



REFERENCES

- 1 Herman, R.G., Kiler, K., Simmons, G.W., Finn, B.P., Bulko, J.B., and Koby Linski, T.P., *J. Catal.* **56**, 407 (1979).
- 2 Kiler, K., Chatikavanij, V., Herman, R.G., and Simmons, G.W., *J. Catal.* **74**, 343 (1982).
- 3 Friedrich, J.B., Young, D.J., and Wainwright, M.S., *J. Catal.* **80**, 14 (1983).
- 4 Friedrich, J.B., Wainwright, M.S., and Young, D.J., *J. Catal.* **80**, 1 (1983).
- 5 Shibata, M., Ohbayashi, Y., and Kawata, N., *J. Catal.* **96**, 296 (1985)
- 6 Chinchen, G.C., Denny, P.J., Parker, D.G., Spencer, M.S., and Whan,D.A., *Appl. Catal.* **30**, 333 (1987).
- 7 Nix, R.M., Rayman, T., Lambert, R.M., Jennings, J.R., and Owen, G., *J. Catal.* **106**, 216 (1987).
- 8 Gasser, D., and Baiker, A., *Appl. Catal.* **48**, 279 (1989).
- 9 Jennings, J.R., Lambert, R.M., Nix, R.M., Owen, G., and Parker, D.G. *Appl. Catal.* **50**, 157 (1989).
- 10 Curry-Hyde, H.E., Sizgek, G.D., Wainwright, M.S., and Young, D.J., *Appl. Catal.* **95**, 65 (1993).
- 11 Inui, T., Kitagawa, K., Takeguchi, T., Hagiwara, T., and Makino, Y., *Appl. Catal.* **94**, 31 (1993).
- 12 Jiang, C.T., Trimm, D.L., Wainwright, M.S., and Cant, N.W., *Appl. Catal.* **93**, 245 (1993).
- 13 Coteron, A., and Hayhurst, A.N., *Appl. Catal.* **101**, 151 (1993).
- 14 Sakurai, H., Tsubota, S., and Haruta, M. *Appl. Catal.* **102**, 125 (1993).
- 15 Fan, L. , and Fujimoto, K. *Appl. Catal.* **106**, L (1993).

- 16 Terlecki-Baricevic, A., Tovanovic, D., Grbic, B., Marinova, T., and Kirilov,-Stefanov, P., *Appl. Catal.* **108**, 115 (1994).
- 17 Fujitani, T., Saito, M., Kanai, Y., Kakumoto, T., Watanabe, T., Nakamura, J., and Uchijima, T., *Catal. Let.* **25**, 271 (1994).
- 18 Kanai, Y., Watanabe, T., Fufitani, T., Saito, M., Makamura, J., and Uchijima, T., *Catal. Let.* **27**, 67 (1994).
- 19 Bailey, S., Froment, G.F., Snoeck, J.W., and Waugh, K.C., *Catal. Let.*, **30**, 99 (1995).
- 20 Hadden, R.A., Lambert, P.J., and Ranson, C., *Appl. Catal.* **122**, L1 (1995).
- 21 Wainwright, M.S., and Trimm, D.L., *Catal. Today* **23**, 29 (1995).
- 22 Fujiwara, M., Kieffer, R., Ando, H., and Souma, Y., *Appl. Catal.* **121**, 113 (1995).
- 23 Psaro, R., Dossi, C., Pergola, R.D., Garlaschelli, L., Calmotti, S., Marengo, S., Bellatreccia, M., and Zanomi, R., *Appl. Catal.* **121**, L19 (1995).
- 24 Breman, B.B., Beenackers, A.A.C.M., Schuurman, H.A., and Oesterholt, E., *Catal. Today* **24**, 5 (1995).
- 25 Skrzypek,J., Stoczyrski,J., and Ledakowicz,S., *Methanol Synthesis science and Engineering* (1994)..
- 26 Chauvel, A., Lefebvre, G., *Petrochemical Processes Technical and Economic Characteristics* **1**, 81 (1989).
- 27 Campbell, J.S. *Ind.Eng.Chem.Prov.Des.Dev.* **9**, 588 (1970).
- 28 Charles N., S. *Heterogeneous Catalysis in Practice*, 295
- 29 Owen,G., Hawkes,C.M., Lloyd,D., Jennings,J.R., Lambert,R.M., and Nix,R.M., *Appl.Catal.* **58**, 69 (1990).
- 30 Jennings,J.R., Lambert,R.M., Nix,R.M., Owen,G., and Shannon,M.D., *Appl.Catal.* **81**, 257 (1992).
- 31 Jennings,J.R., Owen,G., Nix,R.M., and Lambert,R.M., *Appl.Catal.* **82**, 65 (1992).

