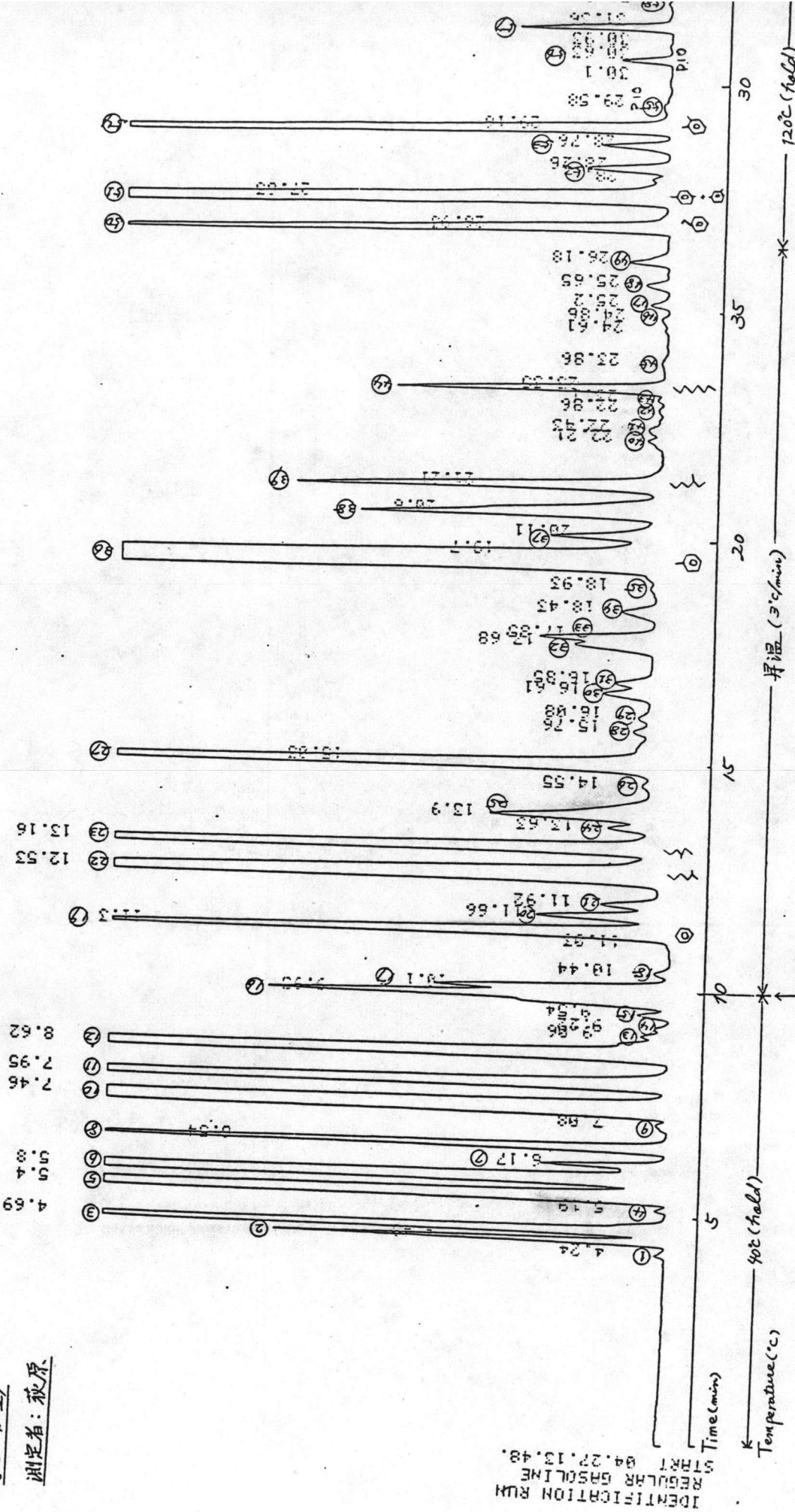
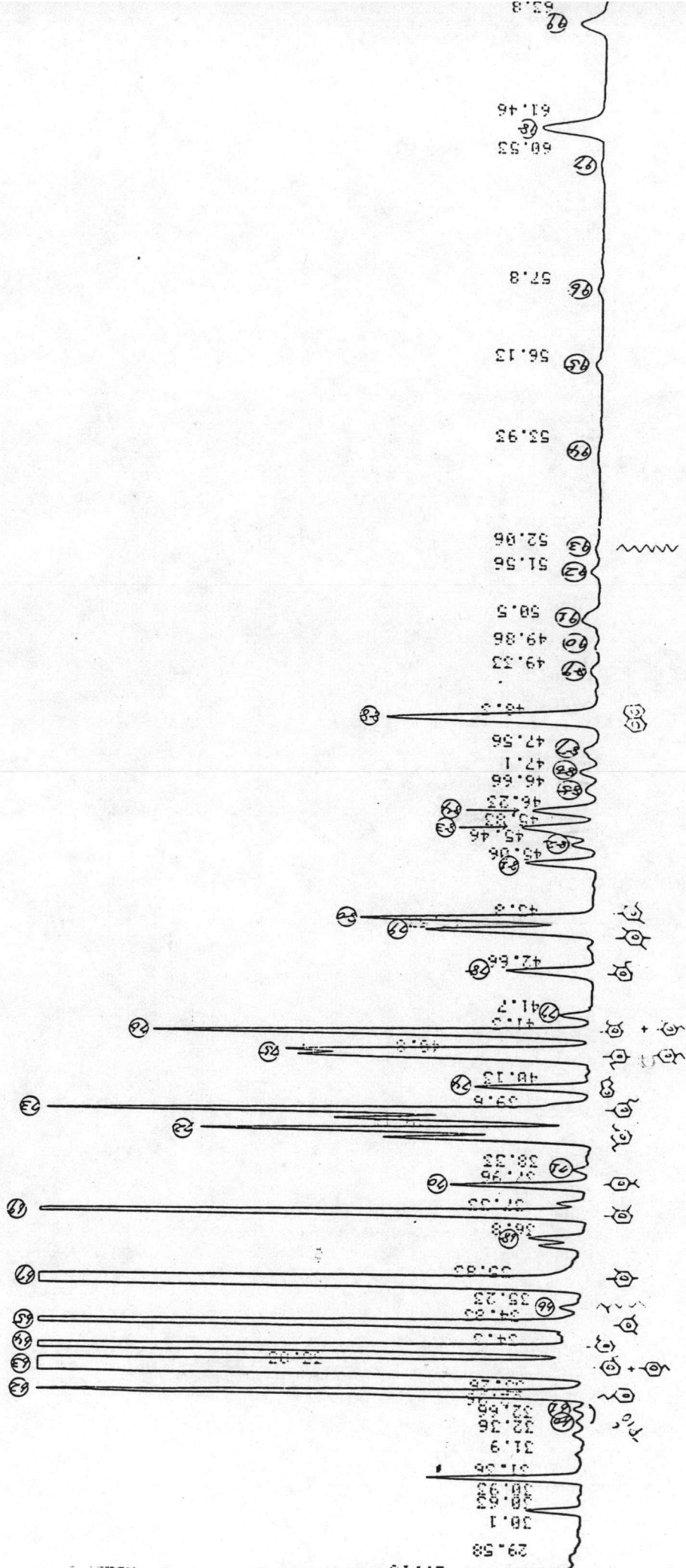


