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APPENDICES

Appendix A Calculations

1. Catalysts Preparation

1.1 Amount of Ni loading

Example Prepared 1 g of 3wt.%Ni/KL catalyst ;

- Amount of Ni (MW = 58.69 g/mole)

$$\begin{aligned} \text{Ni} &= 1 * (3/100) \text{ g} \\ &= 0.03 \text{ g} \end{aligned}$$

- Amount of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (MW = 290.81 g/mole)

$$\begin{aligned} \text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} &= 0.03 * (290.81 / 58.69) \text{ g} \\ &= 0.1486 \text{ g} \end{aligned}$$

- Amount of KL zeolite

$$\begin{aligned} \text{KL zeolite} &= 1 - 0.03 \text{ g} \\ &= 0.97 \text{ g} \end{aligned}$$

1.2 Amount of Mg loading

Example Prepare 1g of 2%Mg-7%Ni/KL catalyst ;

- Amount of Ni (MW = 58.69 g/mole)

$$\begin{aligned} \text{Ni} &= 1 * (7/100) \text{ g} \\ &= 0.07 \text{ g} \end{aligned}$$

- Amount of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (MW = 290.81 g/mole)

$$\begin{aligned} \text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} &= 0.07 * (290.81 / 58.69) \text{ g} \\ &= 0.3468 \text{ g} \end{aligned}$$

- Amount of Mg (MW = 24.305 g/mole)

$$\begin{aligned} \text{Mg} &= 1 * (2/100) \text{ g} \\ &= 0.02 \text{ g} \end{aligned}$$

- Amount of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (MW = 256.42 g/mole)

$$\begin{aligned} \text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} &= 0.02 * (256.41 / 24.305) \text{ g} \\ &= 0.211 \text{ g} \end{aligned}$$

- Amount of KL zeolite

$$\text{KL zeolite} = 1 - 0.07 - 0.02 \text{ g} = 0.91 \text{ g}$$

1.3 Amount of Ca loading

Example Prepare 1g of 2%Ca-7%Ni/KL catalyst ;

- Amount of Ni (MW = 58.69 g/mole)

$$\text{Ni} = 1 * (7/100) \text{ g}$$

$$= 0.07 \text{ g}$$

- Amount of Ni(NO₃)₂.6H₂O (MW = 290.81 g/mole)

$$\text{Ni(NO}_3)_2\cdot 6\text{H}_2\text{O} = 0.07 * (290.81/58.69) \text{ g}$$

$$= 0.3468 \text{ g}$$

- Amount of Ca (MW = 40.075 g/mole)

$$\text{Ca} = 1 * (2/100) \text{ g}$$

$$= 0.02 \text{ g}$$

- Amount of Ca(NO₃)₂.4H₂O (MW = 236.15 g/mole)

$$\text{Ca(NO}_3)_2\cdot 4\text{H}_2\text{O} = 0.02 * (236.15/40.075) \text{ g}$$

$$= 0.1178 \text{ g}$$

- Amount of KL zeolite

$$\text{KL zeolite} = 1 - 0.07 - 0.02 \text{ g}$$

$$= 0.91 \text{ g}$$

2. Conversion and Selectivity

2.1 CH₄ Conversion

$$\text{CH}_4 \text{ conversion} = \frac{\text{CH}_{4,\text{in}} - \text{CH}_{4,\text{out}}}{\text{CH}_{4,\text{in}}} \times 100$$

Where CH_{4,in} = CH₄ fed to the reactor

CH_{4,out} = CH₄ out of reactor

2.2 CO₂ Conversion

$$\text{CO}_2 \text{ conversion} = \frac{\text{CO}_{2,\text{in}} - \text{CO}_{2,\text{out}}}{\text{CO}_{2,\text{in}}} \times 100$$

Where $\text{CO}_{2,\text{in}} = \text{CO}_2$ fed to the reactor

$\text{CO}_{2,\text{out}} = \text{CO}_2$ out of reactor

2.3 H₂ Selectivity

$$\text{H}_2 \text{ selectivity} = \frac{y_{(H_2,\text{out})}}{y_{(H_2,\text{out})} + y_{(CO,\text{out})}} \times 100$$

Where $y_{(H_2,\text{out})}$ = Mole fraction of H₂ in the effluent stream

$y_{(CO,\text{out})}$ = Mole fraction of CO in the effluent stream

2.4 H₂ Production

$$\text{H}_2 \text{ production} = F_{\text{out}} \times y_{(H_2,\text{out})} \text{ ml/min}$$

Then, convert to mole/(min*g-cat)

Where F_{out} = Total flow rate of feed stream that feed to the reactor

$y_{(H_2,\text{out})}$ = Mole fraction of CO in the effluent stream

3. Metal crystallite size

The thickness of crystallite (L) from Scherrer equation;

$$L_{k\bar{h}\bar{l}} = k\lambda / (\beta \cos \theta_0)$$

Where λ = the x-ray wavelength

β = the peak width (expressed in radian)

θ_0 = the angle between the beam and the normal on the reflecting plane (expressed in radian)

k = a constant (or shape factor) (often take as 1)

4. KH zeolite synthesis

Synthesis KH zeolite with molar ratio of SiO₂ : 0.1Al₂O₃ : 4K₂O : 410H₂O

Base on H₂O 60 ml (so, divided by 123)

- Amount SiO_2 (MW = 60.086 g/mole)

$$\begin{aligned}\text{SiO}_2 &= (1 * 60.086) / 123 \text{ g} \\ &= 0.4885 \text{ g}\end{aligned}$$

$$\begin{aligned}\text{So, amount of Ludox HS40 colloidal silica} &= 0.4885 * (40 / 100) \\ &= 1.221 \text{ g}\end{aligned}$$

- Amount of Aluminium Isopropoxide, $\text{C}_9\text{H}_{21}\text{AlO}_3$ (MW = 204.25 g/mole)

$$\begin{aligned}\text{Al} &= (0.1 * 2 * 27) / 123 \text{ g} \quad (\text{MW of Al} = 27 \text{ g/mole}) \\ &= 0.0439 \text{ g}\end{aligned}$$

$$\begin{aligned}\text{So, amount of Aluminium Isopropoxide} &= 0.0439 * (204.25 / 27) \text{ g} \\ &= 0.332 \text{ g}\end{aligned}$$

- Amount of KOH (MW = 56.11)

