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## APPENDIX A

### Experimental Calculation

#### 1. Methane Conversion ( $\Delta X_{CH_4}$ )

$$\Delta X_{CH_4} = \frac{\text{Amount of mole atom of carbon in CO and CO}_2}{\text{Total amount of mole atom of carbon in all gas composition}}$$

From Table C1 in Appendix C, product gas composition at atmospheric pressure, 700 °C, excess steam and catalyst weight of 2 g was as follows:

Feed Flow rate		Product Gas Composition			
CH <sub>4</sub>	H <sub>2</sub> O	(% mole)			
(mole/min)	(mole/min)	H <sub>2</sub>	CO	CH <sub>4</sub>	CO <sub>2</sub>
5.87E-04	0.15	14.59	8.18	71.62	5.62

$$\begin{aligned}\text{Thus, methane conversion } (\Delta X_{CH_4}) &= (8.18 + 5.62)/(8.18 + 5.62 + 71.62) \\ &= 0.162\end{aligned}$$

#### Carbon balance

100 % of methane in experiment

$$\begin{aligned}\text{Total amount of carbon in methane} &= 1 \times 100 \\ &= 100 \text{ mole of C/ } 100 \text{ mole of CH}_4\end{aligned}$$

$$\begin{aligned}\text{Flow rate of carbon inflow} &= \frac{(5.87 \times 10^{-4} \text{ mole of CH}_4/\text{min})}{(100 \text{ mole of CH}_4/100 \text{ mole of C})} \\ &= 5.87 \times 10^{-4} \text{ mole of C/min}\end{aligned}$$

$$\begin{aligned}\text{Flow rate of unconverted methane} &= \text{mole CH}_4 \text{ inflow} - \Delta X_{CH_4} (\text{mole CH}_4 \text{ inflow}) \\ &= 5.87 \times 10^{-4} - (0.162)(5.87 \times 10^{-4}) \\ &= 4.92 \times 10^{-4} \text{ mole of CH}_4/\text{min}\end{aligned}$$

$$\text{Flow rate of unconverted carbon in CH}_4 = 4.92 \times 10^{-4} \text{ mole of C/min}$$

Based on percent of product gas composition of 71.62 % mole of CH<sub>4</sub>, 8.18 % mole of CO and 5.62 % mole of CO<sub>2</sub>

$$\begin{aligned}\text{Flow rate of carbon in CO} &= (4.92 \times 10^{-4}) \times 8.18 / 71.62 \\ &= 5.62 \times 10^{-5} \text{ mole of C/min}\end{aligned}$$

$$\begin{aligned}\text{Flow rate of carbon in CO}_2 &= (4.92 \times 10^{-4}) \times 5.62 / 71.62 \\ &= 3.86 \times 10^{-5} \text{ mole of C/min}\end{aligned}$$

$$\begin{aligned}\text{Thus, flow rate of total carbon outflow} &= (49.2 + 5.62 + 3.86) \times 10^{-5} \\ &= 5.86 \times 10^{-4} \text{ mole of C/min}\end{aligned}$$

## 2. Reaction Rate of Methane ( $-r_{\text{CH}_4}$ )

$$-r_{\text{CH}_4} = \frac{\Delta X_{\text{CH}_4}}{(W/F_{\text{CH}_4})}$$

From the same experimental data, catalyst weight of 2 g and  $5.87 \times 10^{-4}$  mole of CH<sub>4</sub>/min for methane feed rate:

$$\begin{aligned}W/F_{\text{CH}_4} &= (2 \times 10^{-3}) / (5.87 \times 10^{-4}) \\ &= 3.41 \text{ kg/(mole of CH}_4\text{/min)}\end{aligned}$$

From calculation of methane conversion,  $\Delta X_{\text{CH}_4} = 0.162$

$$\begin{aligned}\text{Thus, } -r_{\text{CH}_4} &= 0.162 / 3.41 \\ &= 0.047 \text{ mole of CH}_4\text{/(kg * min)}\end{aligned}$$

