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Appendix A

1. Calculation of the mole composition of Mg/Al/Li/0.2 Pr as a catalyst.

M.W. of MgO	= 40.311
The MgO was used	= 40.311/100 = <u>0.4031 g</u>
M.W. of Al ₂ O ₃	= 101.957
The Al ₂ O ₃ was used	= 101.957/2 = 50.9785
	= 50.9785/100 = <u>0.5098 g</u>
M.W. of LiOH.H ₂ O	= 41.941
The LiOH.H ₂ O was used	= 41.941/100 = <u>0.4194 g</u>
M.W. of Pr(NO ₃) ₃ .6H ₂ O	= 435.02
The Pr(NO ₃) ₃ .6H ₂ O was used	= 435.01 x 0.20
	= 87.004
	= 87.004/100 = <u>0.8700 g</u>

2. Calculation of the flow rate of gases CH₄/O₂ = 1/1 at the room temperature = 27 °c and at velocity 2000 h⁻¹.

The catalyst was weighed 0.2000 g and put in 0.6 cm. I.D. reactor. The height of catalyst in the reactor was 1.2 cm.

Temperature factor at the STP was $(27 + 273.15)/273.15 = 1.0988$

The volume of the catalyst was $\pi \times r^2 \times h$. of cat.

$$= 3.1416 \times 0.3^2 \times 1.2 \text{ cm}^3$$

$$= 0.33929 \text{ cm}^3$$

space velocity = (flow rate) / (vol. of cat.)

$$\text{then, flow rate} = 2000 \text{ h}^{-1} \times 0.33929 \text{ cm}^3$$

$$= 678.5840 \text{ cm}^3 \cdot \text{h}^{-1}$$

that was the total flow rate of two gas of cofeed.

$$\text{Considered at minute level} = 678.5840/60$$

$$= 11.3097 \text{ cm}^3 \cdot \text{min}^{-1} \text{ of cofeed}$$

$$\begin{aligned}\text{The flow rate at the STP} &= 11.3097 \times 1.0988 \\ &= 12.4271 \text{ cm}^3 \cdot \text{min}^{-1}\end{aligned}$$

Thus the only CH flow rate was $12.4271/2 = 6.2135 \text{ cm}^3 \cdot \text{min}^{-1}$

Checked the flow rate five cm at the seconds.

$$\begin{aligned}6.2135 \text{ cm}^3 &= 60 \text{ sec.} \\ 5 \text{ cm}^3 &= (60 \times 5)/6.2135 \\ &= 48.28 \text{ sec.}\end{aligned}$$

The total flow rate at 5 cm^3 was $(60 \times 5)/12.4271 = 24.14 \text{ sec.}$

3. Calculation of CH₄ conversion

$$\begin{aligned}\text{conversion (wt. \%)} &= \frac{\text{feed area of CH}_4 - \text{product area} \times 100}{\text{feed area of CH}_4} \quad \text{of CH}_4 \\ &= \frac{(1738286 - 947718) \times 100}{1738286} = 45.48 \%\end{aligned}$$

4. Calculation of CO and CO₂ products from GC-8A (TCD) to adjust for GC-GOW MAC (FID)

CO does not appear the peak on GOW MAC, but appears on the MS-5A of GC-8A. then it must be adjusted for the GOW MAC. (Fig. A4)

$$\begin{aligned}\text{CO(GOW MAC)} &= \text{CH}_4(\text{in GOW MAC}) \times b \\ b &= \text{area of CO(in GC-8A)} / 1.13 \times \text{area of CH}_4(\text{in GC-8A})\end{aligned}$$

For example on figure

$$\begin{aligned}b &= 47349 / 1.13 \times 590356 \\ &= 0.070977 \\ \text{CO(in GOW MAC)} &= 0.070977 \times 947718 \\ &= 67266.2963\end{aligned}$$

For the GOW MAC at the same temperature(700 °c) :

$$\text{The area } 534481 = 30.38 \text{ wt \%}$$

$$\begin{aligned} \text{Then area } 67266.296 &= 30.38 \times 67266.296 / 534481 \\ &= 3.82 \text{ wt } \% \end{aligned}$$

For CO₂ (FIG - A5)

$$\begin{aligned} \text{CO}_2 \text{ (in GOW MAC)} &= \text{CH}_4 \text{ (in GOW MAC)} \times a \\ a &= \text{area of CO}_2 \text{ in GC-8A} / 1.35 \times \text{area of CH}_4 \text{ in GC-8A} \end{aligned}$$

For example in figure (Fig. A5)

$$\begin{aligned} a &= 57041 / 1.35 \times 792581 \\ &= 0.0533 \end{aligned}$$

$$\begin{aligned} \text{CO}_2 \text{ in GOW MAC} &= 0.0533 \times 947718 \\ &= 50522.9655 \end{aligned}$$

