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APPENDICES

Appendix A Calculation of Methane Conversion and Product Selectivity

A.1 %CH_4 Conversion

1. Definition of CH_4 Conversion

$$\%\ CH_4 Conversion = \frac{Total\ mol\ of\ CH_{4,in} - Total\ mol\ of\ CH_{4,out}}{Total\ mol\ of\ CH_{4,in}} \times 100 \quad (1)$$

2. $Total\ mol\ of\ CH_{4,in}$ can be replaced by the term $Total\ C$ since the source of total carbon are derived from only methane and $Total\ C\ in\ CH_{4,out}$ can be replaced by $C\ in\ unreacted\ CH_4$.

Therefore, the eq. (1) becomes;

$$\%\ CH_4 Conversion = \frac{Total\ C - C\ in\ unreacted\ CH_4}{Total\ C} \times 100 \quad (2)$$

3. Carbon balance with no coke formation:

$Total\ C = Total\ C_{in} = Total\ C_{out}$ (obtained from all carbon in outlet stream)

Hence, $Total\ C - C\ in\ unreacted\ CH_4$ in eq. (2) can be replaced by $Total\ C\ in\ all\ Products$

Thus eq. (2) becomes;

$$\%\ CH_4 Conversion = \frac{Total\ C\ in\ all\ Products}{Total\ C} \times 100 \quad (3)$$

Example; for the reaction in case of the blank tube

1. The resulting peak area from online GC of all chemicals in the exhaust stream listed below:

Table A1 Peak area of exhaust stream

FID					TCD
CH_4	C_2H_6	C_2H_4	CH_3Br	CH_2Br_2	CO
11808.5	0	38.8	1126.4	79.7	932.7

2. Change area to mol by multipling with response factor of each substance.

Table A2 Response factor (obtained from Calibration Data)

Substance	Response factor(mol/area)
CH_4	4.5969E-10
C_2H_6	3.4581E-10
C_2H_4	3.4151E-10
CH_3Br	1.0000E-09
CH_2Br_2	5.0000E-10
CO	5.6853E-10

Table A3 Mol of each chemical species in the exhaust stream

Mol					
CH_4	C_2H_6	C_2H_4	CH_3Br	CH_2Br_2	CO
5.42827E-06	0	1.32506E-08	1.1264E-06	3.985E-08	5.30274E-07

3. Total mol of C was calculated by

   = mol of C_{CH4} + 2(mol of C_{C2H6}) + 2(mol of C_{C2H4}) + mol of C_{CH3Br} + mol of C_{CH2Br2} + mol of C_{CO}

   C in product was calculated by

   = 2(mol of C_{C2H6}) + 2(mol of C_{C2H4}) + mol of C_{CH3Br} + mol of C_{CH2Br2} + mol of C_{CO}

Accordingly, the methane conversion calculated from eq. (3) was shown in the below table

Table A4 Methane conversion

Total mol of C	C in product	**% CH_4 Conversion**
7.15129E-06	1.72302E-06	24.0939

A.2 %CH_3Br Selectivity

$$\%\ CH_3\text{Br Selectivity} = \frac{\text{mol of } CH_3Br}{\text{Total mol of Product}} \times 100$$

Example;

1. Mol of CH_3Br (shown in Table A3)

   = 1.1264E-06 mol

2. Total mol of Product was calculated by

   = mol of C_{C2H6} + mol of C_{C2H4} + mol of C_{CH3Br}+ mol of C_{CH2Br2} + mol of C_{CO}

Table A5 Total mol of Product

Mol					**Total mol of product**
C_2H_6	**C_2H_4**	**CH_3Br**	**CH_2Br_2**	**CO**	
0	1.32506E-08	1.1264E-06	3.985E-08	5.30274E-07	1.70977E-06

$$\%\ CH_3\text{Br Selectivity} = \frac{1.1264E-06}{1.70977E-06} \times 100 = 65.88\ \%$$

A.3 %CO Selectivity

*The conceptual calculation of %CO Selectivity is the same as %CH_3Br Selectivity.

Appendix B Calculation of Catalyst Composition

The Rh/SiO_2 catalyst was prepared by incipient wetness impregnation method which means support containing the same pore volume as the volume of the solution that was added.

Example 2 g of 0.5 wt% Rh/SiO_2 catalyst

= 2 g (Rh_2O_3 + SiO_2) of 0.5 % (Rh^0 w/w to Rh_2O_3 +SiO_2)

Rh_2O_3 form must be involved in this case due to small amount of catalyst prepared.

Step 1: wt. Rh^0		
wt. of Rh^0	0.0100	g
Step 2: wt. Rh_2O_3		
MW of Rh^0	102.9100	g/mol
MW of Rh_2O_3	253.8200	g/mol
wt. of Rh_2O_3	0.0123	g
Step 3: wt SiO_2		
wt. of Support (SiO_2)	1.9877	g
Step 4: wt $RhCl_3*3H_2O$		
MW of $RhCl_3*3H_2O$	263.3103	g/mol
g of $RhCl_3*3H_2O$	0.0256	g
(assay ≥ 99.9% trace metal basis)		
Corrected weight	0.0258	g
Step 5: Lacttice water		
Lattice water	0.0052	ml
(neglible)		
Step 6: Volume of SiO_2		
From BET surface analysis, total pore volume of SiO_2 is 2.1606 ml/g		
Volume of SiO_2	4.2925	ml
Step 7: Water required		
Impregnation volume (100% pore volume)		
Water required for $RhCl_3*3H_2O$	4.2925	ml