## 3. Thiele Modulus ( $\Phi$ )

From criteria of Weisz – Prater:

$$\Phi = \frac{(r_a \rho_s)_{\text{obs}} L^2}{D_{\text{eff}} C_{\text{as}}}$$

From Table C8 in Appendix C, these parameters could be indicated as follows:

$$\text{Observed reaction rate } (r_a)_{\text{obs}} = 0.0027 \text{ mole of CH}_4/(\text{kg} \cdot \text{sec})$$

$$\text{Observed particle density } (\rho_s)_{\text{obs}} = 589.64 \text{ kg/m}^3$$

$$\text{Pore length } (L) = 2.40 \times 10^{-9} \text{ m}$$

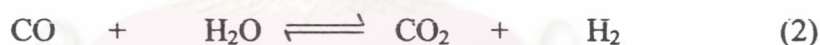
$$\text{Effective diffusivity } (D_{\text{eff}}) = 3.35 \times 10^{-3} \text{ m}^2/\text{sec}$$

$$\text{Concentration at outside particle surface } (C_{\text{as}}^s) = 10.85 \text{ mole of CH}_4/\text{m}^3$$

$$\begin{aligned} \text{Thus, } \Phi &= \frac{(0.0027 \times 589.64) (2.40 \times 10^{-9})^2}{(3.35 \times 10^{-3} \times 10.85)} \\ &= 2.52 \times 10^{-16} \end{aligned}$$

#### 4. Gas Composition in Thermodynamics Equilibrium

From Table C9 in Appendix C, for example, gas composition in thermodynamics equilibrium at 700 °C could be calculated with assumption of thermodynamics model of reaction, which was assumed in two reactions as follows:



Basis: 4.0 of H<sub>2</sub>O/CH<sub>4</sub> ratio, x mole of reacted CH<sub>4</sub> in reaction (1), z mole of reacted CO in reaction (2) and at atmospheric pressure

Thus, amount of gas composition in product (in unit mole) could be indicated as follows:

CH <sub>4</sub>	H <sub>2</sub> O	CO	CO <sub>2</sub>	H <sub>2</sub>	Total
1 - x	4 - x - z	x - z	z	3x + z	5 + 2x

From:  $P_i = y_i \cdot P_T$

When,  $P_i =$  partial pressure of component i

$y_i =$  mole fraction of component i

$P_T =$  total pressure (1 atm.)

Which could be rearranged:  $P_i = y_i \quad (1)$



And then partial pressure of each product gas could be indicated as follows:

$P_{CH_4}$	$P_{H_2O}$	$P_{CO}$	$P_{CO_2}$	$P_{H_2}$
$\frac{(1-x)}{(5+2x)}$	$\frac{(4-x-z)}{(5+2x)}$	$\frac{(x-z)}{(5+2x)}$	$\frac{z}{(5+2x)}$	$\frac{(3x+z)}{(5+2x)}$

From reactions (1) and (2), equilibrium constant ( $K_p$ ) of two reactions could be obtained from Figure 2.6 as follows:

Reaction	$K_p$ at 700 °C
(1)	0.00019
(2)	6.76083

Hence,

$$K_{p1} = P_{CO} \cdot P_{H_2}^3 / P_{CH_4} \cdot P_{H_2O}$$

$$0.00019 = (x-z)(3x+z)^3 / [(1-x)(4-x-z)(5+2x)^2] \quad (2)$$

$$K_{p2} = P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$$

$$6.76083 = z(3x+z) / [(x-z)(4-x-z)] \quad (3)$$

Solving equations (2) and (3) for giving variables that they could be taken to calculate mole fraction ( $y_i$ ) in equation (1). Then, mole fraction of each product gas could be indicated as follows:

x	z	$y_{CH_4}$	$y_{CO}$	$y_{CO_2}$	$y_{H_2}$
0.2705	0.2587	0.3423	0.0057	0.135	0.517

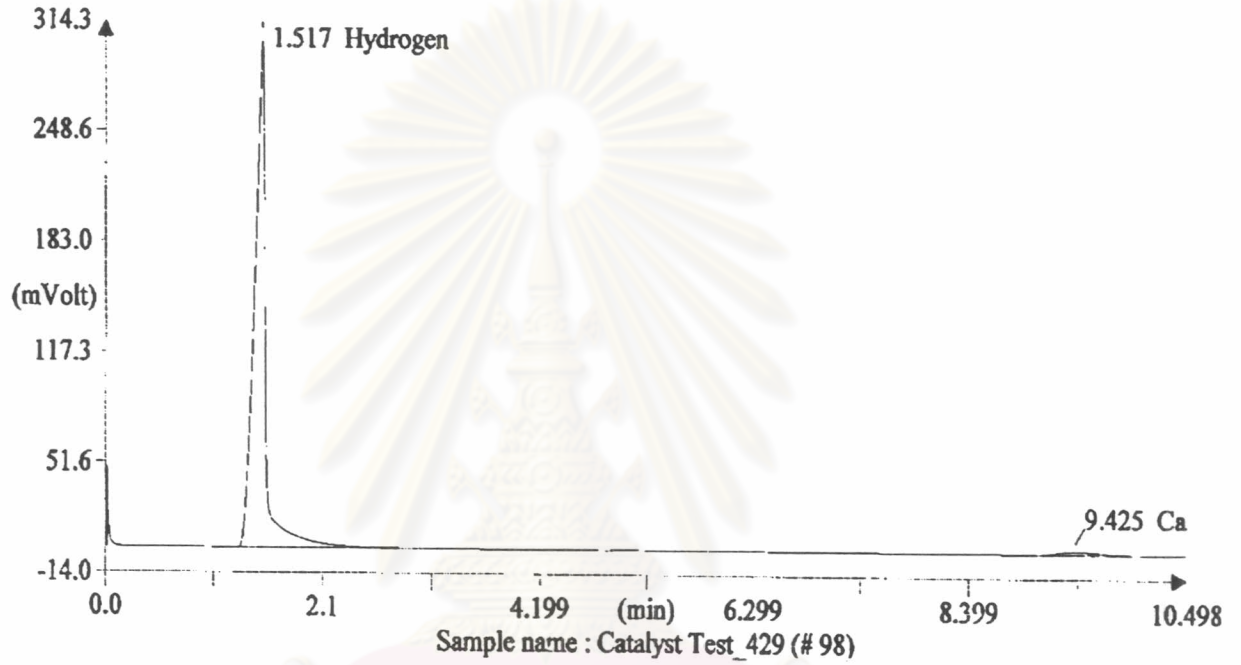
Thus, product gas composition at 700 °C in thermodynamics equilibrium could be indicated as follows:

