REFERENCES

Al-Zahrani, S.M. The effects of kinetics, hydrodynamics and feed conditions on methane coupling using fluidized bed reactor. Catal. Today 64(2001): 219.

Anshits, A.G., A.N. Shigapov, S.N. Veresshchagin and V.N. Shevin. C_2 hydrocarbon formation from methane on silver membrane. Catal. Today 6(1990): 593.

Au, C.T., K.D. Chen and C.F.Ng. The modification of Gd_2O_3 with BaO for the oxidative coupling of methane reactions. Appl. Catal. A. 170(1998): 81-92.

Au, P.C., Y.W. Liu and C.F. Ng. Raman spectroscopic and TPR studies of oxygen species over BaO- and BaX2(X=F, Cl, Br)-promoted Nd2O3catalysts for the oxidative coupling of methane. J. Catal. 176 (1998): 365.

Choudhary, V.R., V.H. Rane and S.T. Chaudhari. Surface properties of rare earth promoted MgO catalysts and their catalytic activity/selectivity in oxidative coupling of methane. Appl. Catal. A 158(1997): 121-136.

Dubois J.L. and C.J. Cameron. Common features of oxidative coupling of methane cofeed catalysts. Appl. Catal. 67(1990): 49-71.

Eng, D.W. The Partial oxidation of methane in a solid electrolyte cell. PhD thesis, Tufts University, 1990.

Filkova D., D. Wolf, G. Gayko, M. Baerns and L. Petrov, Experimental study on the influence of alkaline earth promoters on neodymium oxide performance in the oxidative coupling of methane. Appl. Catal. A 159(1997): 33-44.

Gellings, P.J. and H.J.M. Bouwmeester. Solid state aspects of oxidation catalysis. Catal. Today 58(2000): 1-53.

Guo, X.M., K. Hidajet and C.B. Ching. Simulation of a solid oxide fuel cell for oxidative coupling of methane. Catal. Today 50(1999): 109-116.

Harold, M.P., V.T. Zaspalis, K. Keizer and A.J. Burggraaf. Intermediate product yield enchancement with a catalytic inorganic membrane. Chem. Eng. Sci. 48(1992): 2705-2725

Keller, G.E. and M.M. Bhasin. J. Catal. 73(1982): 9.

Lane, G.S. and E.E. Wolf. J. Catal. 113(1988): 144-163.

Liu, S., X. Tan, K. Li, and R. Hughes. Methane coupling using actalytic membrane reactors. Catal. Rev. 43(2001): 147-198.

Long , R.Q. and H.L. Wan. Oxidative coupling of methane over SrF2/Y2O3 catalyst. Appl. Catal. A 159(1997): 45-58.

Lunsford, J.H., P.G. Hinson, M.P. Rosynek, C. Shi, M. Xu and X. Yang, J. Catal. 147 (1994): 301.

Lunsford, J.H. Catalytic conversion of methane to more useful chemicals and fuels: a challenge for the 21st century. Catal. Today. 63(2000): 165-174.

Mimoun, H., A. Robine, S. Bonnaude and C.J. Cameron. Appl. Catal. 58(1990): 269.

Minh, N.Q. And Takahashi, T. Science and technology of ceramic fuel cells. Amsterdam: Elsevier, 1995.

Mogensen, M. Comparison of solid oxide fuel cells with alternative fuel cells and competitive technologies. In H. L. Tuller, J. Schoonman and I. Riess (eds), Oxygen ion and mixed conductors and their technological applications, pp. 449-469. Appied Sciences, 2001.

Otsuka, K., S. Yokoyama and A. Morikawa, Chem. Lett. (1985): 319-322.

Pak, S., P. Qiu and J.H. Lunsford. Elementary reactions in the oxidative coupling of methane over $Mn/Na_2WO_4/SiO_2$ and $Mn/Na_2WO4/MgO$ catalysts. J. Catal. 179(1998): 222-230.

Palermo, A., J.P. Holgado Vazquez and R.M. Lambert. New efficient catalysts for the oxidative coupling of methane. Catal. Lett. 68(2000): 191-196.