Table B1 The ingredients of prepared catalyst

Loading (wt%)	SiO_2(g)	$RhCl_3*3H_2O$ (g)	Required water (ml)
0.1	2	0.0052	4.3160
0.3	2	0.0258	4.2925
0.5	2	0.0155	4.3052

Appendix C Calibration Data and Feed Flow Calibration

The response factors of methane (CH_4) ethane (C_2H_6) ethylene (C_2H_4), and carbon monoxide (CO) were determined by using the Single Point External Standard assuming analyte response to be linear over a range of concentrations. This method requires a known amount of analytes and record the peak area. The peak area of each substrate was calculated from average areas. The volume of each online injection equals to 2.5 ml which subsequently converted to mol bases on an ideal gas. Then calculate a response factor using an equation below.

$$Response\ Factor = \frac{\text{mol}}{area}$$

Table C1 The response factors calculated from the Single Point External Standard

No./ Retention time	Methane	Ethane	Ethylene	Carbon monoxide
	3.49	4.46	5.02	9.34
1	22225.7	295.6	299.1	180.7
2	22315.9	294.3	297.9	180.5
3	22222.5	297.2	301.1	178.2
4		296.3	300.2	180.4
Area	22254.7	295.85	299.575	179.95
Volume(l)	0.00025	0.0000025	0.0000025	0.0000025
Mol	1.023E-05	1.023E-07	1.023E-07	1.023E-07
Response factor (mol/area)	4.5969E-10	3.4581E-10	3.4151E-10	5.6853E-10

For methyl bromide (CH_3Br) and dibromomethane (CH_2Br_2), the response factors were determined by using the Multiple Point External Standard. The samples used in this method cover the expected analyte concentration range. Use a line fitting algorithm such as point to point, linear least squares, or quadratic least squares to produce a calibration curve. The response factor used for calculation the

products amount were derived from the the reciprocal of slope of calibration curve as shown in Figure C1 and Figure C2.

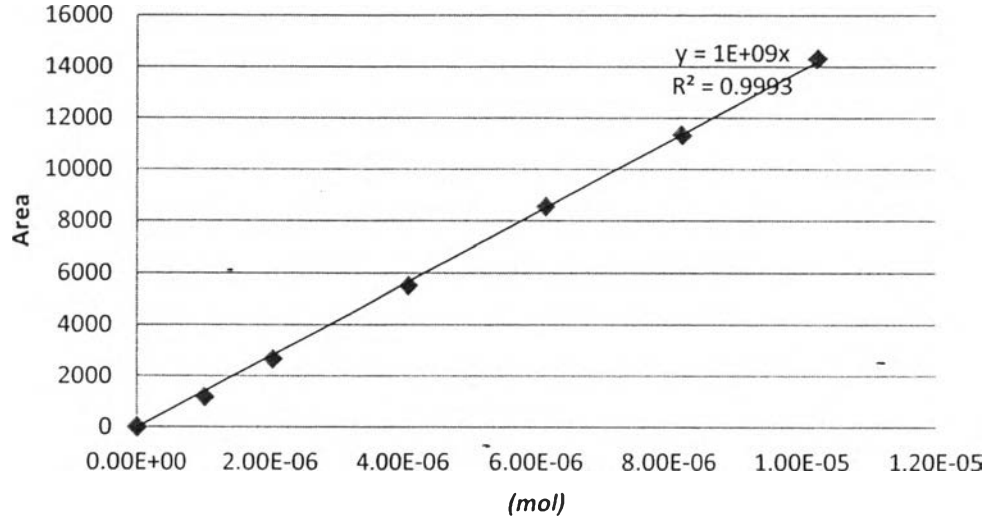

Figure C1 Response factors from GC FID as a function of injection volume of methyl bromide.

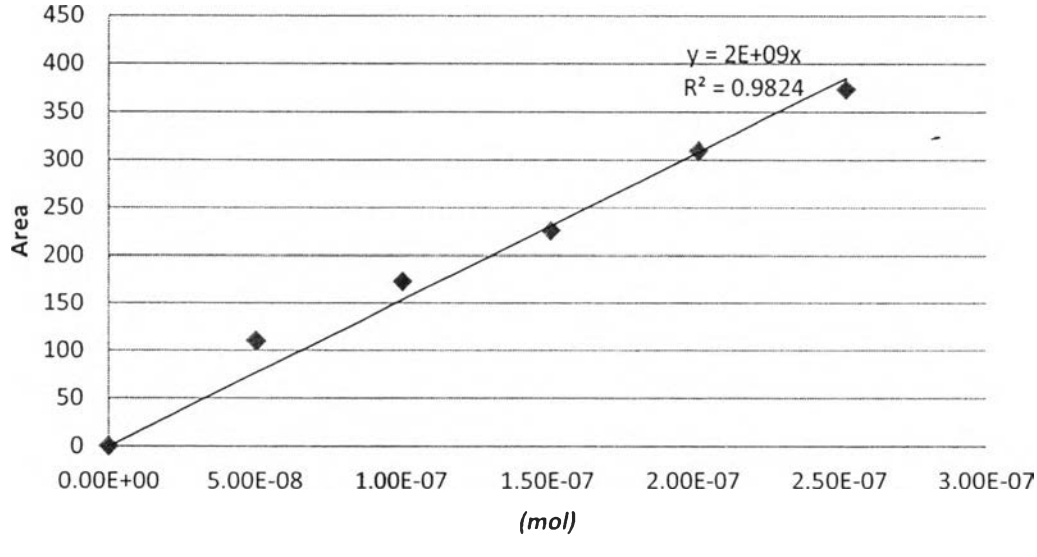

Figure C2 Response factors from GC FID as a function of injection volume of dibromomethanes.