Product Gas Composition (% mole)			
H <sub>2</sub>	CO	CH <sub>4</sub>	CO <sub>2</sub>
51.70	0.57	34.23	13.50

At other temperature, product gas composition could be also calculated with the same method.

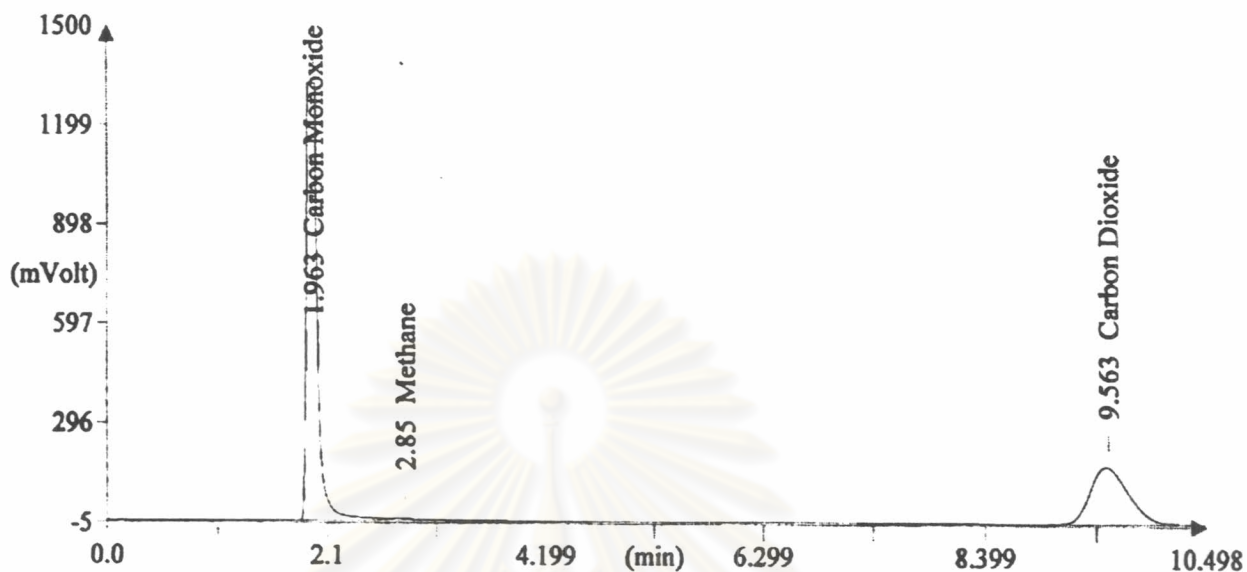
APPENDIX B

Gas Composition Analysis by Gas Chromatograph



Ident. Number (#)	Retention Time (min)	Area (.1 $\mu$ V $\cdot$ sec)	Component Name	Solution Conc (ppm)
1	1.517	22901780	Hydrogen	847953.300
4	9.425	540658	Carbon Dioxide	7.106

Figure B1 Chromatogram of gas composition using thermal conductivity detector (TCD).



Ident. Number (#)	Retention Time (min)	Area (.1* $\mu$ V*sec)	Component Name	Solution Conc (ppm)
1	1.963	103191700	Carbon Monoxid	155399.200
2	2.850	112641	Methane	149.722
3	9.563	43691030	Carbon Dioxide	65713.290

Figure B2 Chromatogram of gas composition using flame ionization detector (FID).

