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APPENDIX A

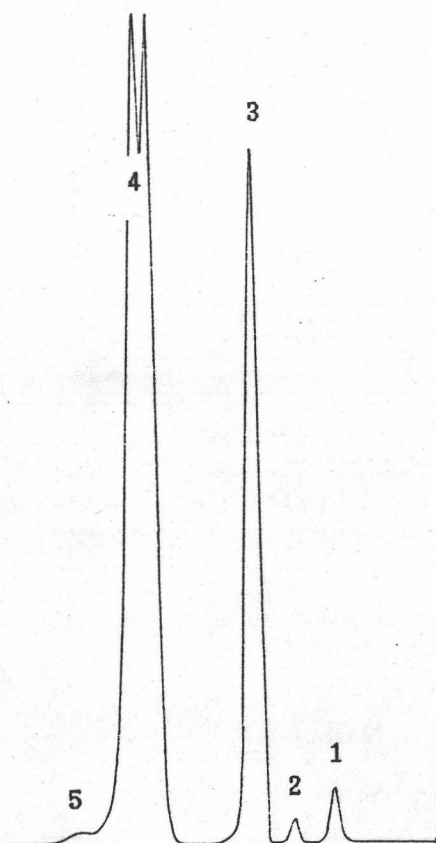## Analytical Method of Gas Chromatograph

i) Analysis of Reactants and Product gas mixture

A Shimudu gas chromatograph model 8 AIT with a thermal conductivity detector (TCD) was used for analyzing the sampling mixture of reactant feed and product gas. The sampling was taked two times for each analysis and seperately injected into MS 5A and porapak Q columns respectively. Each column identified the different components: hydrogen, oxygen, nitrogen, methane and carbon monoxide were analyzed by using column of MS-5A and those of carbon dioxide, water and the others hydrocarbon components such as ethane, ethylene, propane, propylene and methanol were analyzed by using column of Porapak Q. A recorder was used to received signals from detector of Gas Chromatograph and ploted on contineous feeding paper. Finally, the mole fraction of each component in the gas mixture was carried out by the calculation. The operating conditions were detector and column temperature=120°C and 70°C, respectively, detector current=80 mA, Ar carrier flow rate of MS-5A and Porapak Q column = 15 ml/min and 45 ml/min, respectively. The attenuations of recorder for MS-5A and Porapak Q column were 25 mV/(25 cm) and 10 mV/(25 cm), respectively.

ii) Sample peak

column: MS 5A   Porapak Q

1. Hydrogen   1. Carbon dioxide

2. Oxygen   2. Ethylene

3. Nytrogen   3. Ethane
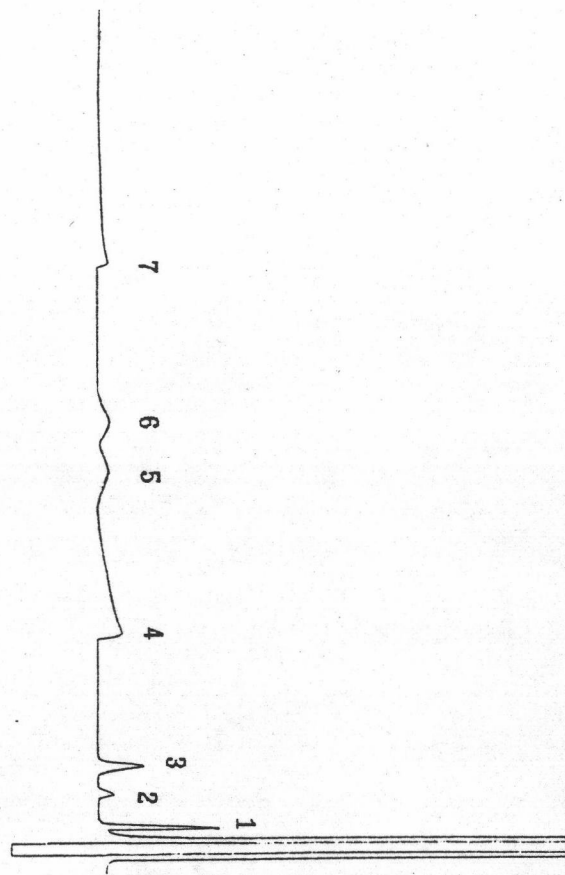
4. Methane   4. Water

5. Carbon monoxide   5. Propylene

                       6. Propane

                       7. Methanol

iii) Sample of Calculation: Mole Fraction of Product Gas

Experimental conditions

Pressure	atmospheric pressure
Temperature	600 $^\circ$C
WHSV	2 g cat./ml s^{-1}
$CH_4:O_2:N_2$	10:1:11
Catalyst	Li/ZnO (Oxidizing form)