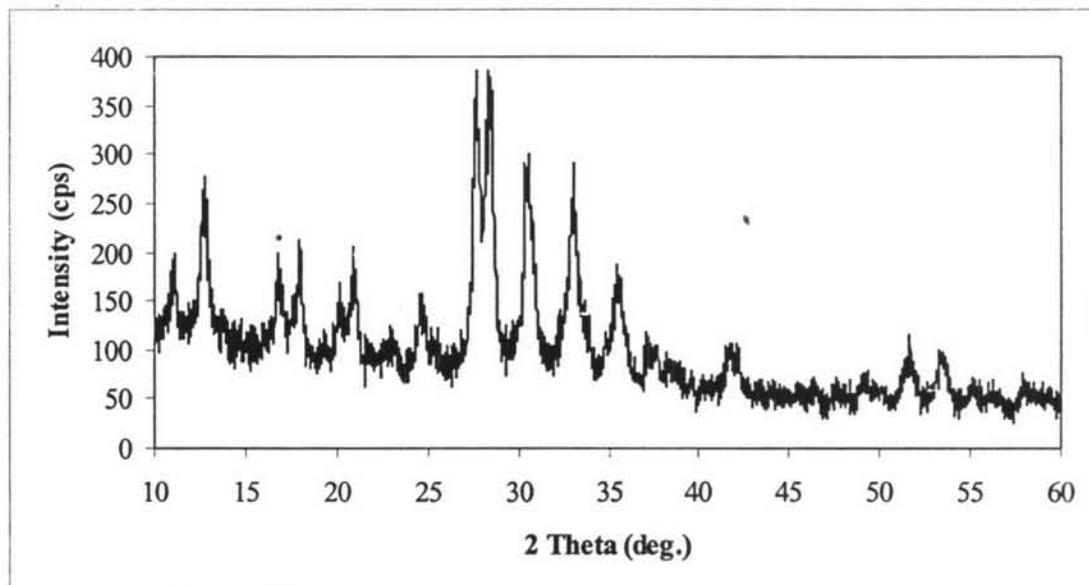
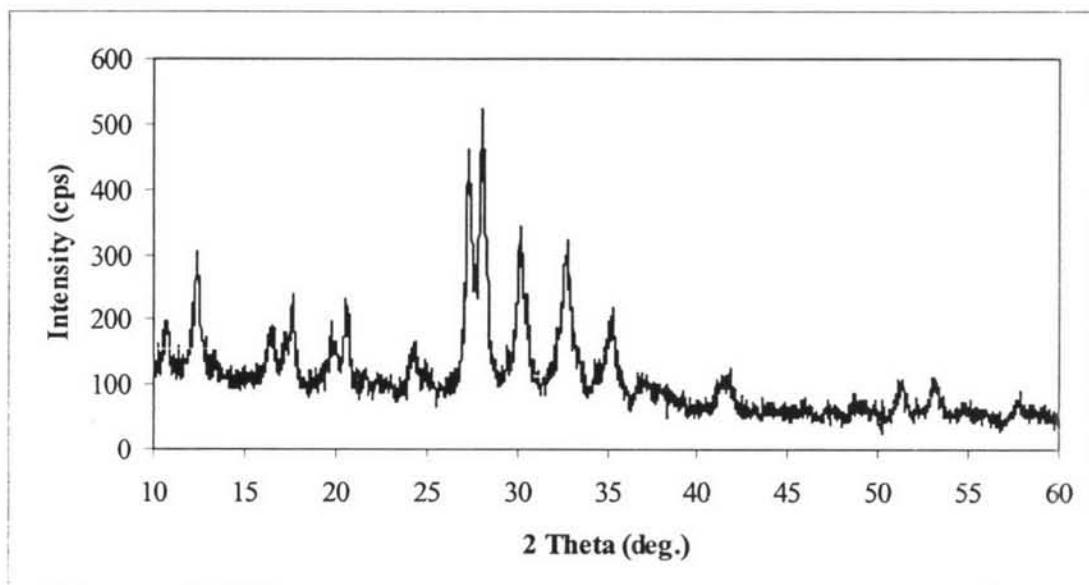
$$\begin{aligned}\text{K} &= (4 * 2 * 39.098) / 123 \text{ g} \quad (\text{MW of K} = 39.098 \text{ g/mole}) \\ &= 2.5429 \text{ g}\end{aligned}$$

$$\begin{aligned}\text{So, amount of KOH} &= 2.5429 * (56.11 / 39.098) \text{ g} \\ &= 3.649 \text{ g}\end{aligned}$$

- Amount of H_2O

$$\begin{aligned}\text{There are H}_2\text{O from Aluminium Isopropoxide} &= 1.221 * (60 / 100) \text{ ml} \\ &= 0.732 \text{ ml}\end{aligned}$$

$$\begin{aligned}\text{So, need H}_2\text{O} &= 60 - 0.732 \text{ ml} \\ &= 59.268 \text{ ml}\end{aligned}$$

Appendix B Effect of time to the KH zeolite crystallization**Figure B1** KH zeolite synthesize with aging time 30 hours.**Figure B2** KH zeolite synthesize with aging time 40 hours.

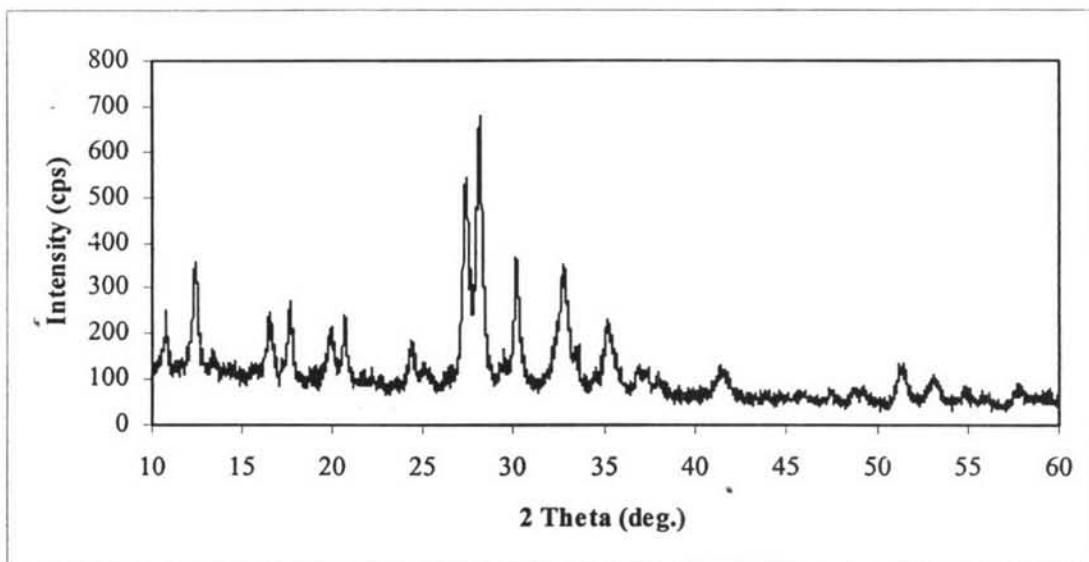


Figure B3 KH zeolite synthesize with aging time 50 hours.