Table C2 The response factors calculated from the Multiple Point External Standard

Chemicals	Retention time	Slope (area/mol)	Response factor (mol/area)
Methyl bromide	12.50	1E+09	1E-09
Dibromomethanes	21.03	2E+09	5E-10

Appendix D Raw Data of Reaction Results

The reaction results as a raw data of GC FID and TCD peak area and calculated data are shown below.

Table D1 The results of the reaction with 20 ml/min of CH_4, 5 ml/min of O_2, 5 ml/min of N_2, 6.5 ml/h of 48 wt% HBr/H_2O, reaction temperature 660 °C, and 2 g of SiO_2

TOS		FID					TCD	%CH_4 Conversion	% Selectivity				
min	h	CH_4	C_2H_6	C_2H_4	CH_3Br	CH_2Br_2	CO		C_2H_6	C_2H_4	CH_3Br	CH_2Br_2	CO
30	0.5	13352.9	0	9.8	315.5	0	2398.6	21.55	0	0.20	18.75	0	81.05
64	1.1	12641.3	0	9.8	683.6	13.5	2316.2	25.74	0	0.17	34.00	0.34	65.50
98	1.6	12912.3	0	9.2	816.1	19.6	2113.3	25.52	0	0.15	40.19	0.48	59.17
132	2.2	12341.9	0	9.9	791.8	18.1	2152.1	26.36	0	0.17	39.05	0.45	60.34
166	2.8	12123.2	0	11.9	889.5	27.2	2217.6	28.04	0	0.19	41.03	0.63	58.16
200	3.3	12120.9	0	11.7	930.4	29.5	2106.8	27.85	0	0.19	43.34	0.69	55.79
234	3.9	11968	0	12.5	986.8	31.8	2079.2	28.50	0	0.20	45.08	0.73	54.00
268	4.5	12667.5	0	9.7	991	30.3	1723	25.49	0	0.17	49.82	0.76	49.25
302	5.0	11898.2	0	11.5	1017.7	33.5	2020	28.60	0	0.18	46.54	0.77	52.52
336	5.6	12240.6	0	10.2	964.3	32.9	1897.8	26.86	0	0.17	46.74	0.80	52.30
370	6.2	12114.9	0	9.8	962.2	30	1807.6	26.54	0	0.17	47.91	0.75	51.17
404	6.7	12070.2	0	7.8	993	31.9	1700.1	26.31	0	0.13	50.20	0.81	48.86
438	7.3	12511.4	0	6.6	891.5	26.3	1733.5	24.78	0	0.12	47.11	0.69	52.08

Table D2 The results of the reaction with 20 ml/min of CH_4, 5 ml/min of O_2, 5 ml/min of N_2, 6.5 ml/h of 48 wt% HBr/H_2O, reaction temperature 660 °C, and 2 g of Al_2O_3

TOS		FID					TCD	%CH_4 Conversion	% Selectivity				
min	h	CH_4	C_2H_6	C_2H_4	CH_3Br	CH_2Br_2	CO		C_2H_6	C_2H_4	CH_3Br	CH_2Br_2	CO
30	0.5	12722	0	15.1	40.7	0	2226.8	18.38	0	0.39	3.10	0	96.50
64	1.1	12509.5	0	18.3	35.6	0	2667.6	21.39	0	0.40	2.28	0	97.31
98	1.6	12979.8	0	14.1	29.2	0	2488.9	19.59	0	0.33	2.02	0	97.65
132	2.2	12406.8	0	22	20.3	0	2713.5	21.67	0	0.48	1.29	0	98.23
166	2.8	12599.9	0	20.1	18	0	2700	21.29	0	0.44	1.15	0	98.41
200	3.3	12544.3	0	19	14	0	2830.3	22.10	0	0.40	0.86	0	98.74
234	3.9	12683.9	0	23.1	0	0	2994.5	22.76	0	0.46	0.00	0	99.54
268	4.5	13425.4	0	16.1	12.8	0	2685.9	20.08	0	0.36	0.83	0	98.82
302	5.0	13824.5	0	20.1	0	0	2621.9	19.14	0	0.46	0	0	99.54
336	5.6	13872.3	0	17.4	0	0	2606.3	18.98	0	0.40	0	0	99.60
370	6.2	13428	0	21.9	0	0	2776.4	20.52	0	0.47	0	0	99.53
404	6.7	13838.2	0	19.8	0	0	2761.7	19.93	0	0.43	0	0	99.57
438	7.3	13763	0	20.4	0	0	2693.1	19.63	0	0.45	0	0	99.55

Table D3 The results of the reaction with 20 ml/min of CH_4, 5 ml/min of O_2, 5 ml/min of N_2, 6.5 ml/h of 48 wt% HBr/H_2O, reaction temperature 660 °C, and 2 g of ZSM-5