Park, S., R.J. Gorte and J.M. Vohs. Applications of heterogeneous catalysis in the direct oxidation of hydrocarbons in a solid-oxide fuel cell. Appl. Catal. A 200(2000): 55-61.

Pujare, N.U. and A.F. Sammells. Methane activation to C2 hydrocarbons species in solid oxide fuel cell. J. Electrochem. Soc. 135(1988): 2544.

Sinev, M.Y., V.N. Korchak and O.V. Krylov. Kinet. Catal. 27(1986): 1274.

Singhal, S.C. Advances in solid oxide fuel cell technology. Solid State Ionics 135(2000): 305-313

Tsai, K.R., D.A. Chen, H.L. Wan, H.B. Zhang, G.D. Lin and P. X. Zhang. Forty years of applied catalysis research at Xiamen University and its interaction with fundamental catalysis research. Catal. Today. 51(1999): 3-23.

Tagawa, T., K.K. Moe, M. Ito and S. Goto. Fuel cell type reactor for chemicals-energy co-generation. Chem. Eng. Sci. 54(1999): 1553-1557.

Tagawa, T., K.K. Moe, T. Hiramatsu and S. Goto. Design of electrode for solid oxide fuel cells reactor. Solid state Ionics 106(1998): 227-235.

Tagawa, T., K. Kuroyanagi, S. Goto, S. Assabumrungrat and P. Praserthdam. Selective oxidation of methane in an SOFC-type reactor: effect of applied potential Chem. Eng. J. 4046(2002): 1-7.

Vayenas, C.G. and R.D. Farr, *Nature* **208** (1980), 593.

Wan, H.L., X.P. Zhou, W.Z. Weng, R.Q. Long, Z.S. Chao, W.D. Zhang, M.S. Chen, J.Z. Luo and S.Q. Zhou. Catalytic performance, structure, surface properties and active oxygen species of the fluoride-containing rare earth (alkaline earth)-based catalysts for the oxidative coupling of methane and oxidative dehydrogenation of light alkanes. Catal. Today. 51(1999): 161-175.

Yide, X., Y. Lin and G Xiexian. Effect of basicity and adding CO2 in the feed on the oxidative coupling of methane over K2O and SrO promoted La2O3/ZnO catalysts. Appl. Catal. A 164(1997): 47-57.

APPENDICES

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

APPENDIX A
CALCULATION OF CATALYST
PREPARATION

Anode Catalyst

Molecular weight

Sm	150.36	g/g mol
Al	26.98	
O	16.00	
N	14.00	
$Sm(NO_3)_3.6H_2O$	444.35	
$Al(NO_3)_3.9H_2O$	374.97	

Catalyst : $Sm_{1.8}Al_{0.2}O_3$

Mw	324.04	g/g mol
Sm content	150.36*1.8/324.04*100	
	= 83.5	%wt
Al content	26.98*0.2/324.04	
	= 1.7	%wt

Catalyst weight: based on 2 g

$Sm(NO_3)_3.6H_2O$	2*0.835/(150.36/444.35)	
	= 4.94	g
$Al(NO_3)_3.9H_2O$	2*0.017/(26.98/374.97)	
	= 0.46	g

Cathode Catalyst

Molecular weight

La	138.9	g/g mol
Sr	87.62	
Mn	54.94	
O	16.00	
N	14.00	
$La(NO_3)_3.6H_2O$	432.9	
$Sr(NO_3)_2$	211.6	
$Mn(NO_3)_3.4H_2O$	312.9	

Catalyst : $La_{0.8}Sr_{0.2}MnO_3$

Mw	231.58	g/g mol
La content	138.9*0.8/231.58*100	
	= 50.0	%wt
Sr content	87.62*0.2/231.58*100	
	= 7.6	%wt
Mn content	54.94/231.58*100	
	= 23.7	%wt