Figure A-2.4 Standard GC-Analysis peak of Hydrocarbons (gasoline fraction) calibrated by Mr. . Hagiwara



(continued)

REPT # 1321
METHOD 41

*... 样品にて確認

Run No.	Carbon No. #	NAME	TIME	CONC (wt%) MK	AREA
* 1	P3	C ₃	4.24	0.0094	81
* 2	P4	i-C ₄	4.48	0.3886	3357
* 3	P4	n-C ₄	4.69	1.9026	16438
4	O5	3M1Bu	5.19	0.0105	91
* 5	P5	i-C ₅	5.4	10.485	90588
* 6	P5	n-C ₅	5.8	9.3927	81151
7	O5	CP	6.17	0.1976	1707
8	O5	2H2Bu	6.54	0.091	7698
9	N5	CP	7.08	0.0175	151
* 10	P6	2MP	7.46	6.7026	57370
* 11	P6	3MP	7.95	3.6537	31568
* 12	P6	n-C ₆	8.62	5.5302	47780
13	O6	T ₂ H'	9.06	0.0108	93
14	O6	C ₂ H'	9.22	0.0069	60
15	O6	3MT ₂ P'	9.54	0.0474	409
* 16	N6	MCP	9.93	0.9078	7843
17	P7	2,2DMP	10.1	0.3826	3306
18	O6	2,3DM2Bu	10.44	0.0216	186
* 19	A6	Benzene	11.3	1.2506	10805
* 20	O7	2,4DMP	11.66	0.2548	2201
21	O7	2,4DMP'	11.92	0.1203	1039
* 22	P7	2MH	12.53	2.7772	23994
* 23	P7	3MH	13.16	2.4518	21183
24	O7	i-H ₃ S	13.63	0.0643	556
25	O7	i-H ₃ S	13.9	0.4457	3851
26	O7	3E2P'	14.55	0.0096	83
* 27	P7	n-C ₇	15.03	1.8557	16033
28	O7	H ₃	15.78	0.0231	199
29	N7	1C ₂ DMCP	16.08	0.0169	146
(30)	N7	MCH	16.61	0.11	950
31	P8	2,2DHH	16.85	0.0726	627
32	N7	ECP	17.68	0.1674	1446
33	P8	2,5DHH	17.85	0.222	1918
34	P8	2,4DHH	18.43	0.0844	729
35	P8	2,23THP	18.93	0.0077	66
* 36	A7	Toluene	19.7	16.9647	146572
37	P8	2,3DHH	20.11	0.2055	1775
38	P8	2MHp+4HHp	20.6	0.7219	6237
39	P8	3MHP	21.21	0.6925	5983
(40)	N8	DMCH	22.21	0.0278	240
41	P9+N8	2,2,4THH+MECP	22.43	0.0261	226
42	N8	MECP	22.86	0.0078	67
43	N8	DMCH	23.1	0.0089	77
* 44	P8	n-C ₈	23.35	0.4115	3555
45	P9	2,4,4THH	23.86	0.0126	109
46	P9	2,3,5THH	24.86	0.0119	102
47	P7	2,2DHH	25.2	0.0312	269
48	P9	2,4DHHp	25.65	0.0432	373
49	P9	2,6DHHp	26.18	0.0749	647
* 50	A8	EBz	26.93	1.0425	9007
* 51	A8	p-Xylene+Xylene	27.63	3.7032	31995
52	P9	4MO	28.26	0.1412	1220
53	P9	2MO	28.76	0.113	976
* 54	A8	o-Xylene	29.16	1.5412	13315
55	O P10	THHP	29.58	0.0077	66
			30.63	0.0665	574
			31.36	0.2189	1891

TABLE A-2. Integrated area and c-wt% of Hydrocarbons analysis in Figure A-2.4

(continued)

* 57	P9	0	n-C ₉	31.36	0.2189	1891
58	N9	0	Alkyl CH	31.9	0.0099	86
59	N9	0	Alkyl CH	32.36	0.0149	129
60	O P10	0	3,2,5THHP	32.66	0.0087	75
61	O P10	0	2,4,2THHP	32.96	0.0113	97
62	A9	0	m-PB ₂	33.26	0.8403	7260
* 63	A9	0	1M3EB ₂ +1M4EB ₂	33.83 (-ET+p-ET)	5.8244	50322
* 64	A9	0	1M2EB ₂	34.3 (o-ET)	2.0232	V 17480
65	A9	0	1,3,5TMB ₂	34.83	1.4672	V 12676
66	O P10	0	THN	35.23	0.0186	161
* 67	A9	0	1,2,4TMB ₂	35.83	5.5761	48176
68	P10+A10	0	1M3EB ₂ +PB ₂	36.8	0.1162	1004
69	A9	0	1,2,3THB ₂	37.33	1.0949	9460
70	A10	0	1M4PB ₂	37.96	0.1862	1609
71	A9	0	Indane	38.33	0.0155	134
72	A10	0	1,3DEB ₂	39.16	0.8465	7314
73	A10	0	1H3-n-P-P ₂	39.6	1.2074	V 10431
74	A10	0	2M1Indane	40.13	0.1626	1405
75	A10	0	1,2,3,4,5P ₂ +1,2,3,4,5P ₂	40.8	0.8631	7457
76	A10	0	1,2,3,4,5P ₂ +1,2,3,4,5P ₂	41.3	0.6789	5865
77	A11	0	1M4+n-BuB ₂	41.7	0.0379	327
78	A10	0	1,2,3,4,5P ₂	42.66	0.1536	1327
* 79	A10	0	1,2,3,5TMB ₂	43.53	0.3008	2599
80	A10	0	1,2,3,5TMB ₂	43.8	0.4029	V 3481
81	A11	0	Isopropyl B ₂	45.06	0.1227	1060
82	A11	0	Aroma	45.46	0.0363	314
83	A10	0	5M1Indane	45.83	0.17	V 1469
84	A10	0	4M1Indane	46.23	0.1156	998
85	A11	0	n-PB ₂	46.66	0.0248	214
86	A10	0	1,2,3,4,5TMB ₂	47.1	0.0326	281
87	A10	0	Tetralin	47.56	0.0404	349
88	A10	0	Naphthalene	48.3	0.5123	4426
89	A12	0	1,2,3,4,5,6,7,8P ₂	49.33	0.0224	194
90	A12	0	Aroma	49.86	0.0022	79
91	A12	0	Aroma	50.5	0.0637	550
92	A12	0	Aroma	51.56	0.0193	167
* 93	P12	0	n-C ₁₂	52.06	0.0078	67
94	A12<	0	unknown	53.93	0.0131	114
95	.	0	.	56.13	0.017	147
96	.	0	.	57.8	0.0164	141
97	.	0	.	60.53	0.0142	123
98	.	0	.	61.46	0.2206	1906
99	.	0	.	63.8	0.1018	879
TOTAL					99.9999	863980