APPENDIX A

SAMPLE OF CALCULATIONS

Preparation 1% Ce-1.31% Cu Catalysts with the Co-Impregnation Method

Reagent : 1) Cerium (III) nitrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$)

Purity 98%; Molecular weight = 434.22 g.

Atomic weight of Cerium = 140.12

2) Copper nitrate $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$

Purity 99%; Molecular weight = 241.54 g

Atomic weight of Copper = 63.54

Support : Alumina ($\gamma\text{-Al}_2\text{O}_3$); type KNH-3

Pore volume = 1.0 ml./g.

From Sumitomo Aluminium Smelting Co.,Ltd.

Calculation for prepared 1% Ce 1.31% Cu / Al_2O_3 (% by weight)

based on : Catalyst = 100 g.

Hence : each 100 gram. of the catalyst is composed of

Cerium 1 g.

Copper 1.31 g.

Aluminium X g.

Then $1 + 1.31 + X = 100$ gram.

Support (X) = 97.69 gram.

The alumina support weight used for all preparations is 3 grams.

1. Cerium (Ce) was prepared from 25 ml. of solution of Cerium nitrate which was prepared by dissolving 10 g. of Cerium nitrate in deionized water.

$$\begin{aligned}\text{Then; Ce content in stock solution} &= 10 \times 140.12 / (434.22 / 0.98) \\ &= 3.1623 \text{ g.}\end{aligned}$$

$$\begin{aligned}\text{Cerium nitrate taken} &= 0.03071 \times 25 / 3.1623 \text{ ml.} \\ \text{from stock solution} &= 0.2429 \text{ ml.}\end{aligned}$$

$$2. \text{ Cooper required} = 3 \times 1.31 / 97.69 = 0.04023 \text{ g.}$$

Copper (Cu) was prepared from 25 ml. of solution of Copper nitrate which was prepared by dissolving 10 g. of Cobalt nitrate in de-ionized water.

$$\begin{aligned}\text{Then; Cu content in stock solution} &= 10 \times 63.54 / (241.60 / 0.99) \\ &= 2.6037 \text{ g.}\end{aligned}$$

$$\begin{aligned}\text{Copper nitrate taken} &= 0.04023 \times 25 / 2.6037 \\ \text{from stock solution} &= 0.3863 \text{ ml.}\end{aligned}$$

The Co-impregnation was performed by Co-impregnate method in this research. As the pore volume of the alumina support is 1 ml./g, the total volume of each reagent used, Ce(NO₃)₃, Cu(NO₃)₂ is made by adding de-ionized water to increase the volume of the impregnation solution volume by 3 ml. for impregnate in 3 grams of support.

APPENDIX B

Table B-1 Shows Specification of Alumina Support (Al_2O_3) Type KNH-3

Chemical Composition	Weight Percent
Al_2O_3	60-70%
SiO_2	30-35%
Fe_2O_3	0.3-0.5%
TiO_2	0.5-0.7%
CaO	0.1-0.2%
MgO	0.2-0.4%
Na_2O	0.3-0.4%
K_2O	0.2-0.3%
$\text{ZrO}_2 + \text{HfO}_2$	0.03-0.04%

Physical Properties	
Bulk Density (g/ml.)	1.3 - 1.5
Apparent Specific Gravity	3.1 - 3.3
Packing Density (lb./ft. ³)	20 - 25
Pore Volume (ml./g)	1.0 - 1.3
Surface Area (m ² /g)	340-350

The operating conditions for gas chromatograph.