Catalyst weight: based on 2 g

$La(NO_3)_3.6H_2O$	2*0.50/(138.9/432.9)	
	= 3.11	g
$Sr(NO_3)_2$	2*0.076/(87.62/211.6)	
	= 0.38	g
$Mn(NO_3)_3.4H_2O$	2*0.237/(54.94/312.9)	
	= 2.70	g

APPENDIX B

CALCULATION OF SPECIFIC SURFACE AREA

From Brunauer-Emmett-Teller (BET) equation

$$\frac{p}{n(1-p)} = \frac{1}{n_m C} + \frac{(C-1)p}{n_m C} \tag{B.1}$$

Where, p = Relative partial pressure of adsorbed gas, P/P_0

P_0 = Saturated vapor pressure of adsorbed gas in the condensed state at the experimental temperature, atm

P = Equilibrium vapor pressure of adsorbed gas, atm

n = Gas adsorbed at pressure P, ml. at the NTP/g of sample

n_m = Gas adsorbed at monolayer, ml. at the NTP/g of sample

C = Exp $[(H_C - H_l)/RT]$

H_C = Heat of condensation of adsorbed gas on all other layers

H_l = Heat of adsorption into the first layer

Assume $C \rightarrow \infty$, then

$$\frac{p}{n(1-p)} = \frac{p}{n_m}$$

$$n_m = n(1-p) \tag{B.2}$$

The surface area, S, of the catalyst is given by

$$S = S_b \times n_m \tag{B.3}$$

From the gas law

$$\frac{P_b V}{T_b} = \frac{P_t V}{T_t} \tag{B.4}$$

Where, P_b = Pressure at 0°C

P_t = Pressure at t°C

T_b = Temperature at 0°C = 273.15 K

T_t = Temperature at t°C = 273.15 + t K

V = Constant volume

Then, $P_b = (273.15/T_t) \times P_t = 1$ atm

Partial pressure

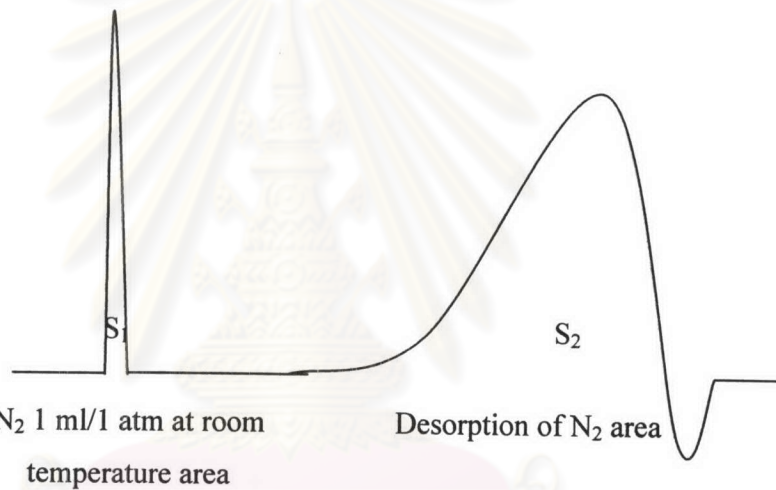$$P = \frac{[\text{Flow of } (He + N_2) - \text{Flow of He}]}{\text{Flow of } (He + N_2)} \quad \text{(B.5)}$$

$$= 0.3 \text{ atm}$$

For nitrogen gas, the saturated vapor pressure equals to

$$P_0 = 1.1 \text{ atm}$$

then, $p = P/P_0 = 0.3/1.1 = 0.2727$

To measure the volume of nitrogen adsorbed, n

N$_2$ 1 ml/1 atm at room temperature area   Desorption of N$_2$ area

$$n = \frac{S_2}{S_1} \times \frac{1}{W} \times \frac{273.15}{T} \text{ ml. /g of catalyst} \quad \text{(B.6)}$$