CAL PM 1
 WIDTH 5
 SLOPE 60
 DRIFT 20
 MIN AR 50
 T-DEL 15
 LOCK 0
 STP TM 70
 ATTN 0
 SPEED 10
 METHOD 41
 SPL WT 100
 IS WT 1

略号の読み方

例. MCP = Methyl Cyclopentane

T₂H' = Trans-(2)Hexene1,3,5TMB₂ = 1,3,5-TriMethyl(Benzene)

P: paraffine, O: olefine, N: naphthene, A: aromatics

文献

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- 2) 中村宗和, 石油学会誌, 46.5/(1973)

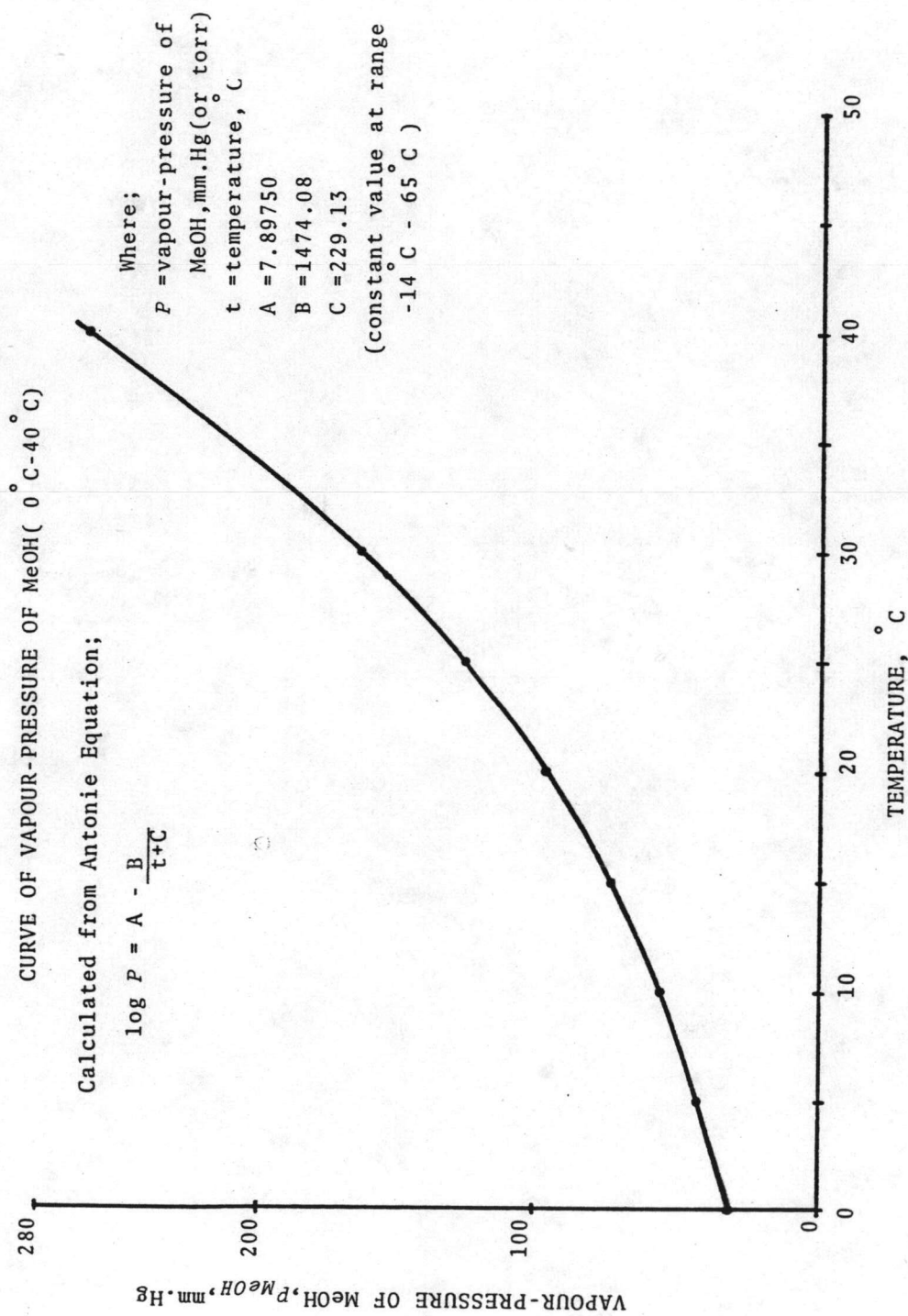
A-4 Vapour Pressure Curve of MeOH at Various Temperatures.

Figure A-3 Curve of vapour pressure of MeOH related to temperature

A-5 BET Surface Area Calculation (22)

From BET equation :

$$\frac{x}{v(1-x)} = \frac{1}{v_m C} + \frac{C-1}{v_m C} \cdot x \quad (\text{A-5.1})$$

where $x =$ ratio of partial pressure $\frac{P}{P_o}$

$P_o =$ saturated vapour pressure of N_2 (or adsorped gas)

$P =$ equilibrium vapour pressure of N_2

$v =$ amount of adsorption at the equilibrium, c.c. at the NTP/gm of sample

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

$$C = \frac{e^{E_1 - E_2/RT}}{e} \quad (\text{A-5.2})$$

where

$E_1 =$ heat of adsorption of the first layer

$E_2 =$ heat of condensation of adsorped gas

assume $C \rightarrow \infty$, then

$$\frac{x}{v(1-x)} = \frac{1}{v_m} \cdot x \quad (\text{A-5.3})$$

let

$$v_m = v_m'$$

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

$v =$ amount of adsorption measuring by GC.

$$x = \frac{P}{P_o}$$

$$\frac{P_b V}{273} = \frac{P_t V}{T}$$

where

V = const volume

P_b = pressure at 0°C

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

T = $273 + t$ k

P_b = $\frac{273}{T} P_t$

P_b = 1 atm

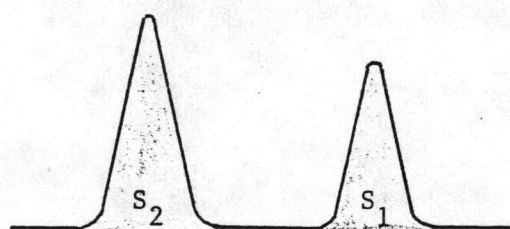
partial pressure P = $\frac{\text{Flow of } (\text{He} + \text{N}_2) - \text{flow of } (\text{He})}{\text{flow of } (\text{He} + \text{N}_2)} \cdot P_b$

= 0.3 atm

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

$$x = \frac{P}{P_o} = \frac{P}{1.1}$$

How to measuring v



1 ml/ 1 atm at room temp.

desorption
of N_2 area

N_2 calibration^(s)
area

$$v = \frac{S_2}{S_1} \times \frac{1 \text{ c.c.}}{W} \times \frac{273.15}{T} \quad \text{c.c./g of cat.}$$