TOS		FID					TCD	%CH_4 Conversion	% Selectivity				
min	h	CH_4	C_2H_6	C_2H_4	CH_3Br	CH_2Br_2	CO		C_2H_6	C_2H_4	CH_3Br	CH_2Br_2	CO
30	0.5	14386.4	0	19.3	0	0	1974.9	14.66	0	0.58	0	0	99.42
64	1.1	12348.1	0	33.8	18.4	0	3382.7	25.71	0	0.59	0.94	0	98.47
98	1.6	13795.2	0	32.2	20.5	0	2950.4	21.33	0	0.64	1.20	0	98.16
132	2.2	12625.8	0	40.6	17	0	3009.8	23.23	0	0.80	0.98	0	98.23
166	2.8	13556.6	0	33.3	22.4	0	2344.1	18.11	0	0.83	1.64	0	97.53
200	3.3	12695.6	0	50.3	20.8	0	2823.8	22.15	0	1.05	1.27	0	97.69
234	3.9	12772.8	0	56.3	21.7	0	2633.1	20.96	0	1.25	1.41	0	97.34
268	4.5	13157.8	0	53.8	20.4	0	2500	19.64	0	1.26	1.40	0	97.34
302	5.0	13557.1	0	55.8	23.5	0	2389.3	18.56	0	1.36	1.68	0	96.96
336	5.6	12495.9	0	62.2	24	0	2606.5	21.23	0	1.39	1.57	0	97.04
370	6.2	12385.9	0	60.8	24.2	0	2617.3	21.44	0	1.35	1.58	0	97.07
404	6.7	12512.8	0	60.9	27.4	0	2573.4	21.03	0	1.38	1.81	0	96.81
438	7.3	12802.3	0	61.3	28.7	0	2463.2	20.00	0	1.44	1.98	0	96.58

Table D4 The results of the reaction with 20 ml/min of CH_4, 5 ml/min of O_2, 5 ml/min of N_2, 6.5 ml/h of 48 wt% HBr/H_2O, reaction temperature 660 °C, and 2 g of Activated carbon

TOS		FID					TCD	%CH_4 Conversion	% Selectivity				
min	h	CH_4	C_2H_6	C_2H_4	CH_3Br	CH_2Br_2	CO		C_2H_6	C_2H_4	CH_3Br	CH_2Br_2	CO
30	0.5	12457.4	0	0	0	0	1827.3	15.36	0	0	0	0	100
64	1.1	11355.6	0	0	0	0	2190.6	19.26	0	0	0	0	100
98	1.6	11136.7	0	0	0	0	2268.3	20.12	0	0	0	0	100
132	2.2	10878.8	0	0	0	0	2186.7	19.91	0	0	0	0	100
166	2.8	11676.7	0	0	0	0	2029.4	17.69	0	0	0	0	100
200	3.3	11412.2	0	0	0	0	2089.6	18.46	0	0	0	0	100
234	3.9	11547.1	0	0	0	0	2004.9	17.68	0	0	0	0	100
268	4.5	10876.1	0	0	0	0	2439	21.71	0	0	0	0	100
302	5.0	10961.2	0	0	0	0	2278.5	20.45	0	0	0	0	100
336	5.6	10990.6	0	0	0	0	2286.4	20.46	0	0	0	0	100
370	6.2	10255.4	0	0	0	0	2417.1	22.57	0	0	0	0	100
404	6.7	10559.8	0	0	0	0	2357.3	21.64	0	0	0	0	100
438	7.3	10869.7	0	0	0	0	2277.3	20.58	0	0	0	0	100

Table D5 The results of the reaction with 20 ml/min of CH_4, 5 ml/min of O_2, 5 ml/min of N_2, 6.5 ml/h of 48 wt% HBr/H_2O, reaction temperature 400 °C

TOS		FID					TCD	%CH_4 Conversion	% Selectivity				
min	h	CH_4	C_2H_6	C_2H_4	CH_3Br	CH_2Br_2	CO		C_2H_6	C_2H_4	CH_3Br	CH_2Br_2	CO
30	0.5	14407.6	0	0	49.6	0	0	0.74	0	0	100	0	0
64	1.1	13885.5	0	0	19	0	0	0.30	0	0	100	0	0
98	1.6	14061.1	0	0	13.3	0	0	0.21	0	0	100	0	0
132	2.2	14630.7	0	0	10.2	0	0	0.15	0	0	100	0	0
166	2.8	14026.6	0	0	12.7	0	0	0.20	0	0	100	0	0
200	3.3	13343.5	0	0	17.2	0	0	0.28	0	0	100	0	0
234	3.9	13498.8	0	0	10.3	0	0	0.17	0	0	100	0	0
268	4.5	13613.5	0	0	12.2	0	0	0.19	0	0	100	0	0
302	5.0	13349.7	0	0	11.6	0	0	0.19	0	0	100	0	0
336	5.6	13486.7	0	0	11.5	0	0	0.19	0	0	100	0	0
370	6.2	13032.5	0	0	14	0	0	0.23	0	0	100	0	0
404	6.7	13108.6	0	0	17.6	0	0	0.29	0	0	100	0	0
438	7.3	13166.3	0	0	13.9	0	0	0.23	0	0	100	0	0

Table D6 The results of the reaction with 20 ml/min of CH_4, 5 ml/min of O_2, 5 ml/min of N_2, 6.5 ml/h of 48 wt% HBr/H_2O, reaction temperature 500 °C