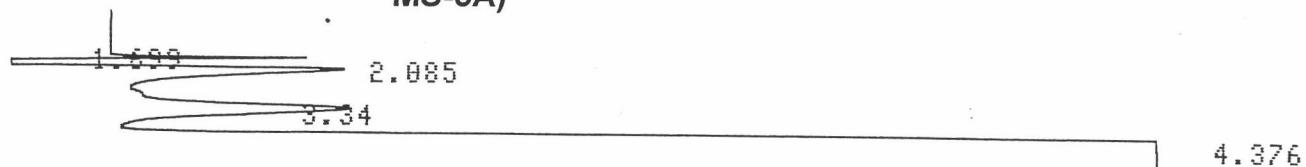
A thermal conductivity detector gas chromatograph (model 8ATP) was used to analyze the concentrations of oxygen, nitrogen, carbon monoxide.

OPERATING CONDITIONS ARE AS FOLLOWS :

GC.	:	SHIMUDZU-GC-8ATP
Detector	:	TCD
Packed column	:	MS-5A / Porapak-Q
Carrier gas	:	Ultra high Purity Helium (99.999%)
Flow rate of Carries gas	:	30 ml. / min.
Column temperature	:	100 °C
Detector temperature	:	110 °C
Injector temperature	:	110 °C
Current	:	80 mA

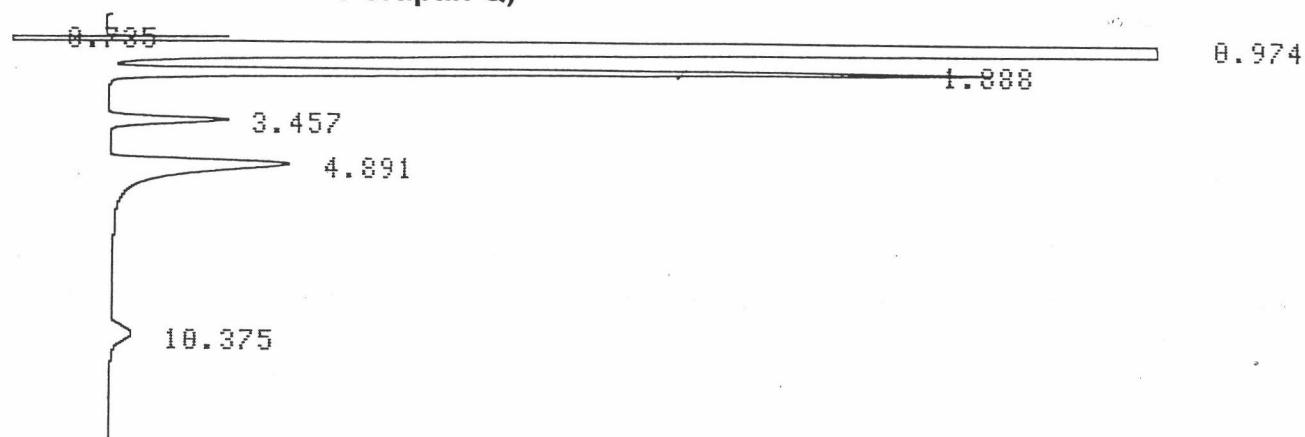
The chromatography from gas analysis are shown in Figure B-1, B-2 respectively.

Figure B-1 Sample of Chromatogram from GC-8ATP (column MS-5A)



CHROMATOGRAM 1 MEMORIZED						
PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	1.699	6843			0.4573	
2	2.085	48316			3.6556	
3	3.34	78927	V		5.3664	
4	4.376	1196388	V		98.5207	
<hr/>						
TOTAL		1321674			100	

Figure B-2 Sample of Chromatogram from GC-8ATP (column Porapak-Q)



CHROMATOGRAM 1 MEMORIZED						
PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	0.735	6416	E		0.3779	
2	0.974	1606586	E		94.6296	
3	1.888	68745	V		4.0491	
4	3.457	3432			0.2022	
5	4.891	11045			0.6506	
6	10.375	1540			0.0907	
<hr/>						
TOTAL		1697763			100	

APPENDIX C

TABLES OF EXPERIMENT

Table 5.1 Catalytic performance of Cu base catalyst

2% Cu	250°C	300°C	350°C	400°C
% Selectivity	0	14.97	13.12	6.93
% Conversion	0.41	2.14	3.82	4.58
%Yield/Pass	0	0.32	0.50	0.32