W = Weight of sample

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

$$S_W = S \times v_m$$

where

$$S = \text{surface area from literature for } N_2$$

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

$$S_W = 4.373 v_m'$$

A-6 Si/V Charged ratio Calculation

$$Na_2O \cdot SiO_2 \cdot H_2O = 69 \text{ g.}$$

(29%)

$$\text{M.W. of Si} = 28.0855$$

$$\text{M.W. of O} = 15.9994$$

$$\text{M.W. } SiO_2 = 60.0843$$

$$\text{M.W. } VCl_3 = 157.30$$

$$\text{Mole of Si used} = \text{wt. } \left(\frac{\% \text{ of Si}}{100} \right) \cdot \frac{\text{M.W. Si}}{\text{M.W. } SiO_2} \cdot \frac{1 \text{ mole}}{\text{M.W. Si}} \quad (\text{A-6.1})$$

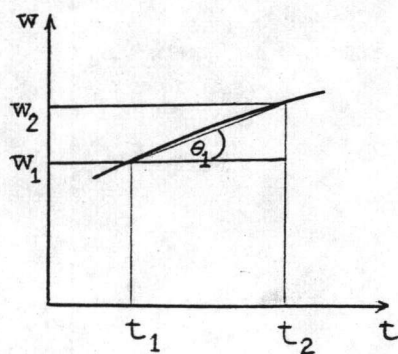
$$= 69 \times \left(\frac{29}{100} \right) \times \frac{1}{60.0843}$$

$$= 0.3330 \text{ mole}$$

$$\text{We must use } VCl_3 = \frac{\text{mole of Si}}{\text{charged ratio } (x)} \text{ M.W. } VCl_3 \quad (\text{A-6.2})$$

$$= \frac{0.3330}{x} 157.30$$

A-7 TPD Calculation

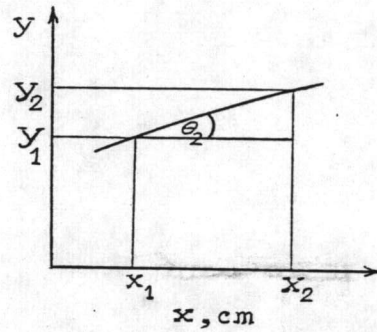


From Figure A-4.1

$$\frac{\Delta w}{\Delta t} = \frac{w_2 - w_1}{t_2 - t_1} + \tan \theta \quad (\text{A-7.1})$$

Figure A-4.1 plot of weight loss vs. time

From Figure A-4.2, the recorder condition was adjusted as follows:



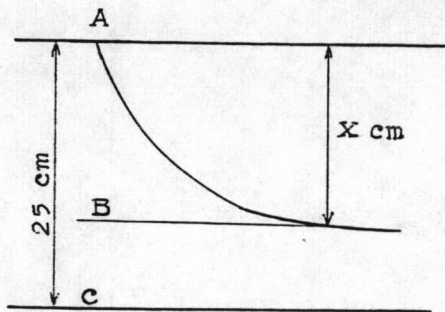
$$\begin{aligned}
 25 \text{ cm} &= a \text{ mg} \\
 y_1 \text{ cm} &= \frac{a}{25} y_1 \text{ ''} \\
 \text{and } y_2 \text{ cm} &= \frac{a}{25} y_2 \text{ ''}
 \end{aligned}$$

Figure A-4.2 Plot of full scale chart relating weight loss to speed chart which is related to time.

$$\begin{aligned}
 \text{speed chart } b \text{ cm} &= 60 \text{ sec} \\
 x_1 \text{ ''} &= \frac{60}{b} \cdot x_1 \text{ sec} \\
 x_2 \text{ ''} &= \frac{60}{b} \cdot x_2 \text{ sec}
 \end{aligned}$$

$$\frac{dw}{dt} = \frac{\frac{a}{25} (y_2 - y_1)}{\frac{60}{b} (x_2 - x_1)} = \frac{ab}{(25 \times 60)} \tan \theta_2 \quad (\text{A-7.2})$$

For TPD curve we plot $(\frac{dw}{dt}) / w_o$ vs. temperature where w_o = dry weight of catalyst and calculated as follows



we set full chart scale = a mg

$$\begin{aligned}
 \text{at } A \text{ position weight of catalyst} &= a \text{ mg} \\
 B \text{ position weight of catalyst} &= \frac{ax}{25} \text{ mg} \\
 \text{weight loss} &= \frac{ax}{25} \text{ mg} \quad (\text{A-7.3})
 \end{aligned}$$

$$\begin{aligned}
 \text{dry weight of catalyst} &= \text{weight of sample before drying} \\
 &- \text{weight loss} \quad \text{mg.} \quad (\text{A-7.4})
 \end{aligned}$$

A-8 Calculation for percentage of MeOH conversion

Assume that the temperature of sampling syringe was 95°C .

volume of syringe = 2 ml.

Hence,

$$\text{volume of MeOH in 2 ml of sample} = 2 \times 10^{-3} (1) \times Y \quad (\text{A-8.1})$$

where $Y = \% \text{ conc. of MeOH in feed stream line.}$

for example, $Y = 20 \% \text{ MeOH}$

$$\begin{aligned} \text{then, volume of MeOH in syringe} &= 2 \times 10^{-3} \times 0.2 \quad 1 \\ &= 0.0004 \quad 1 \end{aligned}$$

The amount of carbon from a 2 ml syringe of feed MeOH calculated as follows:

assume MeOH vapour obey ideal gas law, i.e.,

$$\text{MeOH (at STP) } 22.4 \quad 1 \quad \text{compose with} \quad C = 12 \text{ g}$$

$$\text{MeOH (at STP) } V_1 \quad 1 \quad \text{compose with} \quad C = \frac{12}{22.4} \times V_1 \text{ g} \quad (\text{A-8.2})$$

From the equation of state,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad (\text{A-8.3})$$

Where

P_1, P_2 = total pressure of a system at condition 1 and 2 respectively

V_1, V_2 = total volume of a system at condition 1 and 2 respectively

T_1, T_2 = temperature of a system at condition 1 and 2 respectively

which 1 represents STP condition, 2 represents the consider condition. For this system, we assumed that $P_1 = P_2$ (atmospheric pressure), then

$$V_1 = \frac{V_2 \times T_1}{T_2} \quad (\text{A-8.4})$$

Substituted (A-6.4) into (A-6.2) and absolute temperature (T_1) = 273.2 K, gives

$$C_{\text{MeOH},i} = \frac{12}{22.4} \times \frac{V_2 (273.2)}{(273.2 + t)} \quad \text{g} \quad (\text{A-8.5})$$

where, $C_{\text{MeOH},i}$ = quantity of C for input MeOH
 t = temperature of syringe

The quantity of output MeOH can be calculated from GC analysis which

$$^a \text{calibration factor for MeOH} = 8.085 \times 10^{-4} \quad (\text{unit area/l})$$