Then the wt% of CO₂ is (50522.9655 x 30.38)/534481 or 2.87 wt%

5. Summary of quantitative analysis of the metal elements of catalysts which be measured by ICP

	Mg	Al	Li	Mn	Ce	Pr	Sm
1. Mg/Al/Li/0.2 Ce	320.1	265.3	84.14	-	184.1	-	-
2. Mg/Al/Li/0.2 Pr	314.0	283.1	80.10	-	-	379.5	-
3. Mg/Al/Li/0.2 Sm	281.5	258.0	75.53	-	-	-	366.7
4. Mg/Al/Li/0.5 Pr	376.2	338.3	83.74	-	-	126.0	-
5. Mg/Al/Li/0.1 Pr	380.0	348.9	104.1	-	-	242.2	-
6. Mg/Al/Li/0.3 Pr	256.8	226.3	69.25	-	-	485.3	-
7. Mg/Li/0.3 Pr	274.2	-	74.93	-	-	525.6	-
8. Mn/Al/Li/0.2 Pr	-	207.7	73.08	548.0	-	307.8	-

The unit of the data are mg/liter which would be transferred to mole ratios

$$\text{Number of mole} = \text{wt. (g)} / \text{atomic wt. (g)}$$

For the example of Mg/Al/Li/0.1 Pr ; Mg , Al , Li , Pr have

the atomic weight of 24.312 , 26.98 , 6.939 , 140.91 respectively.

$$\text{mole of Mg} = 3.80/24.312 = 0.156$$

$$\text{mole of Al} = 3.489/26.98 = 0.129$$

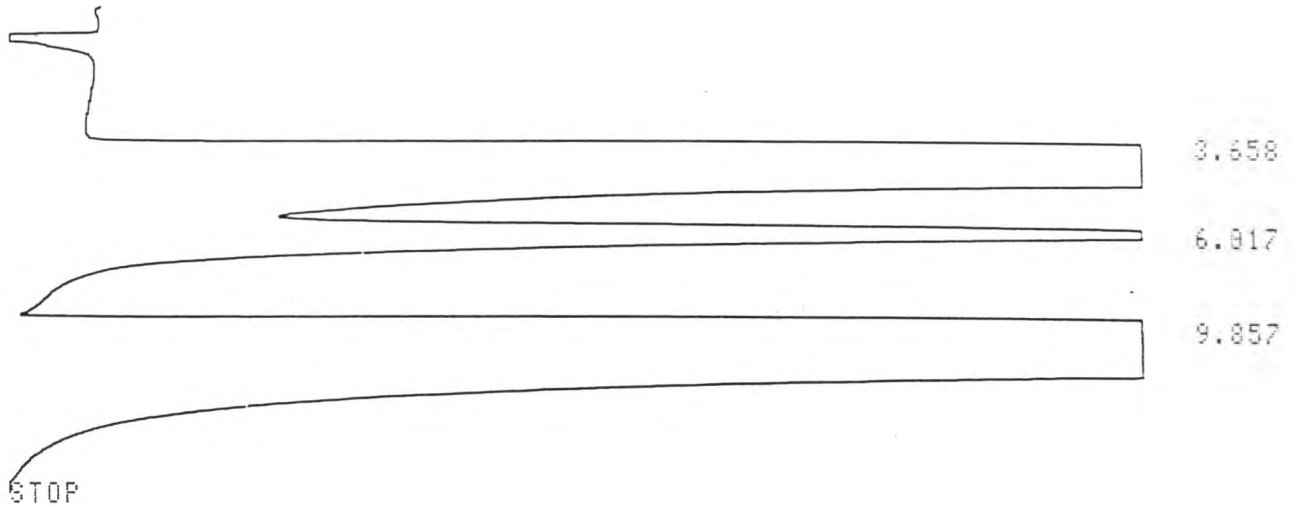
$$\text{mole of Li} = 1.041/6.93 = 0.150$$

$$\text{mole of Pr} = 2.422/140.91 = 0.017$$

Then Mg:Al:Li:Pr is $0.156/0.156:0.129/0.156:0.150/0.156:0.017/0.156 = 1:0.8:1:0.1$