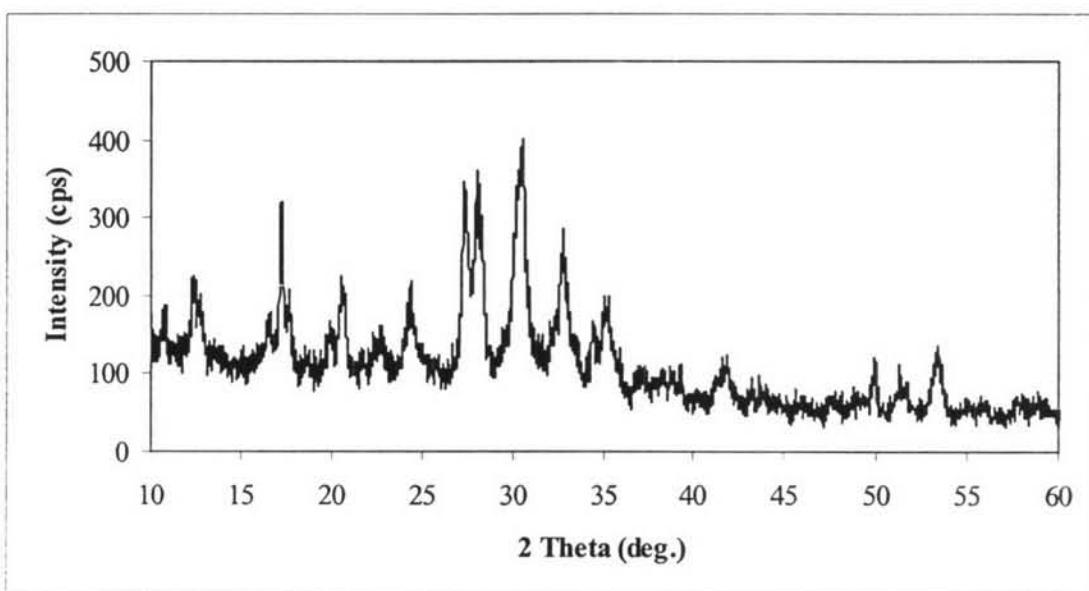


Figure B4 KH zeolite synthesize with aging time 60 hours.

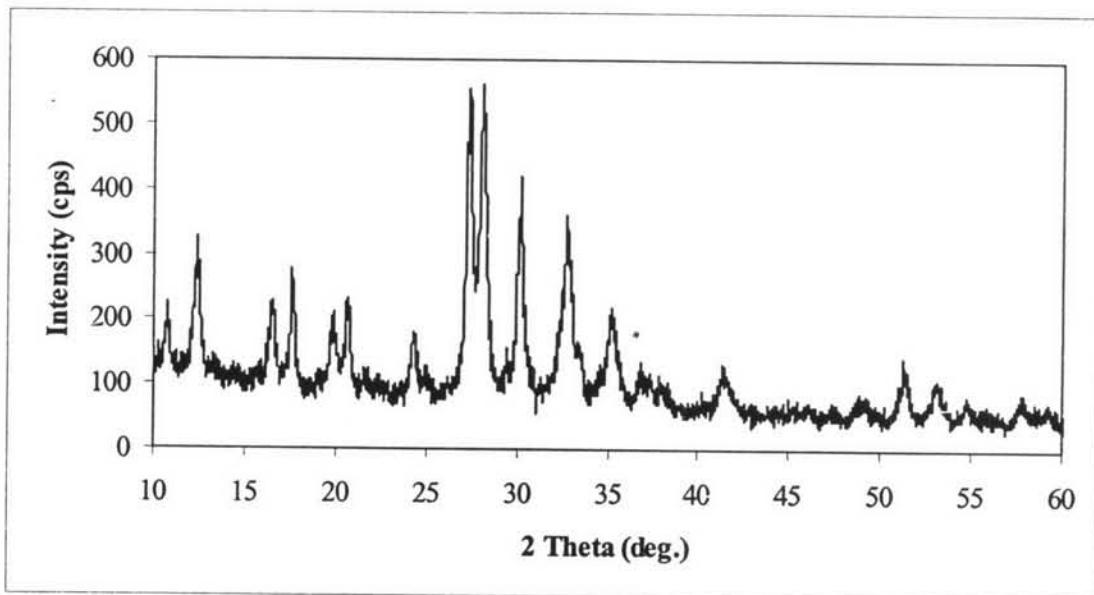


Figure B5 KH zeolite synthesize with aging time 70 hours.

Appendix C Experimental data

Table C1 Effect of Ni loading: CH₄ conversion, CO₂ conversion, H₂ selectivity, H₂ production(mol/g-cat.)*10²

3%Ni/KL		CH ₄			CO ₂			H ₂			
Time	F _{out}	area	y _{out}	%conversion	area	y _{out}	%conversion	y _{out,H2}	y _{out,CO}	Selectivity	Production
33	121.087	141617.5	0.0310	92.32	347580.0	0.0455	88.95	0.5947	0.3288	64.40	87.76
51	121.087	140996.5	0.0311	92.30	343818.0	0.0453	89.00	0.5930	0.3306	64.21	87.51
69	120.731	146358.0	0.0325	91.96	359353.0	0.0477	88.45	0.5902	0.3295	64.18	86.84
87	120.694	152057.5	0.0342	91.54	370000.5	0.0497	87.96	0.5850	0.3311	63.87	86.03
105	120.694	156548.0	0.0353	91.26	378316.0	0.0509	87.68	0.5838	0.3299	63.90	85.86
123	120.656	161034.5	0.0364	90.99	384708.5	0.0519	87.45	0.5829	0.3288	63.94	85.70
141	119.250	164615.5	0.0375	90.84	389685.5	0.0529	87.31	0.5795	0.3301	63.72	84.23
159	119.318	169504.5	0.0386	90.57	396777.5	0.0539	87.08	0.5790	0.3285	63.81	84.21
177	119.318	168803.0	0.0386	90.58	396427.0	0.0540	87.05	0.5775	0.3299	63.65	83.99
195	119.757	173193.5	0.0403	90.13	402829.0	0.0556	86.61	0.5699	0.3342	63.04	83.21
213	119.520	175594.5	0.0408	90.01	404940.5	0.0559	86.56	0.5693	0.3340	63.03	82.95
231	119.283	177273.5	0.0415	89.86	406154.0	0.0564	86.47	0.5664	0.3356	62.79	82.37
249	119.418	181477.5	0.0419	89.77	407417.0	0.0559	86.56	0.5699	0.3323	63.16	82.96
267	119.637	184192.5	0.0434	89.38	409702.5	0.0572	86.23	0.5627	0.3367	62.56	82.09
285	119.233	186129.0	0.0435	89.39	406018.5	0.0564	86.48	0.5662	0.3340	62.89	82.30
300	118.912	189116.0	0.0443	89.23	410975.0	0.0571	86.34	0.5655	0.3332	62.92	81.97