Hence, the amount of C for output MeOH is

$$C_{\text{MeOH},o} = 8.085 \times 10^{-4} \times \text{ITG}_{\text{MeOH}} \times 10^{-6} \times \frac{273.2}{(273.2+95)} \times \frac{12}{22.4} \quad \text{g}$$

where,

$$C_{\text{MeOH},o} = \text{quantity of C for output MeOH} \quad (\text{A-8.6})$$

Then,

$$\begin{aligned} \% \text{ MeOH conversion} &= (2 \times 10^{-3} \times Y) - 8.085 \times 10^{-10} \times \text{ITG}_{\text{MeOH}} \times \frac{100}{(2 \times 10^{-3} \times Y)} \\ &= 100 - \frac{8.085 \times 10^{-5} \times \text{ITG}_{\text{MeOH}}}{2Y} \quad (\text{A-8.7}) \end{aligned}$$

A-9 Calculation for C-wt% of dimethyl ether (DME)

DME can be calculated from GC analysis peak in which the calibration factor for DME is

$$^a \text{calibration factor for DME} = 9.85 \times 10^{-4} \text{ (unit area/l)}$$

a : obtained from calibration data of Mr. Hagiwara, Catalyst Engineering Laboratory, Kyoto University.

Hence, the quantity of C from output DME is

$$C_{\text{DME}} = \frac{24}{22.4} \times (9.85 \times 10^{-4} \times \text{ITG}_{\text{DME}} \times 10^{-6}) \times \frac{273.2}{(273.2+95)} \text{ g} \quad (\text{A-9.1})$$

$$\% \text{ DME} = \frac{C_{\text{DME}}}{C_{\text{MeOH},i} - C_{\text{MeOH},o}} \times 100 \quad (\text{A-9.2})$$

By substituted (A-6.5), (A-6.6) and (A-7.1) into (A-7.2), gives

$$\% \text{ DME} = \frac{(1.97 \times 10^{-7} \times \text{ITG}_{\text{DME}})}{(2Y - 8.085 \times 10^{-7} \times \text{ITG}_{\text{MeOH}})} \quad (\text{A-9.3})$$

A-10 Calculation for percentage of conversion to hydrocarbons.

Basis on 100 % of converted MeOH, then

$$\% \text{ conversion to H.C.} = 100 - \% \text{ DME} \quad (\text{A-10.1})$$

Where H.C = total hydrocarbons.

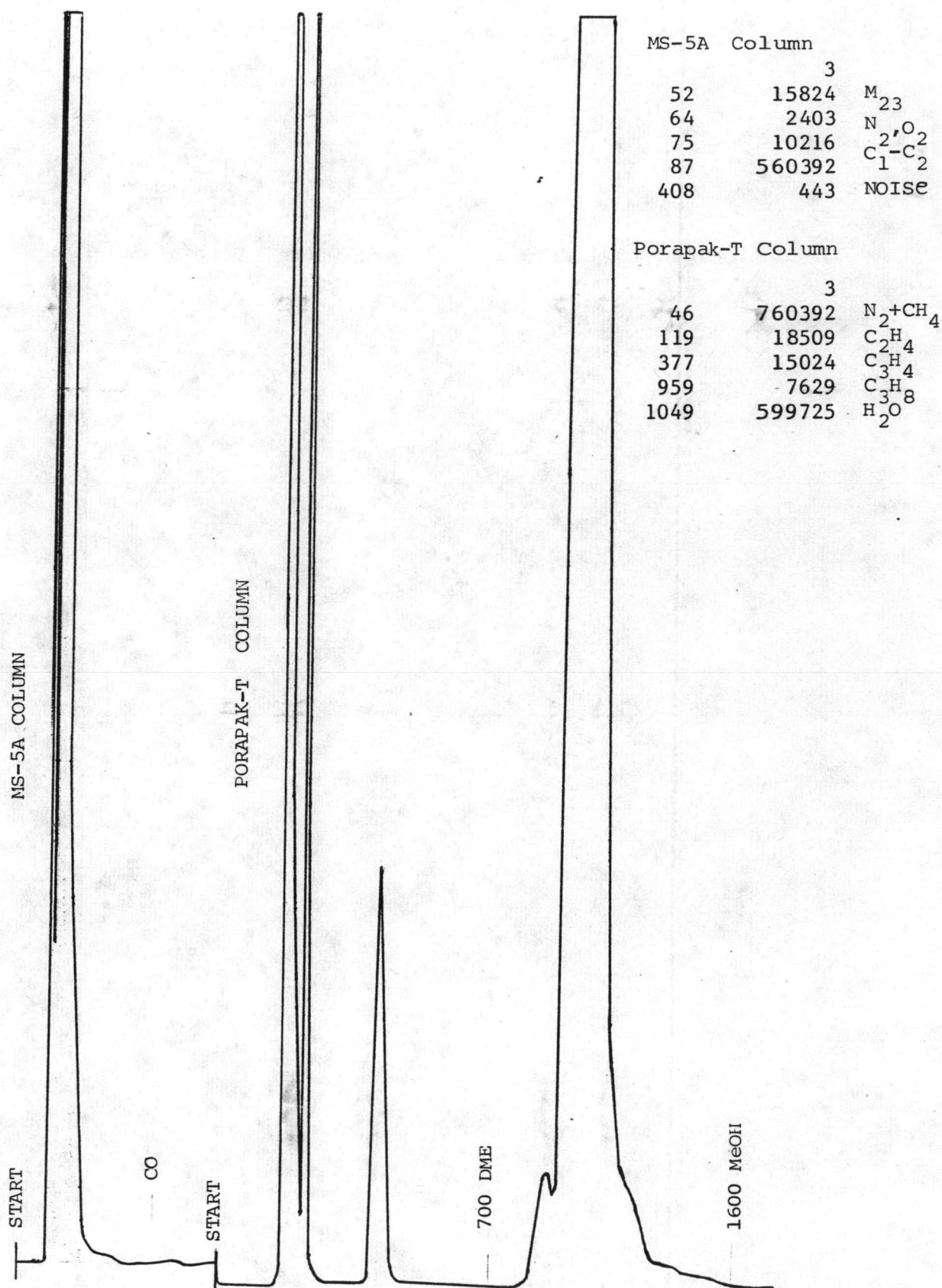


FIGURE A-2.3 GC-Analysis peak of CO, DME, and MeOH

Appendix B

B-1 Prepared sample for XRD measurement.