TOS		FID					TCD	%CH_4 Conversion	% Selectivity				
min	h	CH_4	C_2H_6	C_2H_4	CH_3Br	CH_2Br_2	CO		C_2H_6	C_2H_4	CH_3Br	CH_2Br_2	CO
30	0.5	14349.3	0	0	359.7	27.3	124.3	6.31	0	0	81.01	3.07	15.92
64	1.1	14214.5	0	0	269.3	22.8	88.6	4.82	0	0	81.34	3.44	15.21
98	1.6	14619.4	0	0	302.9	23.4	101.2	5.25	0	0	81.40	3.14	15.46
132	2.2	13774.4	0	0	346.6	31.3	135.9	6.49	0	0	78.86	3.56	17.58
166	2.8	13423.9	0	0	395.1	36	159.1	7.54	0	0	78.46	3.57	17.96
200	3.3	13223.2	0	0	410.8	42	177.5	8.06	0	0	77.11	3.94	18.94
234	3.9	13117.2	0	0	419.9	44.2	185.2	'8.32	0	0	76.72	4.04	19.24
268	4.5	12820.1	0	0	380.2	38.7	158.3	7.67	0	0	77.66	3.95	18.38
302	5.0	13035.8	0	0	359.5	37.3	141.7	7.11	0	0	78.37	4.07	17.56
336	5.6	13355.4	0	0	346.5	33.3	134.2	6.68	0	0	78.85	3.79	17.36
370	6.2	13135	0	0	367.4	34.8	141.8	7.16	0	0	78.94	3.74	17.32
404	6.7	13073.8	0	0	383	39.1	148.4	7.49	0	0	78.66	4.02	17.33
438	7.3	13222.2	0	0	373.2	38.1	147	7.26	0	0	78.43	4.00	17.56

Table D7 The results of the reaction with 20 ml/min of CH_4, 5 ml/min of O_2, 5 ml/min of N_2, 6.5 ml/h of 48 wt% HBr/H_2O, reaction temperature 600 °C

TOS		FID					TCD	%CH_4 Conversion	% Selectivity				
min	h	CH_4	C_2H_6	C_2H_4	CH_3Br	CH_2Br_2	CO		C_2H_6	C_2H_4	CH_3Br	CH_2Br_2	CO
30	0.5	13706.7	0	11.2	1023.3	95.4	391.9	17.12	0	0.29	78.86	3.68	17.17
64	1.1	13409.2	0	7.7	938.9	87.1	372.2	16.29	0	0.22	78.46	3.64	17.68
98	1.6	13782.2	0	6.8	839.9	69.3	343.3	14.50	0	0.22	78.35	3.23	18.21
132	2.2	13618.2	0	0	847.1	70.4	336.3	14.64	0	0	78.91	3.28	17.81
166	2.8	13906	0	0	837.5	67.7	319.1	14.14	0	0	79.55	3.22	17.23
200	3.3	14116.1	0	0	786.5	60.7	296.5	13.18	0	0	79.81	3.08	17.11
234	3.9	14138.1	0	0	812.3	61.7	316.3	13.60	0	0	79.41	3.02	17.58
268	4.5	14311.7	0	0	785.7	58.9	285.2	12.93	0	0	80.40	3.01	16.59
302	5.0	13499.4	0	0	868.7	68.9	336.5	14.99	0	0	79.37	3.15	17.48
336	5.6	13625.1	0	0	848.1	66.2	354.4	14.74	0	0	78.33	3.06	18.61
370	6.2	13743.4	0	0	820.6	64.9	311.1	14.02	0	0	79.68	3.15	17.17
404	6.7	13773	0	0	798.7	62	297.4	13.63	0	0	79.97	3.10	16.93
438	7.3	12714.8	0	0	843.4	71.8	353.1	15.60	0	0	78.09	3.32	18.59

Table D8 The results of the reaction with 20 ml/min of CH_4, 5 ml/min of O_2, 5 ml/min of N_2, 6.5 ml/h of 48 wt% HBr/H_2O, reaction temperature 660 °C

TOS		FID					TCD	%CH_4 Conversion	% Selectivity				
min	h	CH_4	C_2H_6	C_2H_4	CH_3Br	CH_2Br_2	CO		C_2H_6	C_2H_4	CH_3Br	CH_2Br_2	CO
30	0.5	11808.5	0	38.8	1126.4	79.7	932.7	24.09	0	0.77	65.88	2.33	31.01
64	1.1	11710.8	0	30	1518.3	145.9	886	28.21	0	0,49	72.12	3.47	23.93
98	1.6	11834.5	0	30.5	1447	133.2	840.9	27.00	0	0.52	72.27	3.33	23.88
132	2.2	11760.8	0	29.4	1387	124.7	794.6	26.22	0	0.53	72.57	3.26	23.64
166	2.8	11779.8	0	26.4	1362.4	116.5	791.2	25.86	0	0.48	72.49	3.10	23.93
200	3.3	12135.3	0	35.2	1284.4	104.8	801.8	24.57	0	0.67	71.17	2.90	25.26
234	3.9	11844.6	0	33.7	1292.3	103.8	810.4	25.13	0	0.63	71.14	2.86	25.36
268	4.5	11872.4	0	30.7	1294.2	100.6	790.5	24.96	0	0.58	71.72	2.79	24.91
302	5.0	12019.5	0	35.5	1240.9	93.8	810.5	24.29	0	0.69	70.48	2.66	26.17
336	5.6	12012.6	0	34.2	1298.4	97.3	834.7	25.04	0	0.64	70.82	2.65	25.89
370	6.2	12213.1	0	33.4	1256.1	92.9	811.8	24.14	0	0.64	70.75	2.62	25.99
404	6.7	12340.8	0	45.4	1261.8	92.6	879.2	24.48	0	0.85	69.20	2.54	27.41
438	7.3	11796.8	0	40.9	1143.4	84.8	805.3	23.56	0	0.84	68.98	2.56	27.62