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**APPENDIX C**  
**Experimental Data**

**Table C1** The experiment for determination of rate equation at excess steam condition, catalyst weight of 2 g and atmospheric pressure.

Reaction Temperature (°C)	Feed Flow rate		H <sub>2</sub> O/CH <sub>4</sub> Ratio	P <sub>CH<sub>4</sub></sub> =Y <sub>CH<sub>4</sub></sub> *P <sub>T</sub> (atm)	ln(P <sub>CH<sub>4</sub></sub> )	Product Gas Composition (% mole)				Catalyst Weight Flow rate of CH <sub>4</sub> (W/F <sub>CH<sub>4</sub></sub> , kg min/mole)	Methane Conversion (ΔX <sub>CH<sub>4</sub></sub> )	-r <sub>CH<sub>4</sub></sub> = $\frac{\Delta X_{CH_4}}{W/F_{CH_4}}$ (mole/kg min)	ln(-r <sub>CH<sub>4</sub></sub> )
	CH <sub>4</sub> (mole/min)	H <sub>2</sub> O (mole/min)				H <sub>2</sub>	CO	CH <sub>4</sub>	CO <sub>2</sub>				
700	5.87E-04	0.15	255.70	3.90E-03	-5.548	14.59	8.18	71.62	5.62	3.50	0.162	4.61E-02	-3.077
	2.92E-04	0.15	513.38	1.94E-03	-6.243	34.59	7.72	52.53	5.06	7.04	0.196	2.78E-02	-3.583
	2.92E-04	0.15	513.38	1.94E-03	-6.243	36.89	8.00	50.61	4.50	7.04	0.198	2.82E-02	-3.570
	1.46E-04	0.15	1024.37	9.75E-04	-6.933	45.91	6.39	42.38	5.32	14.04	0.216	1.54E-02	-4.173
	7.33E-05	0.15	2047.16	4.88E-04	-7.625	55.54	5.80	35.69	2.97	28.06	0.197	7.03E-03	-4.958
750	4.46E-04	0.15	336.53	2.96E-03	-5.822	37.32	10.92	44.56	7.21	4.61	0.289	6.27E-02	-2.770
	2.78E-04	0.15	539.76	1.85E-03	-6.293	47.33	8.75	35.97	7.95	7.40	0.317	4.28E-02	-3.150
	1.39E-04	0.15	1077.01	9.28E-04	-6.983	54.03	9.27	30.28	6.42	14.76	0.341	2.31E-02	-3.767
	6.97E-05	0.15	2152.36	4.64E-04	-7.675	59.00	7.52	26.41	7.08	29.50	0.356	1.21E-02	-4.417
800	4.25E-04	0.15	352.98	2.83E-03	-5.869	48.41	12.18	30.42	9.00	4.84	0.410	8.48E-02	-2.467
	2.65E-04	0.15	566.14	1.76E-03	-6.341	52.04	12.37	26.29	9.30	7.76	0.452	5.82E-02	-2.843
	1.33E-04	0.15	1129.65	8.84E-04	-7.031	60.79	10.39	21.13	7.69	15.48	0.461	2.98E-02	-3.514
	6.64E-05	0.15	2257.56	4.43E-04	-7.722	64.58	11.86	19.45	4.12	30.95	0.451	1.46E-02	-4.229
850	5.08E-04	0.15	295.12	3.38E-03	-5.691	59.24	19.18	14.05	7.53	4.05	0.655	1.62E-01	-1.820
	4.06E-04	0.15	369.43	2.70E-03	-5.915	68.37	17.86	5.95	7.81	5.06	0.812	1.60E-01	-1.831
	2.53E-04	0.15	592.52	1.68E-03	-6.386	77.74	18.18	1.11	2.98	8.12	0.950	1.17E-01	-2.146
	1.27E-04	0.15	1182.29	8.45E-04	-7.076	77.79	16.94	0.66	4.62	16.21	0.970	5.99E-02	-2.815
	6.35E-05	0.15	2362.76	4.23E-04	-7.768	81.16	15.31	0.76	2.77	32.39	0.960	2.96E-02	-3.519



**Table C2** The experiment for determination of rate equation at non-excess steam condition, catalyst weight of 2 g and atmospheric pressure.