1. Clean glass slide with petroleum ether
2. Put the silicon grease or white grease on the position of cell, Figure B-1
3. Weigh sample about 20-50 mg and put it over the grease
4. Using stainless spatular for well mixing of grease and sample
5. Cleaning the exceed portions on the slide with paper which adsorbes petroleum ether

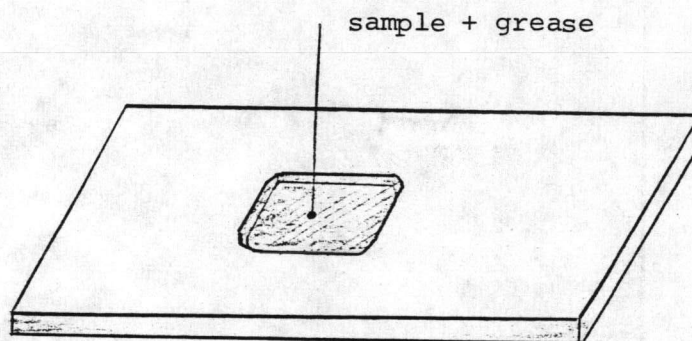


Figure B-1 Prepared slide of sample for XRD measurement

Note: The reason for using silicon grease or vassaline (white grease) as a sample support because:

1. They do not react with sample
2. No evaporate at (XRD) analysis condition
3. They are amorphous, therefore, they are not give XRD peak to interfere the sample peak

B-2 Method of Sample Solution Preparation for Atomic Absorption

B-2.1 Preparation of Sample (Vanadosilicate catalysts)

solution :

1. Weigh 50 mg of sample, 1.2 g of Na_2CO_3 and 0.3 g of H_3BO_3
2. Put all of them (sample, Na_2CO_3 , H_3BO_3) into Pt-crucible and mix together
3. Heat up the mixture in electrical furnace by increasing temperature as follows:

room temperature $\xrightarrow{2 \text{ h}}$ 950°C and hold constant at this point for 30 min.

4. Cool the sample crucible to room temperature and dissolve the fused mixture with 20 ml of 6 N HCl in Pt crucible
5. When fused mixture dissolves completely transfer the solution into 100 ml volumetric flask.
6. Wash the Pt with distilled water and pours into the same volumetric flask and repeat 2-3 times.
7. Make the volume of solution to 100 ml and swirl well for good mixing.
8. Keep the solution in teflon bottle as sample stock solution.

B-2.2 Prepared Standard Solution of Vanadium

1. Weigh 100 mg of VCl_3 and put into 100 ml volumetric flask
2. add 20 ml of 1 N HCl into this flask and make the volume of solution to 100 ml using distilled water.

3. Prepared aliquote of 0.5, 1, 5, 10 and 20 ppm of vanadium standard solution and stock solutions in teflon bottle.

B-2.3 Preparation of Standard Solution of Silicon

1. Take 10 ml of 1000 ppm silicon standard from stock solution and put into 100 ml volumetric flask
2. Add 20 ml of 0.4 N Na_2CO_3 into volumetric flask and make solution to 100 ml (this is 100 ppm Si standard solution)
3. Take 10 ml of 100 ppm Si solution and put into another 100 ml volumetric flask
4. Repeat step 2 (this is 10 ppm Si standard solution)
5. Prepare 200 and 50 ppm Si standard solution by the same method as above.

APPENDIX C

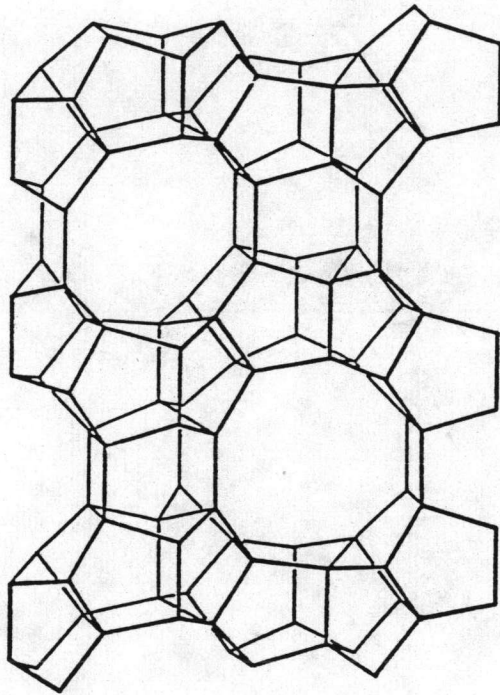


FIGURE C-1 SKELETAL DIAGRAM OF THE (100)-FACE OF THE ZSM-5
UNIT CELL TO SHOW THE NEARLY CIRCULAR APERTURES OF
THE SINUSOIDAL CHANNELS (20)

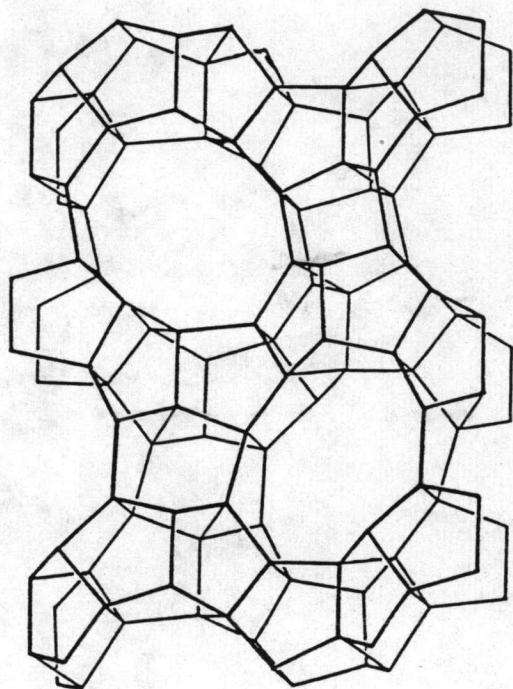


FIGURE C-2 SKELETAL DIAGRAM OF THE (010) - FACE OF THE ZSM-5

UNIT CELL TO SHOW THE ELLIPTICAL APERTURES OF THE

STRAIGHT CHANNELS. (20)

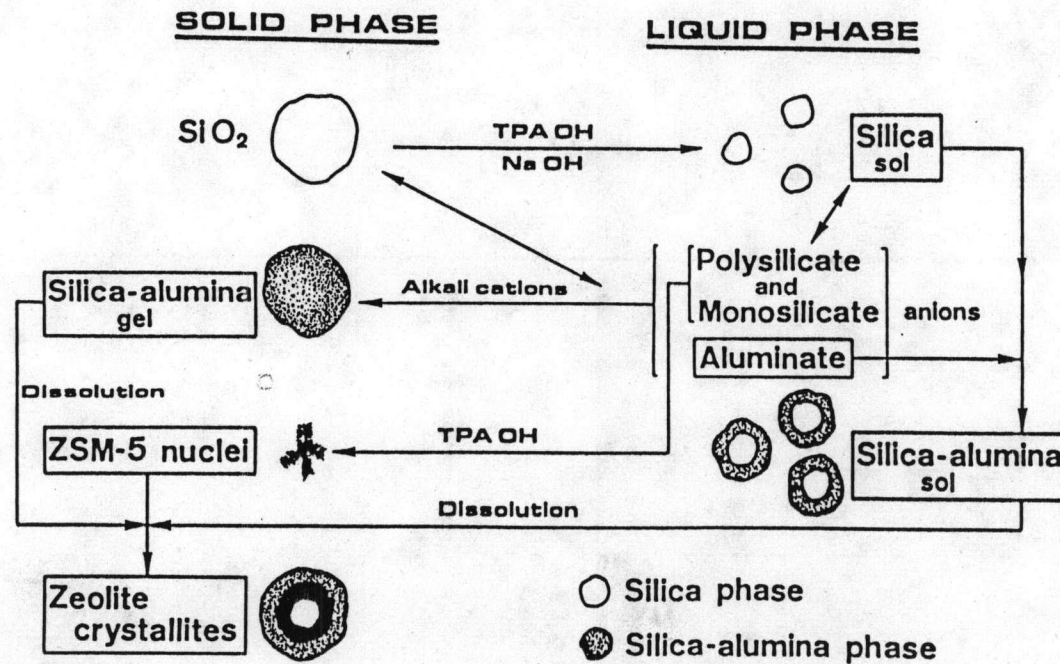


FIGURE C-3 SCHEMATIC REPRESENTATION OF TYPE A SYNTHESIS. THE BLACK RING CORRESPONDS TO AN AL-RICHER ZONE IN THE CRYSTALLITES. (19)