Table D9 The results of the reaction with 20 ml/min of CH_4, 5 ml/min of O_2, 5 ml/min of N_2, 6.5 ml/h of 48 wt% HBr/H_2O, reaction temperature 700 °C

TOS		FID					TCD	%CH_4 Conversion	% Selectivity				
min	h	CH_4	C_2H_6	C_2H_4	CH_3Br	CH_2Br_2	CO		C_2H_6	C_2H_4	CH_3Br	CH_2Br_2	CO
30	0.5	13577.5	16.1	217	1080.7	43.1	1085.7	23.23	0.31	4.11	59.90	1.19	34.21
64	1.1	12464.8	0	94.6	1361.9	84.6	1178.8	27.26	0	1.53	64.52	2.00	31.75
98	1.6	11991.3	0	78.1	1264.9	70.5	1067.6	26.30	0	1.38	65.30	1.82	31.34
132	2.2	11969.3	0	66.5	1368.2	71.8	1038.7	27.11	0	1.12	67.71	1.78	29.22
166	2.8	12360.9	0	76.8	1223.8	62.2	1016.8	24.97	0	1.41	65.72	1.67	31.05
200	3.3	12649	0	78.4	1224.5	57.6	1018.5	24.55	0	1.44	65.76	1.55	31.10
234	3.9	12081	0	69.2	1256	59.5	1046.8	25.83	0	1.24	65.84	1.56	31.20
268	4.5	12324.9	0	67.2	1297.4	59.2	980.8	25.47	0	1.20	67.91	1.55	29.19
302	5.0	11633.5	0	70.9	1221	62.8	1158.6	26.88	0	1.25	62.99	1.62	33.98
336	5.6	11799.8	0	72.2	1175.7	61.1	1080	25.69	0	1.33	63.63	1.65	33.23
370	6.2	11872.8	0	67.7	1244.5	61.1	1095.4	26.32	0	1.20	64.69	1.59	32.37
404	6.7	11953.7	0	62.7	1242.3	61.4	961	25.36	0	1.16	67.39	1.67	29.64
438	7.3	12138.7	0	70.1	1203.6	59	1029.9	25.12	0	1.30	65.22	1.60	31.73

Table D10 The results of the reaction with 20 ml/min of CH_4, 10 ml/min of N_2, 6.5 ml/h of 48 wt% HBr/H_2O, reaction temperature 400 °C, and 2 g of 0.5 wt% Rh/SiO_2-calcined at 450 °C 6 h

TOS		FID					TCD	%CH_4 Conversion	% Selectivity				
min	h	CH_4	C_2H_6	C_2H_4	CH_3Br	CH_2Br_2	CO		C_2H_6	C_2H_4	CH_3Br	CH_2Br_2	CO
30	0.5	14280	0	0	0	0	0	0	0	0	0	0	0
64	1.1	14373.5	0	0	0	0	0	0	0	0	0	0	0
98	1.6	14293.2	0	0	0	0	0	0	0	0	0	0	0
132	2.2	15425.9	0	0	0	0	0	0	0	0	0	0	0
166	2.8	14940.5	0	0	0	0	0	0	0	0	0	0	0
200	3.3	15099.5	0	0	0	0	0	0	0	0	0	0	0
234	3.9	14621	0	0	0	0	0	0	0	0	0	0	0
268	4.5	14783.2	0	0	0	0	0	0	0	0	0	0	0
302	5.0	15310.6	0	0	0	0	0	0	0	0	0	0	0
336	5.6	15593.7	0	0	0	0	0	0	0	0	0	0	0
370	6.2	15549.6	0	0	0	0	0	0	0	0	0	0	0

Table D11 The results of the reaction with 20 ml/min of CH_4, 3.5 ml/min of O_2, 7.5 ml/min of N_2, 6.5 ml/h of 48 wt% HBr/H_2O, reaction temperature 400 °C, and 2 g of 0.5 wt% Rh/SiO_2-calcined at 450 °C 6 h

TOS		FID					TCD	%CH_4 Conversion	% Selectivity				
min	h	CH_4	C_2H_6	C_2H_4	CH_3Br	CH_2Br_2	CO		C_2H_6	C_2H_4	CH_3Br	CH_2Br_2	CO
30	0.5	12113.2	0	0	98.9	0	71.1	2.44	0	0	70.99	0	29.01
64	1.1	12357.6	0	0	113.4	0	45.3	2.39	0	0	81.49	0	18.51
98	1.6	11700.9	0	0	103.1	0	39.1	2.28	0	0	82.26	0	17.74
132	2.2	11889.5	0	0	109.8	0	45.2	2.42	0	0	81.03	0	18.97
166	2.8	11850.3	0	0	109.5	0	44.4	2.41	0	0	81.27	0	18.73
200	3.3	11935.8	0	0	107.7	0	47.9	2.40	0	0	79.82	0	20.18
234	3.9	11848.5	0	0	101.8	0	35.5	2.19	0	0	83.45	0	16.55
268	4.5	11979.8	0	0	108.6	0	44	2.37	0	0	81.28	0	18.72
302	5.0	12245.3	0	0	113	0	43.5	2.39	0	0	82.04	0	17.96
336	5.6	12440.2	0	0	123.1	0	44.9	2.53	0	0	82.82	0	17.18
370	6.2	11616.7	0	0	125.9	0	48.9	2.80	0	0	81.91	0	18.09