Table 5.2 The performance of commercial catalyst

Commercial catalyst	250°C	300°C	350°C	400°C
% Selectivity	70.41	70.09	64.89	70.61
% Conversion	4.48	6.69	9.58	11.13
%Yield/Pass	3.15	4.69	6.22	7.86

Table 5.3.1 Effect of Zn loading on catalytic performance

	Catalysts	250°C	300°C	350°C	400°C
% Selectivity	ZN1	13.08	21.25	12.58	15.56
	ZN2	0	1.03	5.94	3.09
	ZN3	0	19.6	12.34	10.73
% Conversion	ZN1	0.61	1.95	3.46	3.93
	ZN2	1.22	3.00	4.57	5.76
	ZN3	0.09	0.44	1.82	2.64
%Yield/Pass	ZN1	0.08	0.42	0.44	0.61
	ZN2	0	0.03	0.27	0.18
	ZN3	0	0.09	0.23	0.29

Table 5.3.2 Effect of Zn/Cu loading on catalytic performance

	Catalysts	250°C	300°C	350°C	400°C
% Selectivity	ZN4	0	26.03	18.83	7.99
	ZN5	7.98	13.8	11.16	10.52
	ZN6	0	18.61	14.36	20.65
% Conversion	ZN4	0.55	1.18	2.62	4.08
	ZN5	0.85	2.17	4.42	3.93
	ZN6	0.72	1.33	1.94	2.54
%Yield/Pass	ZN4	0	0.31	0.50	0.33
	ZN5	0.07	0.30	0.50	0.41
	ZN6	0	0.30	0.30	0.52

Table 5.4 Effect of Sm loading on the catalytic performance

	Catalyst	250°C	300°C	350°C	400°C
% Selectivity	SM1	-	1.88	5.14	-
	SM4	0	7.72	5.43	4.89
% Conversion	SM1	-	1.91	4.66	-
	SM4	2.23	3.2	9.8	12.78
%Yield/Pass	SM1	-	0.04	0.24	-
	SM4	0	0.25	0.53	0.63

Table 5.5 Effect of Zr loading on the catalytic performance

	Catalysts	250°C	300°C	350°C	400°C
% Selectivity	ZR0.25	14.61	20.33	22.97	28.88
	ZR0.75	5.82	48.95	21.23	18.85
	ZR1.2	55.38	78.82	82.95	20.1
% Conversion	ZR0.25	0.12	0.29	0.78	1.49
	ZR0.75	1.85	3.33	5.02	5.7
	ZR1.2	0.54	1.57	2.19	3.3
%Yield/Pass	ZR0.25	0.02	0.06	0.18	0.43
	ZR0.75	0.11	1.63	1.06	1.07
	ZR1.2	0.30	1.23	1.84	0.66

Table 5.6 Effect of Sm & Zr loading on catalytic performance

	Catalysts	250°C	300°C	350°C	400°C
% Selectivity	SZ1	0	0	2.87	16.05
	SZ2	0	12.74	19.43	20.19
	SZ3	0	14.68	42.78	27.92
% Conversion	SZ1	0.16	0.89	1.03	0.77
	SZ2	0.01	0.44	0.51	0.88
	SZ3	0.51	1.16	1.41	1.72
%Yield/Pass	SZ1	0	0	0.03	0.12
	SZ2	0	0.06	0.10	0.18
	SZ3	0	0.17	0.60	0.48

Table 5.7 Effect of Nd loading on catalytic performance

	Catalysts	250°C	300°C	350°C	400°C
% Selectivity	ND0.25	-	12.07	30.88	-
	ND1	-	4.75	12.83	-
	ND4	-	15.34	16.86	-
% Conversion	ND0.25	-	0.92	1.74	-
	ND1	-	6.48	2.3	-
	ND4	-	7.14	9.39	-
%Yield/Pass	ND0.25	-	1.11	0.54	-
	ND1	-	0.31	0.30	-
	ND4	-	1.10	1.58	-