Reaction Temperature (°C)	Feed Flow rate		H <sub>2</sub> O/CH <sub>4</sub> Ratio	P <sub>CH<sub>4</sub></sub> =Y <sub>CH<sub>4</sub></sub> *P <sub>T</sub> (atm)	P <sub>H<sub>2</sub>O</sub> =Y <sub>H<sub>2</sub>O</sub> *P <sub>T</sub> (atm)	ln (P <sub>CH<sub>4</sub></sub> )	ln (P <sub>H<sub>2</sub>O</sub> )	Product Gas Composition (% mole)				Catalyst Weight Flow rate of CH <sub>4</sub> (W/F <sub>CH<sub>4</sub></sub> , kg min/mole)	Methane Conversion (Δ X <sub>CH<sub>4</sub></sub> )	-r <sub>CH<sub>4</sub></sub> = Δ X <sub>CH<sub>4</sub></sub> (W/F <sub>CH<sub>4</sub></sub> ) (mole/kg min)	ln (-r <sub>CH<sub>4</sub></sub> )
	CH <sub>4</sub> (mole/min)	H <sub>2</sub> O (mole/min)						H <sub>2</sub>	CO	CH <sub>4</sub>	CO <sub>2</sub>				
								H <sub>2</sub>	CO	CH <sub>4</sub>	CO <sub>2</sub>				
700	1.25E-03	2.49E-03	2.0	0.333	0.667	-1.099	-0.405	8.22	0.32	90.69	0.77	1.65	0.0118	0.0072	-4.9384
	1.25E-03	4.98E-03	4.0	0.200	0.800	-1.609	-0.223	9.36	0.20	89.92	0.53	1.65	0.0080	0.0049	-5.3236
	1.25E-03	7.47E-03	6.0	0.143	0.857	-1.946	-0.154	15.04	0.14	84.45	0.38	1.65	0.0061	0.0037	-5.6008
	1.25E-03	9.97E-03	8.0	0.111	0.889	-2.197	-0.118	16.41	0.11	83.18	0.30	1.65	0.0049	0.0030	-5.8140
750	1.18E-03	2.37E-03	2.0	0.333	0.667	-1.099	-0.405	9.49	0.40	89.31	0.79	1.74	0.0132	0.0076	-4.8768
	1.18E-03	4.74E-03	4.0	0.200	0.800	-1.609	-0.223	10.09	0.25	89.13	0.53	1.74	0.0087	0.0050	-5.2961
	1.18E-03	7.11E-03	6.0	0.143	0.857	-1.946	-0.154	17.38	0.18	82.09	0.35	1.74	0.0064	0.0037	-5.5955
	1.18E-03	9.48E-03	8.0	0.111	0.889	-2.197	-0.118	20.73	0.14	78.87	0.27	1.74	0.0051	0.0030	-5.8252
800	1.13E-03	2.26E-03	2.0	0.333	0.667	-1.099	-0.405	10.12	0.45	88.52	0.91	1.82	0.0151	0.0083	-4.7903
	1.13E-03	4.52E-03	4.0	0.200	0.800	-1.609	-0.223	11.07	0.31	88.03	0.59	1.82	0.0101	0.0056	-5.1893
	1.13E-03	6.78E-03	6.0	0.143	0.857	-1.946	-0.154	19.98	0.22	79.41	0.39	1.82	0.0076	0.0042	-5.4746
	1.13E-03	9.04E-03	8.0	0.111	0.889	-2.197	-0.118	22.86	0.18	76.67	0.29	1.82	0.0061	0.0034	-5.6936
850	1.08E-03	2.16E-03	2.0	0.333	0.667	-1.099	-0.405	10.87	0.51	87.62	1.00	1.90	0.0170	0.0089	-4.7217
	1.08E-03	4.32E-03	4.0	0.200	0.800	-1.609	-0.223	11.68	0.37	87.32	0.62	1.90	0.0113	0.0059	-5.1315
	1.08E-03	6.48E-03	6.0	0.143	0.857	-1.946	-0.154	21.59	0.25	77.75	0.41	1.90	0.0084	0.0044	-5.4237
	1.08E-03	8.63E-03	8.0	0.111	0.889	-2.197	-0.118	24.26	0.21	75.23	0.30	1.90	0.0067	0.0035	-5.6476

**Table C3** The experiment about the effect of steam to methane ratio on methane conversion and reaction rate at 850 °C, non-excess steam condition, catalyst weight of 2 g and atmospheric pressure.