Table D12 The results of the reaction with 20 ml/min of CH_4, 5 ml/min of O_2, 5 ml/min of N_2, 6.5 ml/h of 48 wt% HBr/H_2O, reaction temperature 400 °C , and 2 g of 0.5 wt% Rh/SiO_2-calcined at 450 °C 6 h

TOS		FID					TCD	%CH_4 Conversion	% Selectivity				
min	h	CH_4	C_2H_6	C_2H_4	CH_3Br	CH_2Br_2	CO		C_2H_6	C_2H_4	CH_3Br	CH_2Br_2	CO
30	0.5	14919.2	0	0	249.6	0	80.3	4.13	0	0	84.54	0.00	15.46
64	1.1	14256.4	0	0	248.7	8.4	92.7	4.46	0	0	81.38	1.37	17.25
98	1.6	14624.3	0	0	277.8	12	72.4	4.61	0	0	85.49	1.85	12.67
132	2.2	14258.6	0	0	267.2	13	54.7	4.44	0	0	87.66	2.13	10.20
166	2.8	14157.2	0	0	266.1	13.2	52.7	4.44	0	0	87.92	2.18	9.90
200	3.3	14509	0	0	245.3	13.1	35.8	3.92	0	0	90.12	2.41	7.48
234	3.9	14593.9	0	0	256.6	13	38.3	4.07	0	0	90.07	2.28	7.64
268	4.5	14749.6	0	0	252.5	13.1	29.7	3.91	0	0	91.51	2.37	6.12
302	5.0	14777.2	0	0	246	12.9	22.1	3.75	0	0	92.83	2.43	4.74
336	5.6	13857.2	0	0	245.8	12.8	24.8	4.01	0	0	92.30	2.40	5.29
370	6.2	13999.4	0	0	245.6	12.4	20.6	3.93	0	0	93.20	2.35	4.44

Table D13 The results of the reaction with 20 ml/min of CH_4, 6 ml/min of O_2, 4 ml/min of N_2, 6.5 ml/h of 48 wt% HBr/H_2O, reaction temperature 400 °C , and 2 g of 0.5 wt% Rh/SiO_2-calcined at 450 °C 6 h

TOS		FID					TCD	%CH_4 Conversion	% Selectivity				
min	h	CH_4	C_2H_6	C_2H_4	CH_3Br	CH_2Br_2	CO		C_2H_6	C_2H_4	CH_3Br	CH_2Br_2	CO
30	0.5	11798	0	0	120.6	0	177.3	3.92	0	0	54.47	0	45.53
64	1.1	11445.2	0	0	151.9	0	106.6	3.88	0	0	71.48	0	28.52
98	1.6	11298.5	0	0	145.4	0	106.9	3.82	0	0	70.52	0	29.48
132	2.2	11487.1	0	0	153	0	119.3	4.01	0	0	69.29	0	30.71
166	2.8	11775.9	0	0	154.1	0	103.9	3.79	0	0	72.29	0	27.71
200	3.3	12131.8	0	0	158.5	0	96.6	3.69	0	0	74.27	0	25.73
234	3.9	12220.4	0	0	167.9	0	111.1	3.95	0	0	72.66	0	27.34
268	4.5	11701.5	0	0	167.7	0	112.1	4.12	0	0	72.46	0	27.54
302	5.0	11727.8	0	0	168.6	0	105.8	4.07	0	0	73.70	0	26.30
336	5.6	11376.2	0	0	168.1	0	109.9	4.22	0	0	72.90	0	27.10
370	6.2	11590.7	0	0	175.6	6.5	107.8	4.31	0	0	73.12	1.35	25.52

Table D14 The results of the reaction with 20 ml/min of CH_4, 5 ml/min of O_2, 5 ml/min of N_2, 6.5 ml/h of 48 wt% HBr/H_2O, reaction temperature 400 °C , and 2 g of 0.3 wt% Rh/SiO_2-calcined at 450 °C 6 h

TOS		FID					TCD	%CH_4 Conversion	% Selectivity				
min	h	CH_4	C_2H_6	C_2H_4	CH_3Br	CH_2Br_2	CO		C_2H_6	C_2H_4	CH_3Br	CH_2Br_2	CO
30	0.5	11844.5	0	0	122.7	27.4	81.1	3.24	0	0	67.23	7.51	25.26
64	1.1	13557.6	0	0	148.9	0	131.3	3.46	0	0	66.61	0	33.39
98	1.6	11609	0	0	126.2	0	59.5	2.91	0	0	78.86	0	21.14
132	2.2	12479	0	0	129.7	0	50.8	2.69	0	0	81.79	0	18.21
166	2.8	12276.5	0	0	115.7	0	34.4	2.34	0	0	85.54	0	14.46
200	3.3	13041.5	0	0	122.5	0	0	2.00	0	0	100	0	0
234	3.9	12864.1	0	0	119.6	0	0	1.98	0	0	100	0	0
268	4.5	12132.3	0	0	100.5	0	0	1.77	0	0	100	0	0
302	5.0	12140.6	0	0	102.5	0	0	1.80	0	0	100	0	0
336	5.6	11711	0	0	99.6	0	0	1.82	0	0	100	0	0
370	6.2	11592	0	0	103.9	0	0	1.91	0	0	100	0	0