Table 5.8 Effect of Pr loading on the catalytic performance

	Catalysts	250°C	300°C	350°C	400°C
% Selectivity	PR0.25	-	12.36	14.01	-
	PR1	-	13.29	8.71	-
	PR4	-	16.04	16.67	-
% Conversion	PR0.25	-	6.75	11.48	-
	PR1	-	5.91	12.21	-
	PR4	-	3.31	5.71	-
%Yield/Pass	PR0.25	-	0.83	1.61	-
	PR1	-	0.78	1.06	-
	PR4	-	0.53	0.95	-

Table 5.9.1 Effect of Ce loading on the catalytic performance

	Catalysts	250°C	300°C	350°C	400°C
% Selectivity	CE1	2.84	5.16	6.09	2.71
	CE2	1.86	10.98	30.75	20.32
	CE3	0	5.46	5.92	4.99
% Conversion	CE1	0.6	8.92	11.51	21.2
	CE2	5.27	6.56	8.55	15.21
	CE3	0.71	5.01	8.41	12.11
%Yield/Pass	CE1	0.017	0.46	0.71	0.58
	CE2	0.098	0.72	2.63	3.09
	CE3	0	0.27	0.50	0.60

Table 5.9.2 Effect of Ce/Cu loading on catalytic performance

	Catalysts	250°C	300°C	350°C	400°C
% Selectivity	CE4	17.21	44.5	29.58	22.04
	CE5	49.52	63.38	57.04	83.31
	CE6	2.12	9.34	18.04	16.73
	CE7	4.17	18.99	19.39	10
	CE8	1.03	19.08	13.43	13.72
% Conversion	CE4	1.76	3.76	6.81	14.5
	CE5	0.69	4.84	7.45	4.01
	CE6	6.02	7.54	9.47	11.68
	CE7	6.02	7.59	10.38	22.78
	CE8	5.64	7.39	23.57	10.19
%Yield/Pass	CE4	0.30	1.67	2.02	3.19
	CE5	0.34	3.07	4.25	3.34
	CE6	0.13	0.70	1.709	1.95
	CE7	0.25	1.44	2.01	2.28
	CE8	0.06	1.41	3.17	1.40

Table 5.10.1 Effect of pressure on ND4 catalytic performance

Pressure 10 bar	250°C	300°C	350°C	400°C
% Selectivity	-	2.6	2.8	-
%Conversion	-	11.55	14.47	-
%Yield/pass	-	0.30	0.40	-

Table 5.10.2 Effect of pressure on PR0.25 catalytic performance

Pressure 10 bar	250°C	300°C	350°C	400°C
% Selectivity	-	2.05	3.32	-
%Conversion	-	5.27	6.31	-
%Yield/pass	-	0.11	0.21	-

Table 5.10.3 Effect of pressure on ZN1 catalytic performance

Pressure 10 bar	250°C	300°C	350°C	400°C
% Selectivity	-	2.71	1.94	-
%Conversion	-	3.21	6.39	-
%Yield/pass	-	0.08	0.12	-

Table 5.11.1 Effect of N₂O on CU catalyst

	Inject N₂O	250°C	300°C	350°C	400°C
% Selectivity	No N₂O	0	14.97	13.12	6.93
	2.4 cc ,N ₂ O	0	10.30	5.19	5.70
%Conversion	No N₂O	0.41	2.14	3.82	4.58
	2.4 cc ,N ₂ O	0.41	1.40	5.37	7.49
%Yield/pass	No N₂O	0	0.32	0.50	0.32
	2.4 cc ,N ₂ O	0	0.14	0.28	0.43

Table 5.11.2 Effect of N₂O on Commercial catalyst

	Inject N₂O	250°C	300°C	350°C	400°C
% Selectivity	No N₂O	70.41	70.09	64.89	70.61
	1.0 cc ,N ₂ O	79.22	56.03	34.51	70.61
	2.4 cc ,N ₂ O	61.88	88.57	69.13	35.79
%Conversion	No N₂O	4.48	6.69	9.58	11.13
	1.0 cc ,N ₂ O	13.6	9.28	4.84	4.27
	2.4 cc ,N ₂ O	6.81	9.85	9.46	7.99
%Yield/pass	No N₂O	3.15	4.69	6.22	7.86
	1.0 cc ,N ₂ O	10.77	5.20	1.67	0.92
	2.4 cc ,N ₂ O	4.16	8.73	6.54	2.86