Where, S_1 = N$_2$ 1 ml/1 atm at room temperature area

S_2 = Desorption of N$_2$ area

W = Sample weight, g

T = Room temperature, K

Therefore,

$$n_m = \frac{S_2}{S_1} \times \frac{1}{W} \times \frac{273.15}{T} \times (1-p)$$

$$n_m = \frac{S_2}{S_1} \times \frac{1}{W} \times \frac{273.15}{T} \times 0.7272 \quad \text{(B2.1)}$$

Whereas, the surface area of nitrogen gas from literature equal to

S_b = 4.373 m^2/ml of nitrogen gas

Then,

$$S = \frac{S_2}{S_1} \times \frac{1}{W} \times \frac{273.15}{T} \times 0.7272 \times 4.343$$

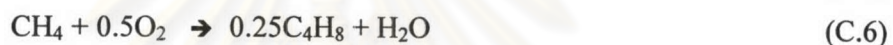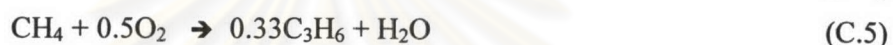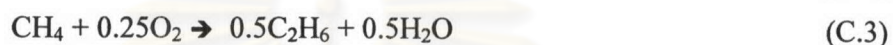$$S = \frac{S_2}{S_1} \times \frac{1}{W} \times \frac{273.15}{T} \times 3.1582 \ \text{m}^2/\text{g} \tag{B.7}$$

APPENDIX C
CALCULATION OF THREORETICAL
VOLTAGE

Involving Reactions

Based on 1 mol CH_4

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \tag{C.1}$$

$$CH_4 + 1.5O_2 \rightarrow CO + 2H_2O \tag{C.2}$$

$$CH_4 + 0.25O_2 \rightarrow 0.5C_2H_6 + 0.5H_2O \tag{C.3}$$

$$CH_4 + 0.5O_2 \rightarrow 0.5C_2H_4 + H_2O \tag{C.4}$$

$$CH_4 + 0.5O_2 \rightarrow 0.33C_3H_6 + H_2O \tag{C.5}$$

$$CH_4 + 0.5O_2 \rightarrow 0.25C_4H_8 + H_2O \tag{C.6}$$

Gibb's Free Energy of Formation, kJ/mol

At 1173 K

CO_2	-396.4
CO	-212.0
C_2H_6	148.24
C_2H_4	133.19
C_3H_6	214.84
C_4H_8	312.31
CH_4	38.34
H_2O	-182.96
O_2	0.0

Calculation

Gibb's free energy change of Eqa. (C.4)

$$\Delta G_{1173\,K} = 0.5 * 133.19 - 182.96 - 38.34 = -154.71 \text{ kJ/mol } CH_4$$

Equation	$\Delta G_{f\,1173\,K}$	Selectivity, %	$\Delta G_{1173\,K}$ * Selectivity/100
C.1	-800.67	4.9	-99.03
C.2	-616.27	16.1	-39.19
C.3	-55.70	6.9	-3.84
C.4	-154.71	10.7	-16.52
C.5	-149.69	4.5	-6.71
C.6	-143.23	5.5	-7.94

Equation	n	Selectivity, %	n * Selectivity/100
C.1	2	4.9	0.24
C.2	1.5	16.1	0.10
C.3	0.25	6.9	0.02
C.4	0.5	10.7	0.05
C.5	0.5	4.5	0.02
C.6	0.5	5.5	0.03

Theoretical voltage, V (or J/coulomb)

$$E_{1173\,K} = -\Delta G_{1173\,K,\,average}/4n_{average}F$$

$$= \frac{-(-99.03-39.19-3.84-16.52-6.71-7.94)*1000}{4*(0.24+0.1+0.02+0.05+0.02+0.03)*96500}$$

$$= 0.976\ V$$

VITA

Mr. Kampol Silpasup was born in Nov 10, 1975 in Bangkok, Thailand. He got his Bachelor's Degree in Chemical Engineering from the Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok in 1997. After had finished his degree, he started work as a process engineer with Thai Plastic and Chemical Co, Ltd, Mab Ta Phut Industrail Estate, Rayong, for two and a half years.