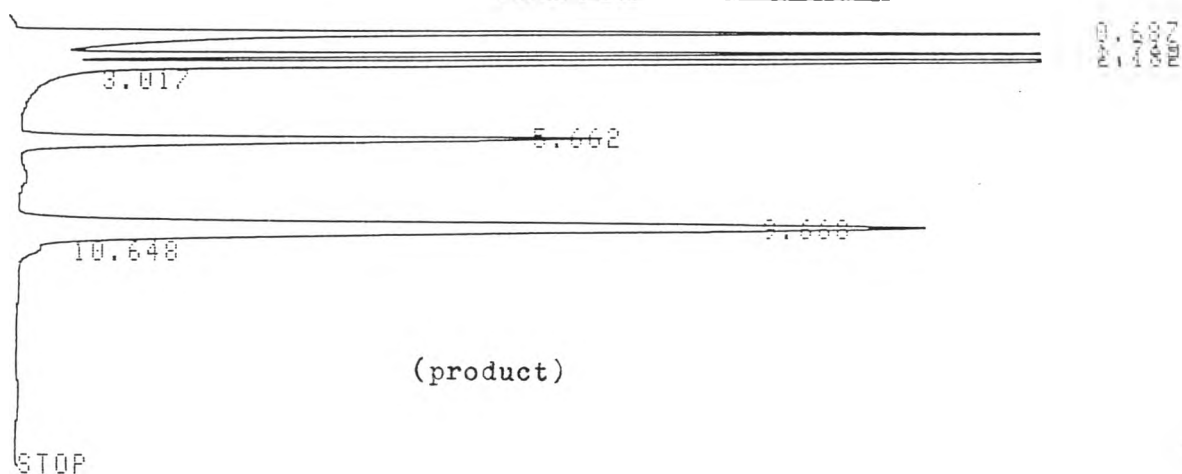
Catalyst : Mg/Al/Li/O₂/Pr

START



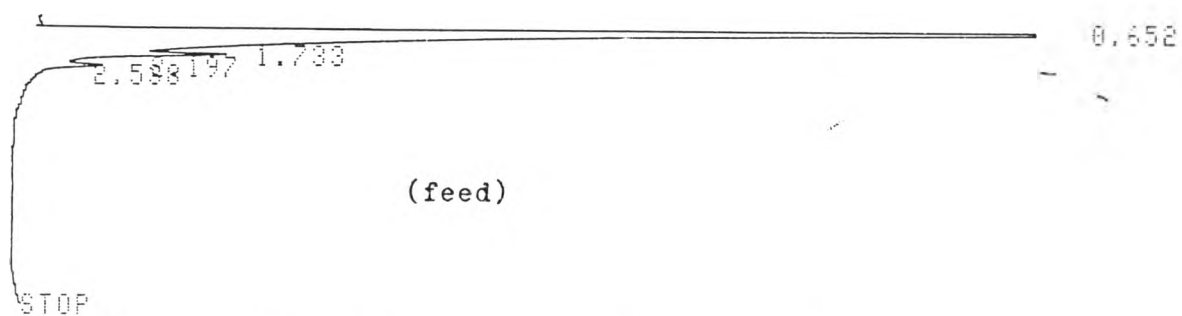
PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	3.658	1380040	S		49.964	O ₂
2	6.017	33427	T		1.2102	N ₂
3	9.857	1348603			48.8258	CH ₄
TOTAL		2762070			100	

Figure A-1 Peaks of feed from MS-5A (TCD) for checking the flow rate of CH₄/O₂ at room temperature



PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	0.687	947718			53.8712	CH ₄
2	1.748	234472	V		13.3281	C ₂ H ₆
3	2.182	534481	SV		30.3816	C ₂ H ₄
4	5.662	11934			0.6784	C ₂ H ₄
5	9.668	30525	S		1.7352	
6	10.648	97	T		0.0055	
TOTAL		1759227			100	