Feed Flow rate		H <sub>2</sub> O/CH <sub>4</sub> Ratio	P <sub>CH<sub>4</sub></sub> =Y <sub>CH<sub>4</sub></sub> *P <sub>T</sub> ( atm )	P <sub>H<sub>2</sub>O</sub> =Y <sub>H<sub>2</sub>O</sub> *P <sub>T</sub> ( atm )	Product Gas Composition ( % mole )				Catalyst Weight Flow rate of CH <sub>4</sub> (W/F <sub>CH<sub>4</sub></sub> , kg min/mole)	Methane Conversion ( Δ X <sub>CH<sub>4</sub></sub> )	-r <sub>CH<sub>4</sub></sub> (mole/kg min)
CH <sub>4</sub> (mole/min)	H <sub>2</sub> O (mole/min)				H <sub>2</sub>	CO	CH <sub>4</sub>	CO <sub>2</sub>			
5.08E-04	1.02E-03	2.0	0.333	0.667	17.05	4.35	69.64	8.96	4.05	0.160	0.050
4.06E-04	8.12E-04	2.0	0.333	0.667	19.64	6.26	63.33	10.77	5.06	0.212	
2.53E-04	5.06E-04	2.0	0.333	0.667	28.26	9.58	59.04	12.12	8.12	0.302	
1.27E-04	2.54E-04	2.0	0.333	0.667	42.78	9.70	34.96	12.57	16.21	0.389	
6.35E-05	1.27E-04	2.0	0.333	0.667	54.97	8.97	23.85	12.22	32.39	0.470	
5.08E-04	2.03E-03	4.0	0.200	0.800	27.96	2.76	59.55	9.73	4.05	0.173	0.050
4.06E-04	1.62E-03	4.0	0.200	0.800	42.84	4.27	44.15	8.74	5.06	0.228	
2.53E-04	1.01E-03	4.0	0.200	0.800	49.13	6.99	34.51	9.38	8.12	0.322	
1.27E-04	5.07E-04	4.0	0.200	0.800	54.96	10.47	23.74	10.83	16.21	0.473	
6.35E-05	2.54E-04	4.0	0.200	0.800	60.81	11.76	16.84	10.59	32.39	0.570	
5.08E-04	3.05E-03	6.0	0.143	0.857	42.83	4.11	46.44	6.62	4.05	0.188	0.062
4.06E-04	2.44E-03	6.0	0.143	0.857	50.83	5.38	37.19	6.60	5.06	0.244	
2.53E-04	1.52E-03	6.0	0.143	0.857	60.47	6.24	25.31	7.98	8.12	0.360	
1.27E-04	7.61E-04	6.0	0.143	0.857	60.37	12.00	18.34	9.29	16.21	0.537	
6.35E-05	3.81E-04	6.0	0.143	0.857	63.81	13.80	12.51	9.88	32.39	0.654	
5.08E-04	4.07E-03	8.0	0.111	0.889	48.00	4.70	41.41	5.89	4.05	0.204	0.073
4.06E-04	3.25E-03	8.0	0.111	0.889	56.38	5.85	30.73	7.04	5.06	0.295	
2.53E-04	2.03E-03	8.0	0.111	0.889	53.93	8.81	25.64	11.62	8.12	0.443	
1.27E-04	1.01E-03	8.0	0.111	0.889	56.83	15.64	16.22	11.30	16.21	0.624	
6.35E-05	5.08E-04	8.0	0.111	0.889	63.11	15.49	11.22	10.18	32.39	0.696	

**Table C4** The experiment about the mechanism of reaction and determination of rate equation by Langmuir-Hinshelwood model at 850 °C, catalyst weight of 2 g and atmospheric pressure.