Table 5.11.3 Effect of N₂O on SM4 catalyst

	Inject N₂O	250°C	300°C	350°C	400°C
% Selectivity	No N₂O	0	7.72	5.43	4.89
	2.4 cc ,N ₂ O	-	-	7.43	-
%Conversion	No N₂O	2.23	3.20	9.80	12.78
	2.4 cc ,N ₂ O	-	-	6.05	-
%Yield/pass	No N₂O	0	0.25	0.53	0.63
	2.4 cc ,N ₂ O	-	-	0.45	-

Table 5.11.4 Effect of N₂O on CE5 catalyst

	Inject N₂O	250°C	300°C	350°C	400°C
% Selectivity	No N₂O	49.52	63.38	57.04	83.31
	0.005cc.N ₂ O	-	50.6	20.71	-
	0.02 cc N ₂ O	-	8.76	11.21	-
	1.0 cc. N ₂ O	0.18	7.17	3.13	0.39
	2.4 cc. N ₂ O	0	8.93	5.53	7.59
	4.8 cc. N ₂ O	-	-	6.2	-
%Conversion	No N₂O	0.69	4.84	7.45	4.01
	0.005cc.N ₂ O	-	2.78	3.56	-
	0.02 cc N ₂ O	-	3.05	4.54	-
	1.0 cc. N ₂ O	2.06	3.75	15.59	21.28
	2.4 cc. N ₂ O	4.85	7.25	8.55	9.3
	4.8 cc. N ₂ O	-	-	8.05	-
%Yield/pass	No N₂O	0.34	3.07	4.25	3.34
	0.005cc.N ₂ O	-	1.10	0.754	-
	0.02 cc N ₂ O	-	0.27	0.51	-
	1.0 cc. N ₂ O	0.004	0.27	0.49	0.30
	2.4 cc. N ₂ O	0	0.65	0.47	0.71
	4.8 cc. N ₂ O	-	-	0.50	-

Table 5.11.5 Effect of N₂O on ND4 catalyst

	Inject N₂O	250°C	300°C	350°C	400°C
% Selectivity	No N₂O	-	15.34	16.86	-
	0.005cc N ₂ O	-	79.25	85.82	-
%Conversion	No N₂O	-	7.14	9.39	-
	0.005cc N ₂ O	-	0.36	0.95	-
%Yield/pass	No N₂O	-	1.10	1.58	-
	0.005cc N ₂ O	-	0.28	0.82	-

Table 5.11.6 Effect of N₂O on ND4 catalyst (Pressure 10 bar)

	Inject N₂O	250°C	300°C	350°C	400°C
% Selectivity	No N₂O	-	2.60	2.80	-
	0.005cc N ₂ O	-	0.90	3.48	-
%Conversion	No N₂O	-	11.55	14.47	-
	0.005cc N ₂ O	-	7.66	7.72	-
%Yield/pass	No N₂O	-	0.30	0.40	-
	0.005cc N ₂ O	-	0.07	0.30	-

Table 5.11.7 Effect of N₂O on PR0.25 catalyst (Pressure 10 bar)

	Inject N ₂ O	250°C	300°C	350°C	400°C
% Selectivity	No N₂O	-	2.05	3.32	-
	0.005cc N ₂ O	-	1.60	4.72	-
%Conversion	No N₂O	-	5.27	6.31	-
	0.005cc N ₂ O	-	2.74	4.05	-
%Yield/pass	No N₂O	-	0.11	0.21	-
	0.005cc N ₂ O	-	0.04	0.19	-

Table 5.11.8 Effect of N₂O on ZN1catalyst (Pressure 10 bar)

	Inject N ₂ O	250°C	300°C	350°C	400°C
% Selectivity	No N₂O	-	2.71	1.94	-
	0.005cc N ₂ O	-	11.97	8.45	-
%Conversion	No N₂O	-	3.21	6.39	-
	0.005cc N ₂ O	-	4.72	8.6	-
%Yield/pass	No N₂O	-	0.09	0.12	-
	0.005cc N ₂ O	-	0.56	0.73	-



VITA

Mr.Kunawut Wattanakij was born on September 25, 1967 at Bangkok, Thailand. He Graduated with a Bachelor Degree of Science (Chemistry) from Chiang Mai University in 1990.