1. Peak height (Peak area for water only)

Column	Injection volume(ml)	Component	Height(mm)
MS 5A	0.3	H_2	20
		O_2	6
		N_2	194
		CH_4	233
		CO	0
Porapak Q	2.5	CO_2	48.5
		C_2H_4	1.5
		C_2H_6	7
		C_3H_6	0
		C_3H_8	0
		H_2O (Area)	82.5 mm^2

2. Convert peak height to volume using calibration curve

MS 5A Column (0.3 ml)

Component	H_2	O_2	N_2	CH_4	CO
Volume(ml)	1.75E-3	3.05E-3	1.78E-1	1.21E-1	0

Total analytical volume = 0.3034 ml

Porapak Q Column (2.5 ml)

Component	CO_2	C_2H_4	C_2H_6	C_3H_6	C_3H_8	H_2O
Volume(ml)	3.79E-2	8.94E-4	7.81E-3	0	0	13.2E-5

Total analytical volume = 0.0756 ml

3. Volume balance for two columns analysis

Basis : 2.5 ml gas mixture in Porapak Q column

    convert 0.3 ml in MS 5A to 2.5 ml

MS 5A Column (2.5 ml)

Component	H_2	O_2	N_2	CH_4	CO	
Volume(ml)	0.0146	0.0254	1.4844	1.0044	0	--->Total=2.5289

Total analytical volume in Porapak Q column   =0.0756

2.4533

adjust 2.5289 ml to 2.4533 ml.

Therefore, in 2.5 ml gas mixture consist of the follows:

Component	H_2	O_2	N_2	CH_4	CO_2	C_2H_4	C_2H_6	H_2O
Volume(ml)	0.0141	0.0247	1.4401	0.9744	3.79E-2	8.94E-4	7.81E-3	13.2E-5

4. Convert volume to mole using ideal gas law

Comp.	H_2	O_2	N_2	CH_4	CO_2	C_2H_4	C_2H_6	H_2O
Mole	5.67E-7	9.90E-7	5.77E-5	3.91E-5	1.52E-6	3.58E-8	3.13E-7	7.36E-7

5. Weight each component into mole fraction or % by mole

Comp.	H_2	O_2	N_2	CH_4	CO_2	C_2H_4	C_2H_6	H_2O
Mole	0.56%	0.98%	57.18%	38.69%	1.51%	0.04%	0.31%	0.73%

APPENDIX B

Example of Calculation

To calculate the term of performance of catalytic reaction such as conversion and selectivty, the mass balance of each compound which involved the reaction have been done in order to find out the rate of formation of products or consumption of reactants (flow reactor; mole/time). These component balances calculated by using the mole fraction of each compound in reactant feed and product gas from gas chromatograph (see APPENDIX A) and volumetric flow rate at entrance and exit of reactor. In experiment, the entrance volumetric flow rate was succeeded by using electrical mass flow meter, especially, the pressure of reaction was higher than atmospheric pressure up to 30 atg. The exit volumetric flow rate have been measured by using soap-film meter directly at atmospheric pressure of reaction. And at higher pressure than atmospheric pressure, the exit gas of reactor was reduced by needle valve to atmospheric pressure and the exit volumetric flow rate was calculated from the mass balance crossing valve with no temperature change; $P_1 v_1 = P_2 v_2$ where P = pressure, v = volumetric flow rate, 1 = at exit of reactor before reducing, and 2 = at atmospheric pressure, 1 atm.

The following example of calculation are experimentals

at atmospheric pressure (0 atg) and 10 atg which both rections used reactant feed number 2. The mole fraction or mole percentage of these reactants and products gas mixture are the follows:

Component		(% by mole)	
	Reactant#2	(0 atg)	(10 atg)
H_2	---	0.56	0.23
O_2	4.44	0.98	0.31
N_2	58.50	57.18	58.59
CH_4	37.06	38.69	38.62
CO	---	---	---
CO_2	---	1.51	1.51
C_2H_4	---	0.04	0.11
C_2H_6	---	0.31	0.23
C_3H_6	---	---	---
C_3H_8	---	---	---
H_2O	---	0.73	0.40

The flow rate of these experiments are the follows:

	1.Volumetric flow rate, ml/s		2.Pressure balance, ml/s	3.Convert to $0^{\circ}C$, ml/s		4. Mole flow rate, mole/s	
	in	out	out	in	out	in	out
0 atg	1.365	1.011	0.092	1.214	0.082	5.3E-5	3.6E-6
10 atg	1.309	1.015	1.015	1.164	0.902	5.1E-5	4.0E-5

1.Volumetric flow rate (ml/s) : The measurement of mass

flow meter at reactor entrance (in) and soap-film meter at reactor exit (out).