Table C2 Effect of Ni loading: CH₄ conversion, CO₂ conversion, H₂ selectivity, H₂ production(mol/g-cat.)*10²

5%Ni/KL		CH ₄			CO ₂			H ₂			
Time	F _{out}	area	y _{out}	%conversion	area	y _{out}	%conversion	y _{out,H2}	y _{out,CO}	Selectivity	Production
33	122.481	101265.0	0.0214	94.48	337826.3	0.0427	89.20	0.6100	0.3258	65.19	91.08
51	120.851	98091.3	0.0208	94.71	325483.7	0.0410	89.72	0.6128	0.3254	65.32	90.27
69	120.851	103307.7	0.0221	94.37	328546.3	0.0419	89.51	0.6079	0.3281	64.94	89.55
87	120.407	113053.0	0.0249	93.69	290999.3	0.0383	90.49	0.5937	0.3431	63.37	87.12
105	119.991	116332.0	0.0255	93.52	291392.7	0.0382	90.49	0.5943	0.3420	63.47	86.86
123	119.291	118757.3	0.0262	93.39	292926.0	0.0386	90.43	0.5923	0.3429	63.33	86.06
141	119.408	120769.3	0.0266	93.28	293475.7	0.0387	90.41	0.5923	0.3424	63.35	86.15
159	119.413	122050.3	0.0271	93.15	294417.3	0.0392	90.29	0.5883	0.3454	62.99	85.57
177	120.106	124286.0	0.0278	92.95	293923.3	0.0393	90.22	0.5844	0.3485	62.64	85.51
195	120.670	126776.0	0.0280	92.86	295596.7	0.0391	90.24	0.5826	0.3503	62.42	85.66
213	120.815	128188.7	0.0286	92.71	294711.3	0.0393	90.17	0.5854	0.3467	62.79	86.17
231	121.345	128969.7	0.0287	92.66	297613.0	0.0396	90.07	0.5860	0.3457	62.88	86.65
249	121.470	131527.7	0.0293	92.51	299020.7	0.0397	90.02	0.5851	0.3459	62.83	86.60
267	122.019	132346.0	0.0300	92.27	299902.7	0.0407	89.74	0.5768	0.3525	62.05	85.77
285	121.643	131539.0	0.0295	92.45	294418.7	0.0394	90.09	0.5834	0.3477	62.65	86.49
300	120.975	133801.7	0.0300	92.36	297606.7	0.0398	90.05	0.5828	0.3475	62.64	85.92

Table C3 Effect of Ni loading: CH₄ conversion, CO₂ conversion, H₂ selectivity, H₂ production(mol/g-cat.)*10²

7%Ni/KL		CH ₄			CO ₂			H ₂			
Time	F _{out}	area	y _{out}	%conversion	area	y _{out}	%conversion	y _{out,H2}	y _{out,CO}	Selectivity	Production
33	121.500	86753.0	0.0183	95.35	264602.5	0.0333	91.57	0.6192	0.3293	65.28	91.68
51	121.456	89038.0	0.0189	95.20	270485.5	0.0343	91.32	0.6185	0.3284	65.32	91.54
69	121.449	90728.5	0.0193	95.10	276533.5	0.0350	91.13	0.6175	0.3282	65.30	91.39
87	121.147	92462.5	0.0196	95.03	276757.5	0.0350	91.16	0.6172	0.3282	65.29	91.12
105	120.631	94428.0	0.0200	94.96	277174.5	0.0350	91.21	0.6174	0.3277	65.33	90.76
123	119.444	96041.5	0.0204	94.90	276638.0	0.0351	91.29	0.6149	0.3297	65.10	89.49
141	120.394	97550.0	0.0206	94.80	272735.5	0.0344	91.38	0.6159	0.3291	65.18	90.36
159	120.311	99196.0	0.0210	94.70	268629.5	0.0340	91.48	0.6138	0.3312	64.96	89.99
177	120.311	100678.5	0.0220	94.47	265733.0	0.0346	91.32	0.6011	0.3424	63.71	88.13
195	120.311	102422.5	0.0221	94.43	262610.5	0.0338	91.51	0.6043	0.3398	64.01	88.60
213	120.311	103520.5	0.0223	94.38	258948.5	0.0333	91.65	0.6042	0.3402	63.98	88.58
231	120.228	103424.0	0.0226	94.31	271041.5	0.0354	91.14	0.6004	0.3417	63.73	87.96
249	121.109	107022.5	0.0228	94.22	264779.0	0.0337	91.50	0.6047	0.3388	64.09	89.25
267	119.950	105821.0	0.0229	94.25	265187.0	0.0342	91.44	0.6029	0.3400	63.94	88.13
285	119.624	108467.5	0.0233	94.17	255939.5	0.0328	91.83	0.6032	0.3407	63.91	87.94
300	119.297	110494.5	0.0237	94.08	259485.5	0.0332	91.76	0.6057	0.3374	64.22	88.06

Table C4 Effect of Ni loading: CH₄ conversion, CO₂ conversion, H₂ selectivity, H₂ production(mol/g-cat.)*10²

9%Ni/KL		CH ₄			CO ₂			H ₂			
Time	F _{out}	area	y _{out}	%conversion	area	y _{out}	%conversion	y _{out,H2}	y _{out,CO}	Selectivity	Production
33	121.330	74790.0	0.0159	95.95	351186.0	0.0451	88.91	0.6227	0.3163	66.33	92.07
51	121.555	79033.5	0.0169	95.70	343176.0	0.0442	89.14	0.6194	0.3196	65.99	91.75
69	121.555	81912.5	0.0175	95.53	340398.5	0.0439	89.19	0.6180	0.3205	65.86	91.55
87	121.780	83855.0	0.0181	95.38	339392.0	0.0440	89.18	0.6145	0.3234	65.54	91.20
105	121.841	86321.5	0.0186	95.24	334635.0	0.0435	89.28	0.6129	0.3250	65.36	91.01
123	121.901	88571.0	0.0191	95.12	330651.0	0.0428	89.45	0.6125	0.3256	65.30	90.99
141	121.863	90168.5	0.0194	95.04	326922.5	0.0423	89.58	0.6115	0.3268	65.18	90.81
159	121.990	90511.0	0.0196	94.99	317914.5	0.0412	89.83	0.6090	0.3302	64.85	90.54
177	121.966	91916.0	0.0198	94.93	314141.0	0.0406	89.98	0.6096	0.3299	64.89	90.62
195	121.767	93287.0	0.0204	94.78	316002.5	0.0414	89.80	0.6020	0.3362	64.17	89.33
213	121.995	94978.0	0.0209	94.65	314449.5	0.0415	89.75	0.5986	0.3390	63.85	88.99
231	121.995	95664.5	0.0212	94.59	311479.5	0.0413	89.81	0.5965	0.3410	63.63	88.69
249	122.223	96822.5	0.0210	94.63	308976.0	0.0401	90.07	0.6028	0.3361	64.21	89.80
267	121.848	97261.0	0.0210	94.62	300893.5	0.0390	90.37	0.6047	0.3353	64.33	89.80
285	121.473	98739.0	0.0215	94.53	297416.5	0.0387	90.48	0.6019	0.3379	64.04	89.11
300	121.258	101299.0	0.0220	94.41	297738.5	0.0387	90.50	0.6022	0.3371	64.11	89.00