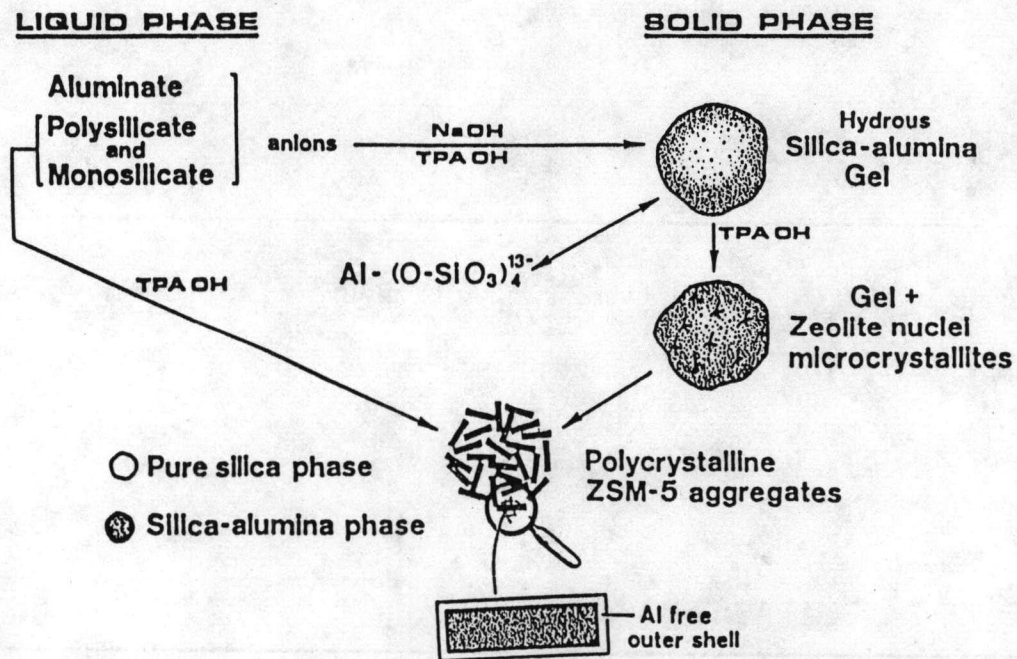


FIGURE C-4 SCHEMATIC REPRESENTATION OF TYPE B SYNTHESIS (19)

APPENDIX D

D-1 Data for study of effect of Si/V charged ratio at 300 °C

Reaction condition : SV = 2000 h⁻¹, 300 °C, 20 % MeOH, 1 h on stream

Si/V (charged ratio)	∞	3200 ^b	1000	400	200	90	40
H.C products (C-Wt%) ^a							
C ₁	0.27	0.30	0.28	0.38	0.74	0.96	80.38
C _{2,O}	8.80	7.90	8.94	7.00	11.28	26.75	11.01
C _{2,P}	0.10	0.10	Tr.	0.22	0.10	0.09	Tr.
C _{3,O}	7.39	7.30	6.80	6.43	8.22	27.10	8.33
C _{3,P}	2.78	3.30	3.25	3.77	2.62	1.45	-
C _{4,O}	10.80	9.50	11.35	10.37	13.45	11.83	-
C _{4,P}	10.62	10.00	10.44	12.40	8.69	4.32	-
C _{5(O,P)}	14.94	13.10	15.21	15.16	14.63	5.77	0.28
C _{6(O,P)}	12.27		11.59	11.42	10.85	5.48	-
C _{7(O,P)}	5.87	26.60	6.25	4.64	5.15	3.35	-
C _{8(O,P)}	4.06		4.87	4.10	4.04	2.23	-
C _{9⁺(O,P)}	2.52		1.26	0.93	2.37	1.33	-

(continue D-1)

A ₆ (Benz.)	0.49	0.60	0.57	0.60	0.56	0.10	-
A ₇ (Tolue.)	1.14	2.10	1.49	1.84	1.08	0.42	-
A ₈	7.18	8.20	7.72	8.55	6.84	3.42	-
A ₉	7.24	6.20	6.75	8.30	6.24	3.21	-
A ₁₀ ⁺	3.56	4.80	3.23	3.82	3.11	2.23	-
MeOH (% conv.)	99.22	100.00	100.00	100.00	100.00	83.97	33.64
DME (C-wt%)	0.12	-	-	-	-	25.69	31.32
CO (C-wt%)	-	-	-	-	-	-	-

a : A = Aromatic, e.g. A₆ = Benzene, A₇ = Toluene, O = olefins, p = paraffins.

b : data obtained from (9)

D-2 Data for study of effect of Si/V changed ratio at 360 °C

Reaction condition: SV = 2000 h⁻¹, 360 °C, 20 % MeOH, 1 h on stream

Si/V (charged ratio)	∞	1600 ^a	400	200	90	40
H.C products (C-wt%)						
C ₁	0.60	0.41	0.65	0.63	2.40	67.65
C _{2,O}	7.02	7.01	7.87	7.78	8.68	11.63
C _{2,P}	0.10	0.10	0.11	0.07	0.13	2.28
C _{3,O}	19.30	16.50	16.99	19.90	21.07	5.90
C _{3,P}	3.39	4.05	3.93	2.91	2.16	0.63
C _{4,O}	19.04	17.59	18.08	21.06	21.45	1.06
C _{4,P}	8.73	10.13	9.43	8.18	5.33	Tr.
C _{5(O,P)}	12.17	12.61	11.81	6.62	12.16	10.79
C _{6(,P)}	8.19	7.79	7.98	13.37	6.66	-
C _{7(O,P)}	2.13	2.05	2.17	2.09	1.93	-
C _{8(O,P)}	1.74	2.12	1.52	1.64	1.85	-
C _{9⁺(O,P)}	0.48	0.53	0.41	0.53	0.57	-
A ₆	0.92	0.93	0.93	0.91	0.88	0.06
A ₇	2.60	2.78	2.90	2.20	1.85	-
A ₈	7.26	8.47	7.90	6.95	7.51	-

(continue D-2)

A ₉	5.08	5.31	5.79	4.15	4.35	-
A ₁₀ ⁺	1.26	1.46	1.56	1.10	1.03	-
MeOH (% conv.)	100.00	100.00	100.00	100.00	100.00	44.81
DME (C-wt%)	-	-	-	-	-	14.26
CO (C-wt%)	-	-	-	-	-	-

a : reaction temperature = 370 °C

D-3 Data for study effect of space velocity

Reaction condition: 300°C, 20 % MeOH, 1 h on stream.