2. **Pressure balance** : The real volumatic flow rate at exit of reactor which calculated from the mass balance crossing valve with no temperature change; $P_1 v_1 = P_2 v_2$

where P = pressure, v = volumetric flow rate, 1=at exit of reactor before reducing, and 2 = at atmospheric pressure, 1 atm.

3. **Convert to 0°C (ml/s)** : The conversion of volumetric flow rate in 1.(in) and 2.(out) at room temperature to standard temperature, 0°C, using ideal gas relation; $v_1/T_1 = v_2/T_2$

where v_1 = volumetric flow rate at room temperature,

   v_2 = volumetric flow rate at standard temperature,

   T_1 = room temperature;K , T_2 = 273 K

4. **Mole flow rate (mole/s)** :The conversion of volumetric flow rate to mole rate using equation of state of ideal gas; $n = P v / R T$ where P=atmospheric pressure, v=volumetric flow rate, R=gas constant and T=273 K.

Material balance

The flow-reactor was operated at steady state therefore the material balance of each component used the mole rate at entrance and exit of each component. These can calculate form mole fraction of gas mixture and total mole rate at entrance and exit of reactor as the follows:

Experiment at 0 atg

Total mole flow rate, mole/s	Entrance	Exit
	5.1E-5	4.0E-5

	[A]	[B]	[C]	[D]	
		[A]*5.1E-5		[C]*4.0E-5	[D]-[B]
Component	Reactant#2	Mole in	Exp.#14	Mole out	
	(% mole)	(mole/s)	(% mole)	(mole/s)	(mole/s)
H_2	---	---	0.56	2.2E-7	2.2E-7
O_2	4.44	2.3E-6	0.98	3.9E-7	-1.9E-6
N_2	58.50	3.0E-5	57.18	2.3E-5	-7.2E-6
CH_4	37.06	1.9E-5	38.69	1.5E-5	-3.6E-6
CO	---	---	---	---	---
CO_2	---	---	1.51	6.0E-7	6.0E-7
C_2H_4	---	---	0.04	1.4E-8	1.4E-8
C_2H_6	---	---	0.31	1.2E-7	1.2E-7
C_3H_6	---	---	---	---	---
C_3H_8	---	---	---	---	---
H_2O	---	---	0.73	2.9E-7	2.9E-7

B.1 Conversion

Conversion = Mole rate of conversion / Mole rate of feed

Methane conversion = (3.6E-6/1.9E-5)*100 = 4.34 %

Oxygen conversion = (1.9E-6/2.3E-6)*100 = 82.88 %

B.2 Carbon Compound Selectivity

Carbon compound i selectivity

= Gram atoms of carbon compound i in products/

Total gram atoms of carbon in products

Carbon compound selectivity of CO_2

= 6.0E-7/(6.0E-7 + 2*1.4E-8 + 2*1.2E-7)

= 0.7258 = 72.58 %

Carbon compound selectivity of C_2H_4

= 2*1.4E-8/(6.0E-7 + 2*1.4E-8 + 2*1.2E-7)

= 0.0342 = 3.42 %

Carbon compound selectivity of C_2H_6

= 2*1.2E-7/(6.0E-7 + 2*1.4E-8 + 2*1.2E-7)

= 0.2400 = 24.00 %

B.3 Product Distribution

Products distribution of each component

= Moles of each produced component in product gas/

Total moles of produced compound of product gas

Produced Component	Produced mole	Product Distribution (%)
H_2	2.2E-7	17.68 %
CO	---	---
CO_2	6.0E-7	48.23 %
C_2H_4	1.4E-8	1.12 %
C_2H_6	1.2E-7	9.64 %
C_3H_6	---	---
C_3H_8	---	---
H_2O	2.9E-7	23.31 %
Total	1.244E-6	

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