Table C5 Effect of Ni loading: CH₄ conversion, CO₂ conversion, H₂ selectivity, H₂ production(mol/g-cat.)*10²

11%Ni/KL		CH ₄			CO ₂			H ₂			
Time	F _{out}	area	y _{out}	%conversion	area	y _{out}	%conversion	y _{out,H2}	y _{out,CO}	Selectivity	Production
33	119.760	76035.5	0.0160	95.99	322941.5	0.0406	90.11	0.6258	0.3177	66.35	91.32
51	119.689	75379.5	0.0161	95.96	309268.5	0.0397	90.35	0.6205	0.3237	65.73	90.51
69	119.474	78753.5	0.0169	95.77	309800.5	0.0399	90.30	0.6184	0.3248	65.57	90.04
87	119.849	81078.5	0.0174	95.62	316123.0	0.0408	90.05	0.6167	0.3250	65.51	90.08
105	120.287	83012.0	0.0179	95.47	324317.5	0.0423	89.64	0.6149	0.3249	65.44	90.13
123	119.579	84728.5	0.0183	95.41	333090.5	0.0433	89.47	0.6171	0.3214	65.78	89.92
141	119.643	86533.0	0.0188	95.29	344684.5	0.0450	89.05	0.6159	0.3204	65.81	89.79
159	119.311	87527.0	0.0189	95.26	348665.5	0.0454	89.01	0.6172	0.3185	65.99	89.74
177	119.502	89115.5	0.0196	95.10	352027.0	0.0466	88.69	0.6108	0.3230	65.44	88.95
195	119.759	91144.0	0.0200	94.96	351631.0	0.0466	88.69	0.6092	0.3242	65.30	88.90
213	120.054	92601.5	0.0204	94.86	352377.5	0.0469	88.58	0.6076	0.3251	65.17	88.89
231	120.581	93892.5	0.0208	94.75	349246.0	0.0465	88.63	0.6058	0.3270	64.98	89.01
249	119.838	93783.5	0.0206	94.83	347553.5	0.0460	88.78	0.6087	0.3246	65.24	88.90
267	119.095	94663.5	0.0207	94.82	340703.0	0.0448	89.14	0.6088	0.3257	65.17	88.36
285	121.100	93582.5	0.0204	94.81	337642.0	0.0443	89.13	0.6101	0.3251	65.26	90.04
300	120.756	95789.5	0.0209	94.71	336583.0	0.0441	89.18	0.6095	0.3254	65.21	89.70

Table C6 Effect of Ni loading: CH₄ conversion, CO₂ conversion, H₂ selectivity, H₂ production(mol/g-cat.)*10²

13%Ni/KL		CH ₄			CO ₂			H ₂			
Time	F _{out}	area	y _{out}	%conversion	area	y _{out}	%conversion	y _{out,H2}	y _{out,CO}	Selectivity	Production
33	121.625	71160.5	0.0151	96.11	300016.0	0.0381	90.41	0.6197	0.3271	65.48	91.84
51	120.841	72612.0	0.0153	96.08	307343.5	0.0386	90.33	0.6226	0.3235	65.83	91.66
69	120.841	75729.5	0.0162	95.86	319844.0	0.0407	89.80	0.6198	0.3234	65.74	91.25
87	120.841	78326.5	0.0168	95.71	334812.0	0.0427	89.30	0.6198	0.3207	65.94	91.25
105	120.264	79728.5	0.0171	95.66	340114.0	0.0434	89.18	0.6205	0.3191	66.08	90.93
123	120.114	81071.0	0.0174	95.57	342953.5	0.0439	89.04	0.6189	0.3198	65.97	90.58
141	120.114	83350.0	0.0179	95.45	345461.0	0.0441	89.00	0.6181	0.3199	65.93	90.46
159	119.965	85024.0	0.0183	95.34	344118.0	0.0442	88.98	0.6159	0.3215	65.74	90.04
177	120.682	86398.5	0.0186	95.24	343652.0	0.0441	88.96	0.6150	0.3222	65.65	90.43
195	120.640	88851.5	0.0192	95.09	342969.0	0.0442	88.94	0.6125	0.3241	65.43	90.03
213	120.639	90217.0	0.0196	95.00	339351.5	0.0439	89.03	0.6102	0.3264	65.18	89.68
231	120.435	92544.0	0.0205	94.77	335315.5	0.0441	88.98	0.6007	0.3346	64.26	88.13
249	119.316	92191.0	0.0206	94.79	329487.0	0.0436	89.22	0.5966	0.3391	63.79	86.68
267	118.884	95644.5	0.0212	94.65	324909.5	0.0428	89.47	0.5986	0.3374	63.98	86.68
285	118.883	93730.0	0.0204	94.86	316401.5	0.0411	89.87	0.6078	0.3307	64.78	88.04
300	118.760	97210.0	0.0212	94.68	314614.0	0.0408	89.96	0.6067	0.3314	64.69	87.78

Table C7 Effect of Ni loading: CH₄ conversion, CO₂ conversion, H₂ selectivity, H₂ production(mol/g-cat.)*10²

15%Ni/KL		CH ₄			CO ₂			H ₂			
Time	F _{out}	area	y _{out}	%conversion	area	y _{out}	%conversion	y _{out,H2}	y _{out,CO}	Selectivity	Production
33	122.740	68681.0	0.0142	96.39	257408.0	0.0318	91.97	0.6253	0.3287	65.55	93.53
51	122.635	64717.0	0.0135	96.59	251179.0	0.0311	92.14	0.6248	0.3306	65.40	93.36
69	122.174	66838.0	0.0139	96.48	256090.5	0.0318	92.01	0.6246	0.3297	65.45	92.98
87	122.157	68438.5	0.0144	96.37	247675.0	0.0309	92.22	0.6238	0.3309	65.34	92.83
105	121.727	71106.0	0.0151	96.21	268039.0	0.0337	91.54	0.6179	0.3332	64.97	91.64
123	121.689	72575.0	0.0153	96.16	267944.0	0.0336	91.59	0.6201	0.3311	65.19	91.94
141	122.030	73551.0	0.0157	96.05	263691.5	0.0334	91.61	0.6152	0.3357	64.70	91.47
159	122.030	75102.5	0.0159	95.98	263696.0	0.0332	91.64	0.6162	0.3346	64.81	91.62
177	122.030	76928.5	0.0165	95.83	262320.5	0.0336	91.56	0.6102	0.3397	64.24	90.73
195	122.402	78128.0	0.0167	95.78	261834.5	0.0333	91.60	0.6121	0.3379	64.43	91.30
213	122.254	79103.5	0.0170	95.71	259617.0	0.0331	91.65	0.6105	0.3394	64.27	90.95
231	122.107	80547.5	0.0172	95.66	273262.0	0.0346	91.28	0.6091	0.3391	64.24	90.62
249	121.896	80561.0	0.0174	95.62	263239.0	0.0338	91.51	0.6082	0.3406	64.10	90.35
267	122.140	80385.5	0.0173	95.64	269505.5	0.0345	91.31	0.6099	0.3383	64.33	90.78
285	121.748	81353.0	0.0173	95.64	255923.0	0.0324	91.86	0.6125	0.3377	64.46	90.87
300	121.356	83559.0	0.0179	95.50	260545.5	0.0332	91.69	0.6103	0.3386	64.31	90.24