SV, h ⁻¹	500		1000			4000			8000		
	∞	400	∞	400	200	∞	400	200	∞	400	200
Si/V (charged ratio)	∞	400	∞	400	200	∞	400	200	∞	400	200
H.C products (C-wt%)											
C ₁	0.88	0.36	0.27	0.31	0.54	0.23	0.26	0.44	0.28	0.24	0.47
C _{2,O}	5.51	5.16	5.61	4.92	7.75	10.29	8.69	12.31	13.22	11.75	16.11
C _{2,P}	0.15	0.22	0.12	0.18	0.15	0.06	0.09	0.08	0.05	0.08	0.06
C _{3,O}	5.24	4.43	5.18	4.06	6.46	11.01	7.46	11.35	18.15	11.83	20.48
C _{3,P}	3.92	5.45	2.98	4.50	4.06	1.91	2.97	2.22	1.76	2.53	1.78
C _{4,O}	9.85	6.40	8.06	7.15	10.11	13.64	11.22	13.17	13.67	12.26	13.04
C _{4,P}	11.41	14.90	10.06	13.82	11.98	8.74	11.24	8.23	8.35	10.33	7.33
C _{5(O,P)}	13.49	13.97	14.79	14.51	14.65	14.95	15.52	13.91	11.07	13.16	10.11
C _{6(O,P)}	10.28	11.22	11.92	11.84	10.89	12.50	11.91	11.70	10.85	11.41	9.89
C _{7(O,P)}	4.69	4.48	5.45	5.42	4.71	5.78	5.07	5.36	5.09	4.75	4.45
C _{8(O,P)}	2.56	2.10	3.21	2.79	2.75	4.36	3.68	3.87	3.54	3.58	3.04
C _{9⁺(O,P)}	1.28	0.89	1.61	1.56	1.63	2.97	2.30	2.81	2.79	2.46	2.52
A ₆	0.55	0.48	0.55	0.46	0.53	0.46	0.54	0.42	0.23	0.35	0.25
A ₇	2.23	2.30	1.76	2.00	1.59	0.77	1.16	0.84	0.59	0.88	0.60
A ₈	10.40	10.59	8.80	9.78	8.90	5.79	7.50	6.41	5.03	6.38	5.01

(continue D-3)

A ₉	11.96	11.64	9.33	11.10	9.11	4.64	7.20	4.77	3.61	5.49	3.39
A ₁₀ ⁺	5.61	5.42	4.31	5.60	4.19	1.90	3.18	2.12	1.74	2.50	1.50
MeOH (% conv.)	100.00	100.00	100.00	100.00	100.00	98.46	99.67	97.62	90.30	94.71	90.17
DME (C-wt%)	-	-	-	-	-	0.14	-	0.59	7.12	3.40	8.14
CO	-	-	-	-	-	-	-	-	-	-	-

D-4 Data for study of effect of reaction temperature

Reaction condition: $SV = 2000 \text{ h}^{-1}$, 20 % MeOH, 1 h on stream

Temperature, ° C	260	280	330		390	420
Si/V (charged ratio)	1600	1600	1600	90	90	90
H,C products (C-wt%)						
C ₁	1.48	0.30	0.37	1.48	4.18	8.71
C _{2,O}	50.22	13.64	6.46	10.31	10.69	12.13
C _{2,P}	Tr.	0.13	0.10	0.11	0.14	0.39
C _{3,O}	41,53	6.25	11.16	15.08	27.92	26.93
C _{3,P}	1.81	3.46	3.58	1.99	1.90	1.28
C _{4,O}	0.71	8.06	15.25	17.58	20.58	14.33
C _{4,P}	3.84	9.66	10.83	6.83	2.02	1.12
C _{5(O,P)}	0.09	13.32	15.15	13.96	8.47	4.80
C _{6(O,P)}		11.98	10.24	9.08	4.33	2.66
C _{7(O,P)}	0.14	7.16	3.57	3.32	0.87	0.73
C _{8(O,P)}		4.31	2.93	3.37	0.82	0.41
C _{9⁺(O,P)}		2.84	1.30	1.50	0.14	0.05
A ₆	-	0.33	0.78	0.78	0.83	0.97
A ₇	-	0.88	1.93	1.28	2.71	4.16

(continue D-4)

A ₈	0.05	7.42	7.83	6.89	9.19	13.33
A ₉	0.09	6.26	6.29	4.84	4.37	6.87
A ₁₀ ⁺	0.06	4.00	2.25	1.63	0.85	1.59
MeOH (% conv.)	88.69	98.00	100.00	99.50	100.00	100.00
DME (C-wt%)	74.19	0.84	-	-	-	-
CO (C-wt%)	-	-	-	-	-	-

D-5 Data for study of effect of MeOH concentration

Reaction condition: Si/V = 1600, SV = 2000 h⁻¹, 300 °C, 1 h on stream.

MeOH conc., %	5	10	40	100
H.C products (C-wt%)				
C ₁	0.25	0.27	0.31	0.38
C ₂ ,O	8.21	8.71	13.81	13.61
C ₂ ,P	0.12	0.17	0.13	0.18
C ₃ ,O	9.19	7.10	6.70	9.20
C ₃ ,P	3.33	3.83	3.49	5.83
C ₄ ,O	13.24	10.38	8.60	9.67
C ₄ ,P	11.17	11.93	9.29	15.16
C ₅ (O,P)	14.62	14.81	13.04	14.78
C ₆ (O,P)	10.45	11.32	11.92	10.90
C ₇ (O,P)	4.23	5.01	7.05	4.41
C ₈ (O,P)	2.97	3.05	4.21	2.28
C ₉ ⁺ (O,P)	1.41	1.66	2.81	0.79
A ₆	0.66	0.56	0.31	0.40
A ₇	1.85	1.64	0.84	0.96
A ₈	8.75	8.76	7.22	4.70
A ₉	7.02	7.56	6.10	4.15
A ₁₀ ⁺	2.53	3.25	4.18	2.59
MeOH (% conv.)	100.00	100.00	98.20	96.94
DME (C-wt%)	-	-	0.68	9.09
CO (C-wt%)	-	-	-	-

VITA

Mr. Dhongchai Medhanavyn was born on June 20, 1956, in Nakornpratom, Thailand. He graduated with a Bachelor Degree of Science in Chemistry from Ramkhamhaeng University in 1978 and continued his work as a government official at the Ministry of Commerce, Div. of Fuel Control. In 1980, he obtained permission from his office to study for a Master Degree in Chemical Engineering at Chulalongkorn University and in 1982, he received a scholarship from the Ministry of Education of Japan (MONBUSHO) as a graduate research students to do part of his dissertation in the Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University for 18 months. He was granted the Master Degree in 1984 from Chulalongkorn University.