Table D15 The results of the reaction with 20 ml/min of CH_4, 5 ml/min of O_2, 5 ml/min of N_2, 6.5 ml/h of 48 wt% HBr/H_2O, reaction temperature 400 °C , and 2 g of 0.3 wt% Rh/SiO_2-calcined at 900 °C 10 h

TOS		FID					TCD	%CH_4 Conversion	% Selectivity				
min	h	CH_4	C_2H_6	C_2H_4	CH_3Br	CH_2Br_2	CO		C_2H_6	C_2H_4	CH_3Br	CH_2Br_2	CO
30	0.5	12510.7	0	0	38.5	0	0	0.66	0	0	100	0	0
64	1.1	12193.2	0	0	53.7	0	0	0.95	0	0	100	0	0
98	1.6	11643.9	0	0	43.6	0	0	0.81	0	0	100	0	0
132	2.2	11884	0	0	35.7	0	0	0.65	0	0	100	0	0
166	2.8	11605.1	0	0	44.5	0	0	0.83	0	0	100	0	0
200	3.3	11827.1	0	0	40.5	0	0	0.74	0	0	100	0	0
234	3.9	12069	0	0	43.3	0	0	0.77	0	0	100	0	0
268	4.5	11584.8	0	0	49.7	0	0	0.92	0	0	100	0	0
302	5.0	11840.5	0	0	42.4	0	0	0.77	0	0	100	0	0
336	5.6	12069	0	0	51.9	0	0	0.93	0	0	100	0	0
370	6.2	11863	0	0	48.9	0	0	0.89	0	0	100	0	0

Table D16 The results of the reaction with 20 ml/min of CH_4, 5 ml/min of O_2, 5 ml/min of N_2, 6.5 ml/h of 48 wt% HBr/H_2O, reaction temperature 400 °C , and 2 g of 0.5 wt% Rh/SiO_2-calcined at 900 °C 10 h

TOS		FID					TCD	%CH_4 Conversion	% Selectivity				
min	h	CH_4	C_2H_6	C_2H_4	CH_3Br	CH_2Br_2	CO		C_2H_6	C_2H_4	CH_3Br	CH_2Br_2	CO
30	0.5	12697.1	0	0	35	0	50.7	1.08	0	0	54.84	0	45.16
64	1.1	12016.6	0	0	44.3	0	0	0.80	0	0	100	0	0
98	1.6	11789.8	0	0	35.9	0	0	0.66	0	0	100	0	0
132	2.2	11564.5	0	0	38.7	0	0	0.72	0	0	100	0	0
166	2.8	11757.2	0	0	41	0	0	0.75	0	0	100	0	0
200	3.3	11958.6	0	0	50.2	0	0	0.90	0	0	100	0	0
234	3.9	12146	0	0	45.3	0	0	0.80	0	0	100	0	0
268	4.5	12367.4	0	0	53	0	0	0.92	0	0	100	0	0
302	5.0	12521.7	0	0	45.8	0	0	0.79	0	0	100	0	0
336	5.6	12569.5	0	0	49.1	0	0	0.84	0	0	100	0	0
370	6.2	12024.1	0	0	57.8	0	0	1.03	0	0	100	0	0

Table D17 The results of the reaction with 20 ml/min of CH_4, 5 ml/min of O_2, 5 ml/min of N_2, 6.5 ml/h of 48 wt% HBr/H_2O, reaction temperature 400 °C , and 2 g of SiO_2

TOS		FID					TCD	%CH_4 Conversion	% Selectivity				
min	h	CH_4	C_2H_6	C_2H_4	CH_3Br	CH_2Br_2	CO		C_2H_6	C_2H_4	CH_3Br	CH_2Br_2	CO
30	0.5	15083.4	0	0	194.7	7.8	25.6	2.98	0	0	91.34	1.83	6.83
64	1.1	14822.8	0	0	161.7	7	41.1	2.69	0	0	85.75	1.86	12.39
98	1.6	14377.4	0	0	126.4	0	0	1.88	0	0	100	0	0
132	2.2	13460.6	0	0	102.3	0	0	1.63	0	0	100	0	0
166	2.8	13803.8	0	0	99.5	0	0	1.54	0	0	100	0	0
200	3.3	13922.4	0	0	103.4	0	0	1.59	0	0	100	0	0
234	3.9	14279	0	0	94.9	0	0	1.43	0	0	100	0	0
268	4.5	13355.4	0	0	93	0	0	1.49	0	0	100	0	0
302	5.0	13660.7	0	0	97	0	0	1.52	0	0	100	0	0
336	5.6	13766.7	0	0	93.2	0	0	1.45	0	0	100	0	0
370	6.2	13844.6	0	0	94.7	0	0	1.47	0	0	100	0	0

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