Table C8 Effect of Mg promoter: CH₄ conversion, CO₂ conversion, H₂ selectivity, H₂ production(mol/g-cat.)*10²

2%Mg-7%Ni/KL		CH ₄			CO ₂			H ₂			
Time	F _{out}	area	y _{out}	%conversion	area	y _{out}	%conversion	y _{out,H2}	y _{out,CO}	Selectivity	Production
33	105.650	180240.0	0.0359	92.18	359523.0	0.0420	91.18	0.4589	0.4633	49.76	59.08
51	113.611	180445.0	0.0363	91.50	352381.0	0.0415	90.61	0.4551	0.4671	49.35	63.01
69	121.571	179883.0	0.0361	90.94	350117.0	0.0412	90.03	0.4563	0.4664	49.45	67.60
87	121.709	170032.0	0.0341	91.45	336679.0	0.0395	90.43	0.4574	0.4690	49.37	67.84
105	121.846	168102.0	0.0337	91.51	332546.0	0.0392	90.51	0.4563	0.4708	49.21	67.75
123	123.385	155297.0	0.0308	92.15	318224.0	0.0371	90.90	0.4614	0.4707	49.50	69.38
141	124.923	155990.0	0.0319	91.78	319146.0	0.0383	90.49	0.4459	0.4840	47.95	67.88
159	123.212	148342.0	0.0303	92.30	312123.0	0.0374	90.84	0.4468	0.4855	47.92	67.08
177	121.500	148922.0	0.0302	92.42	311553.0	0.0371	91.04	0.4503	0.4824	48.28	66.68
195	122.167	147295.0	0.0302	92.38	315893.0	0.0380	90.76	0.4449	0.4868	47.75	66.23
213	122.167	144497.0	0.0301	92.41	306134.0	0.0374	90.91	0.4371	0.4954	46.87	65.07
231	122.833	143155.0	0.0306	92.25	310694.0	0.0389	90.49	0.4261	0.5044	45.79	63.78
249	122.786	139644.0	0.0303	92.33	310410.0	0.0394	90.37	0.4202	0.5100	45.17	62.88
267	122.700	139183.0	0.0303	92.32	314153.0	0.0402	90.20	0.4227	0.5068	45.48	63.21
285	122.700	139194.0	0.0302	92.36	324005.0	0.0412	89.95	0.4280	0.5007	46.09	64.00
300	122.700	139907.0	0.0303	92.33	331693.0	0.0421	89.72	0.4280	0.4996	46.14	63.99

Table C9 Effect of Mg promoter: CH₄ conversion, CO₂ conversion, H₂ selectivity, H₂ production(mol/g-cat.)^{*}10²

3%Mg-7%Ni/KL		CH ₄			CO ₂			H ₂			
Time	F _{out}	area	y _{out}	%conversion	area	y _{out}	%conversion	y _{out,H2}	y _{out,CO}	Selectivity	Production
33	123.571	133017.0	0.0284	93.30	352840.0	0.0441	88.88	0.5199	0.4077	56.05	78.29
51	122.419	130571.0	0.0276	93.53	356791.0	0.0443	88.94	0.5066	0.4215	54.59	75.58
69	122.419	131623.0	0.0278	93.50	359145.0	0.0444	88.90	0.5034	0.4244	54.25	75.09
87	122.419	133010.0	0.0286	93.29	355153.0	0.0448	88.80	0.5132	0.4133	55.39	76.56
105	122.419	134601.0	0.0290	93.20	389866.0	0.0493	87.68	0.5070	0.4146	55.01	75.64
123	121.267	136235.0	0.0293	93.21	399896.0	0.0503	87.54	0.5099	0.4105	55.39	75.35
141	121.300	135052.0	0.0293	93.19	398099.0	0.0507	87.45	0.5082	0.4118	55.24	75.12
159	121.357	137841.0	0.0297	93.12	403012.0	0.0508	87.41	0.5083	0.4112	55.27	75.17
177	121.821	138979.0	0.0299	93.03	403243.0	0.0509	87.35	0.5072	0.4120	55.18	75.30
195	121.821	139221.0	0.0301	92.98	403188.0	0.0511	87.29	0.5063	0.4125	55.11	75.16
213	122.286	141406.0	0.0304	92.89	404116.0	0.0510	87.28	0.5065	0.4121	55.14	75.49
231	122.285	142311.0	0.0306	92.85	404565.0	0.0510	87.28	0.5064	0.4121	55.13	75.46
249	122.285	142163.0	0.0305	92.86	403501.0	0.0508	87.32	0.5060	0.4126	55.08	75.41
267	122.285	144896.0	0.0311	92.72	404679.0	0.0510	87.28	0.5048	0.4131	54.99	75.23
285	122.285	144349.0	0.0310	92.74	398410.0	0.0502	87.47	0.5037	0.4151	54.82	75.06
300	121.643	145588.0	0.0313	92.72	393469.0	0.0496	87.69	0.5019	0.4172	54.60	74.40

Table C10 Effect of Mg promoter: CH₄ conversion, CO₂ conversion, H₂ selectivity, H₂ production(mol/g-cat.)*10²