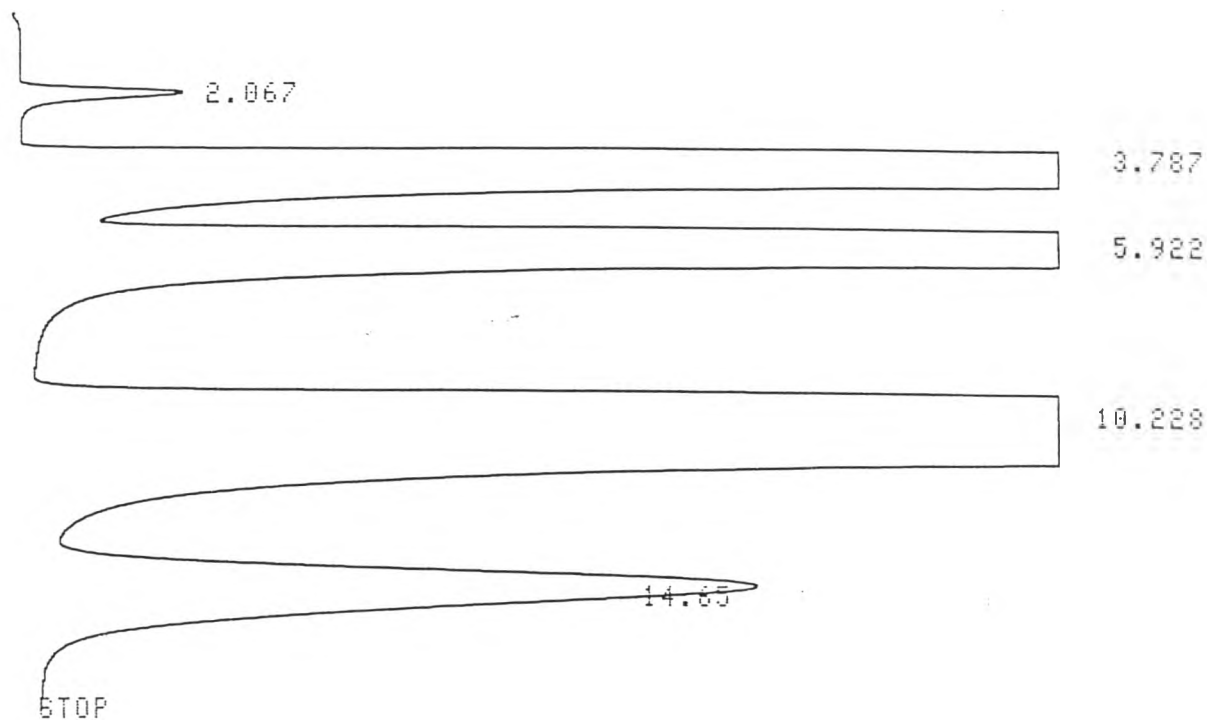
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PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	0.652	1738268	S		99.9274	CH ₄
2	1.733	814	T		0.0198	
3	2.197	414	T		0.0198	
TOTAL		1739530			100	

Figure A-2 Peaks of products and feed from Gow Mac (FID) at temperature of 700°C, space velocity of 2000 h⁻¹

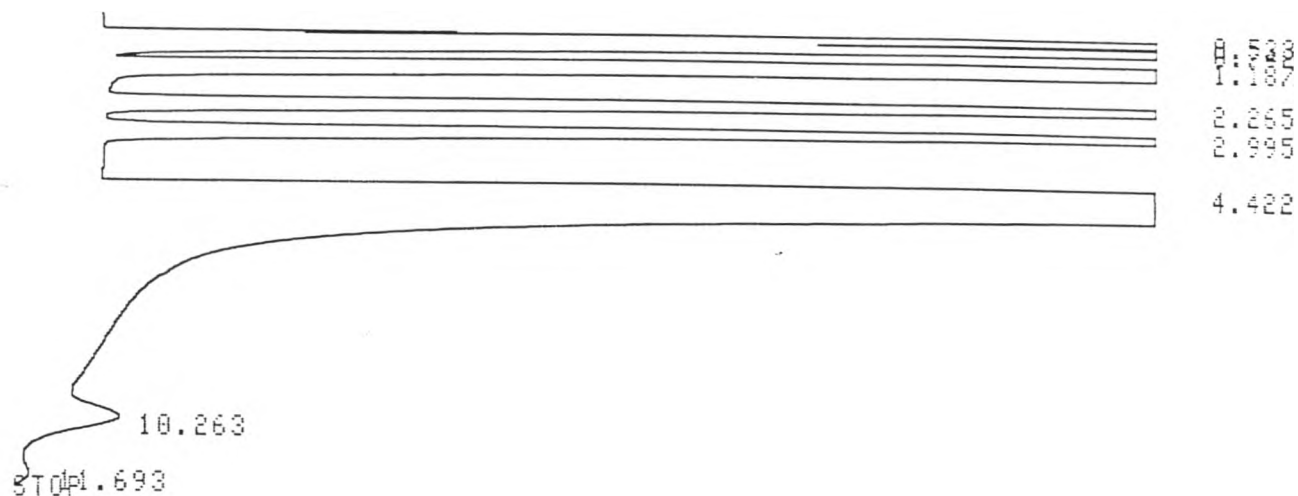
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PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	2.067	2997			0.204	
2	3.787	569401			38.7508	<i>Dz</i>
3	5.922	259289	V		17.646	<i>CH₄</i>
4	10.228	590356	V		40.1769	
5	14.65	47349	V		3.2224	<i>CO</i>
TOTAL		1469392			100	

Figure A-3 Peaks of product from M8-5A at temperature of 700°C and space velocity of 2000 h⁻¹

START



PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	0.533	474584			23.0803	} air and O ₂
2	0.742	349900	V		17.0166	
3	1.187	792581	V		38.5454	- CH ₄
4	2.265	57041	V		2.7741	- CO ₂
5	2.995	27277	V		1.3266	
6	4.422	352324			17.1345	- H ₂ O
7	10.263	2410			0.1172	
8	11.693	108			0.0052	
TOTAL		2056225			100	

Figure A-4 Peaks of product from Porapak Q (TCD) at temperature of 700°C and space velocity of 2000 h⁻¹



VITA

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