Feed Flow rate		H <sub>2</sub> O/CH <sub>4</sub> Ratio	P <sub>CH<sub>4</sub></sub> =Y <sub>CH<sub>4</sub></sub> *P <sub>T</sub> ( atm )	P <sub>H<sub>2</sub>O</sub> =Y <sub>H<sub>2</sub>O</sub> *P <sub>T</sub> ( atm )	Product Gas Composition ( % mole )				Catalyst Weight Flow rate of CH <sub>4</sub> (W/F <sub>CH<sub>4</sub></sub> , kg min/mole)	Methane Conversion ( Δ X <sub>CH<sub>4</sub></sub> )	-r <sub>CH<sub>4</sub></sub> (mole/kg min)
CH <sub>4</sub> (mole/min)	H <sub>2</sub> O (mole/min)				H <sub>2</sub>	CO	CH <sub>4</sub>	CO <sub>2</sub>			
5.08E-04	1.02E-03	2.0	0.333	0.667	17.05	4.35	69.64	8.96	4.05	0.160	0.050
4.06E-04	8.12E-04	2.0	0.333	0.667	19.64	6.26	63.33	10.77	5.06	0.212	
2.53E-04	5.06E-04	2.0	0.333	0.667	28.26	9.58	50.04	12.12	8.12	0.302	
1.27E-04	2.54E-04	2.0	0.333	0.667	42.78	9.70	34.96	12.57	16.21	0.389	
6.35E-05	1.27E-04	2.0	0.333	0.667	54.97	8.97	23.85	12.22	32.39	0.470	
5.08E-04	2.03E-03	4.0	0.200	0.800	27.96	2.76	59.55	9.73	4.05	0.173	0.050
4.06E-04	1.62E-03	4.0	0.200	0.800	42.84	4.27	44.15	8.74	5.06	0.228	
2.53E-04	1.01E-03	4.0	0.200	0.800	49.13	6.99	34.51	9.38	8.12	0.322	
1.27E-04	5.07E-04	4.0	0.200	0.800	54.96	10.47	23.74	10.83	16.21	0.473	
6.35E-05	2.54E-04	4.0	0.200	0.800	60.81	11.76	16.84	10.59	32.39	0.570	
5.08E-04	3.05E-03	6.0	0.143	0.857	42.83	4.11	46.44	6.62	4.05	0.188	0.062
4.06E-04	2.44E-03	6.0	0.143	0.857	50.83	5.38	37.19	6.60	5.06	0.244	
2.53E-04	1.52E-03	6.0	0.143	0.857	60.47	6.24	25.31	7.98	8.12	0.360	
1.27E-04	7.61E-04	6.0	0.143	0.857	60.37	12.00	18.34	9.29	16.21	0.537	
6.35E-05	3.81E-04	6.0	0.143	0.857	63.81	13.80	12.51	9.88	32.39	0.654	
5.08E-04	4.07E-03	8.0	0.111	0.889	48.00	4.70	41.41	5.89	4.05	0.204	0.073
4.06E-04	3.25E-03	8.0	0.111	0.889	55.38	5.85	30.73	7.04	5.06	0.295	
2.53E-04	2.03E-03	8.0	0.111	0.889	53.93	8.81	25.64	11.62	8.12	0.443	
1.27E-04	1.01E-03	8.0	0.111	0.889	56.83	15.64	16.22	11.30	16.21	0.624	
2.53E-04	0.15	592.52	1.68E-03	0.998	77.74	18.18	1.11	2.98	8.12	0.950	
1.27E-04	0.15	1182.29	8.45E-04	0.999	77.79	16.94	0.66	4.62	16.21	0.970	5.99E-02
6.35E-05	0.15	2362.76	4.23E-04	0.999	81.16	15.31	0.76	2.77	32.39	0.960	2.96E-02



**Table C5** Calculation of variables for determination of rate equation at excess steam condition, catalyst weight of 2 g and atmospheric pressure.

Reaction Temperature (°C)	1/T	ln k	k	CH <sub>4</sub> Order	ln k <sub>o</sub>	k <sub>o</sub>	-Ea/R	Ea (cal/mole)
700	1.03E-03	1.6466	5.1893	0.9080	11.264	7.796E+04	-9423.7	18,726.78
750	9.78E-04	1.9430	6.9797	0.8918				
800	9.32E-04	2.4854	12.0059	0.9567				
850	8.90E-04	2.9094	18.3458	0.9235				

**Table C6** Calculation of variables for determination of rate equation at non-excess steam condition, catalyst weight of 2 g and atmospheric pressure.

Reaction Temperature (°C)	1/T	ln k	k	CH <sub>4</sub> Order	H <sub>2</sub> O Order	ln k <sub>o</sub>	k <sub>o</sub>	-Ea/R	Ea (cal/mole)
700	1.03E-03	-3.7565	0.02337	0.9128	0.4413	0.8247	2.2812	-4549.7	9,041.16
750	9.78E-04	-3.6260	0.02662	0.9776	0.4357				
800	9.32E-04	-3.5938	0.02749	0.9331	0.4224				
850	8.90E-04	-3.5072	0.02998	0.9519	0.4157				

**Table C7** The experiment about the effect of catalyst weight on methane conversion, hydrogen to carbon monoxide ratio and product gas composition at 850 °C,  $1.27 \times 10^{-4}$  mole/min of methane feed rate, 0.15 mole/min of steam feed rate and atmospheric pressure.

Catalyst Weight (g)	Product Gas Composition (% mole)				Methane Conversion ( $\Delta X_{CH_4}$ ), (%)	H <sub>2</sub> /CO Ratio
	H <sub>2</sub>	CO	CH <sub>4</sub>	CO <sub>2</sub>		
2.0561	77.15	12.66	6.60	3.59	71.11	6.10
5.0395	86.10	11.36	2.14	0.40	84.59	7.58
8.0898	85.22	12.57	1.82	0.39	87.69	6.78
10.0882	86.20	13.05	0.50	0.26	96.40	6.61