4%Mg-7%Ni/KL		CH ₄			CO ₂			H ₂			
Time	F _{out}	area	y _{out}	%conversion	area	y _{out}	%conversion	y _{out,H2}	y _{out,CO}	Selectivity	Production
33	119.625	142461.0	0.0307	92.84	378436.0	0.0479	87.83	0.5044	0.4170	54.74	73.53
51	119.625	146452.0	0.0315	92.67	373798.0	0.0471	88.03	0.5012	0.4203	54.39	73.06
69	119.646	149804.0	0.0319	92.56	365511.0	0.0457	88.39	0.5032	0.4192	54.55	73.37
87	119.646	150393.0	0.0323	92.48	379865.0	0.0478	87.85	0.5027	0.4173	54.64	73.29
105	119.667	151562.0	0.0328	92.36	390641.0	0.0495	87.40	0.5014	0.4163	54.63	73.12
123	120.000	153221.0	0.0331	92.25	394494.0	0.0500	87.24	0.5009	0.4159	54.64	73.26
141	120.000	153377.0	0.0331	92.26	388005.0	0.0491	87.48	0.4998	0.4180	54.46	73.09
159	120.000	154357.0	0.0336	92.15	389779.0	0.0497	87.32	0.4956	0.4211	54.06	72.48
177	120.333	155828.0	0.0338	92.08	387230.0	0.0492	87.41	0.4950	0.4220	53.98	72.59
195	120.400	157293.0	0.0344	91.93	384528.0	0.0493	87.38	0.4898	0.4265	53.45	71.86
213	120.467	156761.0	0.0338	92.08	381124.0	0.0481	87.68	0.4957	0.4224	53.99	72.77
231	120.626	159211.0	0.0343	91.94	380593.0	0.0481	87.68	0.4952	0.4225	53.96	72.79
249	120.626	159730.0	0.0344	91.91	373684.0	0.0472	87.90	0.4936	0.4248	53.74	72.55
267	120.626	161454.0	0.0348	91.82	377221.0	0.0477	87.77	0.4932	0.4242	53.76	72.51
285	120.626	161412.0	0.0348	91.83	376516.0	0.0475	87.81	0.4881	0.4295	53.19	71.76
300	120.786	162229.0	0.0349	91.78	358449.0	0.0453	88.38	0.4879	0.4319	53.05	71.82

Table C11 Effect of Mg promoter: CH₄ conversion, CO₂ conversion, H₂ selectivity, H₂ production(mol/g-cat.)*10²

5%Mg-7%Ni/KL		CH ₄			CO ₂			H ₂			
Time	F _{out}	area	y _{out}	%conversion	area	y _{out}	%conversion	y _{out,H2}	y _{out,CO}	Selectivity	Production
33	119.467	266798.0	0.0603	87.29	324960.0	0.0431	87.87	0.4217	0.4749	47.04	61.40
51	119.100	262676.0	0.0594	87.52	326171.0	0.0433	87.86	0.4220	0.4753	47.03	61.26
69	119.100	264222.0	0.0600	87.40	326397.0	0.0435	87.81	0.4196	0.4769	46.80	60.90
87	119.100	262842.0	0.0590	87.60	323112.0	0.0426	88.05	0.4255	0.4729	47.36	61.76
105	119.100	263099.0	0.0596	87.48	322195.0	0.0428	87.99	0.4202	0.4774	46.81	60.99
123	118.733	260633.0	0.0588	87.68	320276.0	0.0424	88.14	0.4222	0.4765	46.98	61.09
141	119.667	261135.0	0.0596	87.41	320383.0	0.0429	87.90	0.4157	0.4817	46.32	60.62
159	119.667	261201.0	0.0590	87.55	318888.0	0.0422	88.10	0.4219	0.4769	46.94	61.52
177	119.667	262193.0	0.0591	87.52	319726.0	0.0423	88.08	0.4226	0.4760	47.03	61.63
195	120.600	262410.0	0.0592	87.40	319297.0	0.0423	87.99	0.4217	0.4768	46.94	61.98
213	120.400	262611.0	0.0590	87.47	319100.0	0.0421	88.07	0.4242	0.4748	47.19	62.24
231	120.400	262800.0	0.0596	87.35	320279.0	0.0426	87.92	0.4186	0.4793	46.62	61.42
249	120.400	263905.0	0.0597	87.31	321255.0	0.0426	87.90	0.4197	0.4779	46.76	61.58
267	120.400	263878.0	0.0615	86.94	321202.0	0.0439	87.55	0.4018	0.4928	44.92	58.96
285	120.400	261876.0	0.0598	87.30	317358.0	0.0425	87.94	0.4157	0.4820	46.31	60.99
300	120.400	263082.0	0.0596	87.34	317019.0	0.0421	88.05	0.4203	0.4780	46.79	61.67

Table C12 Effect of Ca promoter: CH₄ conversion, CO₂ conversion, H₂ selectivity, H₂ production(mol/g-cat.)*10²

2%Ca-7%Ni/KL		CH ₄			CO ₂			H ₂			
Time	F _{out}	area	y _{out}	%conversion	area	y _{out}	%conversion	y _{out,H2}	y _{out,CO}	Selectivity	Production
33	120.917	157968.0	0.0447	89.24	222575.0	0.0370	90.77	0.4080	0.5102	44.43	60.13
51	120.500	148287.0	0.0418	89.99	205903.0	0.0340	91.54	0.4075	0.5167	44.09	59.85
69	120.500	152709.0	0.0434	89.61	208614.0	0.0347	91.36	0.4014	0.5205	43.54	58.95
87	120.500	156101.0	0.0445	89.33	211513.0	0.0354	91.20	0.3981	0.5220	43.27	58.46
105	120.500	159551.0	0.0459	89.00	214348.0	0.0362	91.00	0.3922	0.5257	42.73	57.60
123	120.500	161769.0	0.0464	88.89	216599.0	0.0364	90.94	0.3938	0.5234	42.93	57.82
141	120.500	163733.0	0.0471	88.72	219340.0	0.0370	90.80	0.3926	0.5233	42.87	57.66
159	120.500	166153.0	0.0479	88.53	220854.0	0.0373	90.71	0.3913	0.5235	42.78	57.46
177	120.063	168605.0	0.0486	88.40	223934.0	0.0378	90.62	0.3913	0.5223	42.83	57.25
195	120.063	169994.0	0.0491	88.27	225506.0	0.0382	90.53	0.3897	0.5229	42.70	57.02
213	120.063	172718.0	0.0499	88.08	228500.0	0.0387	90.40	0.3891	0.5222	42.69	56.93
231	120.063	174052.0	0.0510	87.84	231601.0	0.0398	90.14	0.3833	0.5260	42.16	56.09
249	120.063	175363.0	0.0508	87.88	237233.0	0.0403	90.02	0.3928	0.5162	43.21	57.47
267	121.308	176873.0	0.0520	87.46	237191.0	0.0409	89.76	0.3852	0.5219	42.46	56.94
285	120.500	176567.0	0.0518	87.60	242526.0	0.0417	89.63	0.3869	0.5197	42.68	56.81
300	120.500	177486.0	0.0519	87.57	245371.0	0.0421	89.53	0.3864	0.5196	42.65	56.74

Table C13 Effect of Ca promoter: CH₄ conversion, CO₂ conversion, H₂ selectivity, H₂ production(mol/g-cat.)*10²

3%Ca-7%Ni/KL		CH ₄			CO ₂			H ₂			
Time	F _{out}	area	y _{out}	%conversion	area	y _{out}	%conversion	y _{out,H2}	y _{out,CO}	Selectivity	Production
33	116.500	181248.0	0.0536	87.67	471798.0	0.0818	80.27	0.4363	0.4283	50.46	61.94
51	116.550	175591.0	0.0516	88.13	444642.0	0.0766	81.53	0.4349	0.4369	49.89	61.77
69	116.550	169300.0	0.0495	88.61	425138.0	0.0729	82.42	0.4378	0.4398	49.89	62.18
87	116.550	170045.0	0.0495	88.61	415993.0	0.0710	82.87	0.4387	0.4407	49.89	62.32
105	116.550	170434.0	0.0502	88.46	409240.0	0.0706	82.97	0.4318	0.4474	49.11	61.33
123	116.550	172096.0	0.0520	88.03	403409.0	0.0715	82.76	0.4146	0.4619	47.30	58.88
141	116.550	172990.0	0.0520	88.03	399741.0	0.0705	83.00	0.4151	0.4623	47.31	58.96
159	116.550	174145.0	0.0522	87.99	396312.0	0.0696	83.20	0.4152	0.4629	47.28	58.98
177	116.550	176495.0	0.0532	87.77	394586.0	0.0697	83.19	0.4106	0.4665	46.81	58.32
195	116.550	177302.0	0.0534	87.71	396432.0	0.0701	83.10	0.4113	0.4652	46.92	58.41
213	116.692	177689.0	0.0535	87.67	398108.0	0.0703	83.02	0.4120	0.4641	47.02	58.59
231	116.467	180892.0	0.0546	87.46	395232.0	0.0699	83.15	0.4100	0.4655	46.83	58.20
249	116.600	180445.0	0.0544	87.49	394658.0	0.0697	83.18	0.4089	0.4671	46.68	58.10
267	116.600	182132.0	0.0534	87.71	394658.0	0.0679	83.62	0.4210	0.4577	47.91	59.82
285	116.600	181115.0	0.0558	87.16	382569.0	0.0691	83.33	0.3927	0.4824	44.87	55.80
300	116.769	182911.0	0.0540	87.56	379860.0	0.0657	84.12	0.4146	0.4656	47.10	59.00

Table C14 Effect of Ca promoter: CH₄ conversion, CO₂ conversion, H₂ selectivity, H₂ production(mol/g-cat.)*10²

4%Ca-7%Ni/KL		CH ₄			CO ₂			H ₂			
Time	F _{out}	area	y _{out}	%conversion	area	y _{out}	%conversion	y _{out,H2}	y _{out,CO}	Selectivity	Production
33	119.933	140863.0	0.0372	91.07	185895.0	0.0288	92.68	0.4204	0.5136	45.01	61.44
51	119.933	139921.0	0.0372	91.07	180306.0	0.0281	92.86	0.4187	0.5160	44.80	61.20
69	119.933	140352.0	0.0375	91.01	181907.0	0.0285	92.76	0.4170	0.5170	44.65	60.95
87	119.933	141288.0	0.0383	90.81	182798.0	0.0290	92.62	0.4093	0.5234	43.89	59.83
105	119.933	141561.0	0.0384	90.78	184161.0	0.0293	92.55	0.4095	0.5229	43.92	59.85
123	119.933	142012.0	0.0376	90.97	185007.0	0.0287	92.70	0.4242	0.5095	45.43	62.00
141	119.933	143024.0	0.0389	90.66	185808.0	0.0296	92.47	0.4080	0.5235	43.80	59.63
159	121.500	144146.0	0.0387	90.59	187317.0	0.0295	92.40	0.4166	0.5152	44.71	61.68
177	121.000	144833.0	0.0389	90.57	187756.0	0.0296	92.41	0.4168	0.5147	44.75	61.46
195	121.000	145616.0	0.0391	90.52	189264.0	0.0298	92.35	0.4166	0.5144	44.75	61.43
213	123.308	145725.0	0.0391	90.35	191334.0	0.0301	92.13	0.4183	0.5126	44.94	62.86
231	121.000	147589.0	0.0399	90.34	192797.0	0.0305	92.17	0.4140	0.5157	44.53	61.04
249	121.000	147518.0	0.0401	90.28	192101.0	0.0306	92.14	0.4131	0.5162	44.46	60.92
267	121.000	149020.0	0.0405	90.20	194422.0	0.0309	92.06	0.4132	0.5154	44.49	60.92
285	121.000	148526.0	0.0404	90.21	191779.0	0.0306	92.15	0.4116	0.5174	44.30	60.69
300	120.643	148291.0	0.0404	90.25	192971.0	0.0308	92.12	0.4110	0.5179	44.25	60.42

Table C15 Effect of Ca promoter: CH₄ conversion, CO₂ conversion, H₂ selectivity, H₂ production(mol/g-cat.)*10²

5%Ca-7%Ni/KL		CH ₄			CO ₂			H ₂			
Time	F _{out}	area	y _{out}	%conversion	area	y _{out}	%conversion	y _{out,H2}	y _{out,CO}	Selectivity	Production
33	119.857	171885.0	0.0382	91.26	425995.0	0.0555	86.45	0.4921	0.4141	54.30	71.88
51	119.857	163522.0	0.0360	91.76	406829.0	0.0526	87.18	0.4927	0.4187	54.06	71.96
69	119.304	168221.0	0.0371	91.56	406221.0	0.0525	87.26	0.4917	0.4188	54.01	71.49
87	118.750	169902.0	0.0374	91.52	407094.0	0.0526	87.29	0.4908	0.4191	53.94	71.03
105	119.000	173387.0	0.0390	91.14	421511.0	0.0556	86.53	0.4833	0.4221	53.38	70.09
123	119.000	175120.0	0.0388	91.19	424238.0	0.0551	86.65	0.4906	0.4155	54.14	71.15
141	119.000	175859.0	0.0390	91.14	418770.0	0.0545	86.81	0.4886	0.4180	53.89	70.85
159	119.000	176885.0	0.0391	91.11	411209.0	0.0534	87.07	0.4876	0.4199	53.73	70.70
177	119.667	177517.0	0.0393	91.02	403725.0	0.0525	87.22	0.4848	0.4234	53.38	70.70
195	119.500	177096.0	0.0390	91.10	395725.0	0.0512	87.56	0.4851	0.4247	53.32	70.64
213	119.500	178965.0	0.0396	90.96	388199.0	0.0504	87.74	0.4807	0.4293	52.83	70.01
231	119.500	179515.0	0.0397	90.93	381957.0	0.0496	87.94	0.4784	0.4323	52.53	69.66
249	119.357	180402.0	0.0398	90.93	376202.0	0.0487	88.17	0.4782	0.4333	52.46	69.56
267	119.350	183001.0	0.0410	90.66	367634.0	0.0483	88.27	0.4678	0.4430	51.36	68.04
285	119.350	179642.0	0.0398	90.94	355256.0	0.0461	88.79	0.4752	0.4388	51.99	69.12
300	119.350	180227.0	0.0399	90.91	355391.0	0.0461	88.80	0.4729	0.4411	51.74	68.78

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