**Table C8** Calculation of Thiele modulus ( $\Phi$ ) in the effect of diffusion on rate of reaction.

Observed reaction rate ( $r_a$ ) <sub>obs</sub> , mole/kg sec	Observed particle density ( $\rho_s$ ) <sub>obs</sub> , kg/m <sup>3</sup>	Pore length (L), m	Effective diffusivity ( $D_{eff}$ ), m <sup>2</sup> /sec	Concentration at outside particle surface ( $C_{as}^s$ ), mole/m <sup>3</sup>	$\Phi = \eta\phi^2 = \frac{(r_a\rho_s)_{obs} L^2}{D_{eff} C_{as}^s}$
8.33E-04	589.64	2.40E-09	3.35E-03	10.85	7.79E-17
8.33E-04	589.64	2.40E-09	3.35E-03	10.84	7.79E-17
1.03E-03	589.64	2.40E-09	3.35E-03	10.84	9.66E-17
1.22E-03	589.64	2.40E-09	3.35E-03	10.84	1.14E-16
3.33E-03	589.64	2.40E-09	3.35E-03	10.85	3.12E-16
2.70E-03	589.64	2.40E-09	3.35E-03	10.85	2.52E-16
2.67E-03	589.64	2.40E-09	3.35E-03	10.84	2.49E-16
1.95E-03	589.64	2.40E-09	3.35E-03	10.85	1.82E-16
9.98E-04	589.64	2.40E-09	3.35E-03	10.84	9.33E-17
4.93E-04	589.64	2.40E-09	3.35E-03	10.85	4.61E-17

**Table C9** The experiment for determination of thermodynamics model of reaction at 700-850 °C, steam to methane ratio of 4.0,  $1.27 \times 10^{-4}$  to  $1.46 \times 10^{-4}$  mole/min of methane feed rate,  $5.07 \times 10^{-4}$  to  $5.86 \times 10^{-4}$  mole/min of steam feed rate and catalyst weight of 5 g.

Reaction Temperature (°C)	Product Gas Composition (% mole)				Methane Conversion ( $\Delta X_{CH_4}$ ), (%)	H <sub>2</sub> /CO Ratio
	H <sub>2</sub>	CO	CH <sub>4</sub>	CO <sub>2</sub>		
700	36.48	5.22	48.34	9.96	23.90	6.98
Equilibrium	51.70	0.57	34.23	13.50	29.13	90.70
750	47.61	6.96	35.22	10.20	32.76	6.84
Equilibrium	60.74	1.67	23.65	13.94	39.76	36.38
800	57.04	8.86	24.26	9.85	43.54	6.44
Equilibrium	68.55	4.26	13.24	13.95	57.90	16.09
850	65.57	11.38	15.14	7.90	56.02	5.76
Equilibrium	72.17	7.53	7.91	12.39	71.58	9.58

## APPENDIX D

### Preparation of Nickel Magnesia Solid Solution Catalyst ( $\text{Ni}_{0.03}\text{Mg}_{0.97}\text{O}$ )

The nickel-magnesia solid solution catalyst containing low nickel has shown excellent stability and no carbon deposition in the methane reforming by carbon dioxide. It was also found that the small nickel metal particle interaction with support surface is effective for the inhibition of carbon formation.

Nickel magnesia solid solution was prepared by the co-precipitation method. For example of preparation 5 g. of catalyst, From mixed aqueous solution of nickel acetate (0.8929 g.) and magnesium nitrate (29.95 g.) in distilled water 240 cc. The solution was stirred well at 60°C. The solution was mixed rapidly with potassium carbonate solution for 30 min., their mixed carbonate was deposited by potassium carbonate aqueous solution (16.53 g. in distilled water 120 cc. or concentration 1.0 M). After being filtered and washed with hot water (1 l.), The precipitate was dried overnight at 120°C, and then the catalyst was calcined in air at 950°C for 20 h. After calcination the catalyst was pressed at 600kg/cm<sup>2</sup> and sieved for 20/40 mesh. Then the catalyst was in the form  $\text{Ni}_{0.03}\text{Mg}_{0.97}\text{O}$ . (MW = 41.34)

#### Steps of preparation

1. Preparing the aqueous solution of  $\text{Ni}(\text{CH}_3\text{COO})_2$  and  $\text{Mg}(\text{NO}_3)_2$  for 0.5 mole/L being stirred at 60°C.
2. Preparing the aqueous solution of  $\text{K}_2\text{CO}_3$  for 1 mole/L.
3. Mixing two solutions immediately and keep always 60°C for 30 min.
4. Washing with hot water (90°C) for 1 litres.
5. Drying overnight at 120°C.
6. Calcination at 950°C for 20 h.
7. Pressing at 600kg/cm<sup>2</sup> and sieving 20/40 mesh.

**VITA**

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