REFERENCES

Aboul-Gheit, A.K., Hanafy, S.A., Aboul-Enein, A.A., and Ghoneim, S.A., (2011) Para-xylene maximization: Part IX—Activation of toluene methylation catalysts with palladium. Journal of the Taiwan Institute of Chemical Engineers, 42 (5), 860-867.

Conley, B.L., Tenn Iii, W.J., Young, K.J.H., Ganesh, S.K., Meier, S.K., Ziatdinov, V.R., Mironov, O., Oxgaard, J., Gonzales, J., Goddard Iii, W.A., and Periana, R.A. (2006) Design and study of homogeneous catalysts for the selective, low temperature oxidation of hydrocarbons. Journal of Molecular Catalysis A: Chemical 251(1-2), 8-23.

Crabtree, R. H. (1995) Aspects of Methane Chemistry. Chemical Reviews 95(4), 987-1007.

Degirmenci, V., Uner, D., and Yilmaz, A., (2005) Methane to higher hydrocarbons via halogenation. Catalysis Today, 106 (1-4), 252-255.

Degirmenci, V., Uner, D., and Yilmaz, A. (2009) Selective methane bromination over sulfated zirconia in SBA-15 catalysts. Catalysis Today 142(1-2), 30-33.

Ding, K., Metiu, H., and Stucky, G.D., (2013) The Selective High-Yield Conversion of Methane Using Iodine-Catalyzed Methane Bromination. ACS Catalysis 3(3), 474-477.

Lersch, P., and F. Bandermann (1991) Conversion of chloromethane over metal-exchanged ZSM-5 to higher hydrocarbons. Applied Catalysis 75(1), 133-152.

Lin, R., Ding, Y., Gong, L., Li, J., Chen, W., Yan, L., and Lu, Y., (2009) Oxidative bromination of methane on silica- supported non-noble metal oxide catalysts. Applied Catalysis A: General 353(1), 87-92.

Liu, Z., Li, W., and Zhou, X., (2010) Product oriented oxidative bromination of methane over Rh/SiO2 catalysts. Journal of Natural Gas Chemistry 19(5), 522-529.

Lorkovic, I.M., Yilmaz, A., Yilmaz, G.A., Zhou, X.P., Laverman, L.E., Sun, S., Schaefer, D.J., Weiss, M., Noy, M.L., Cutler, C.I., Sherman, J.H., McFarland, E.W., Stucky, G.D., and Ford, P.C., (2004) A novel integrated process for the functionalization of methane and ethane: Bromine as mediator. Catalysis Today 98(1-2 SPEC. ISS.), 317-322.

Lunsford, J.H. (1995) The Catalytic Oxidative Coupling of Methane. Angewandte Chemie International Edition in English 34(9), 970-980.

Lunsford, J.H. (2000) Catalytic conversion of methane to more useful chemicals and fuels: A challenge for the 21st century. Catalysis Today 63(2-4), 165-174.

Olah, G.A., Gupta, B., Felberg, J.D., Ip, W.M., Husain, A., Karpeles, R., Lammertsma, K., Melhotra, A.K., and Trivedi, N.J., (1985) Selective Monohalogenation of Methane over Supported Acid or Platinum Metal Catalysts and Hydrolysis of Methyl Halides over y-Alumina-Supported Metal Oxide/Hydroxide Catalysts. A Feasible Path for the Oxidative Conversion of Methane into Methyl Alcohol/Dimethyl Ether. Journal of the American Chemical Society **107**(24), 7097-7105.

Olah, G.A., and Mo, Y. K. (1972) Electrophilic reaction at single bonds. XIII. Chlorination and chlorolysis of alkanes in antimony pentafluoride-chlorine-fluorosulfuryl chloride solution at low temperature. Journal of the American Chemical Society 94(19), 6864-6865.

Reid, R.C., Prausnitz, J.M., and Sherwood, T.K., (1977) The Properties of Gases and Liquids. New York, McGraw-Hill.

Wang, K.X., Xu, H.F., Li, W.S., and Zhou, X.P., (2005) Acetic acid synthesis from methane by non-synthesis gas process. Journal of Molecular Catalysis A: Chemical 225(1), 65-69.

Wang, K.X., Xu, H.F., Li, W.S., Au, C.T., and Zhou, X.P., (2006) The synthesis of acetic acid from methane via oxidative bromination, carbonylation, and hydrolysis. Applied Catalysis A: General 304(0), 168-177.

Weissman, M. and Benson, S.W. (1984) Pyrolysis of methyl chloride, a pathway in the chlorine-catalyzed polymerization of methane. International Journal of Chemical Kinetics 16(4), 307-333.

Xu, H., Wang, K., Li, W., and Zhou, X., (2005) Dimethyl ether synthesis from methane by non syngas process. Catalysis Letters 100(1-2),53-57.

Yang, F., Liu, Z., Li, W., Wu, T., and Zhou, X., (2008) The Oxidative Bromination of Methane Over Rh/SiO2 Catalyst. Catalysis Letters 124(3-4), 226-232.

Zhou, X.-P., Yilmaz, A., Yilmaz, G.A., Lorkovic, I.M., Laverman, L.E., Weiss, M., Sherman, J.H., McFarland, E.W., Stucky, G.D., and Ford, P.C., (2003) An integrated process for partial oxidation of alkanes. Chemical Communications(18), 2294-2295.

Zhou, X.-P., Ouyang, Q., Yin, S.-F., Chen, L., and Au, C.-T., (2013) A new catalytic process for high-efficiency synthesis of p-xylene by methylation of toluene with CH3Br. AIChE Journal, 59 (2), 532-540.

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 barium oxide and tungsten oxide on silica catalysts were prepared by 2 techniques, incipient wetness impregnation and sol-gel technique.

B1 Incipient wetness impregnation method.

Support containing the same pore volume as the volume of the solution that was added.

Example 5 g of 1Ba/SiO_2-I catalyst (0.40%wt Ba/SiO_2)

= 5 g (BaO + SiO_2) of 0.40 % (Ba^0 w/w to BaO +SiO_2)

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

Step 1: wt. Ba^0

wt. of Ba^0	0.0200	g

Step 2: wt. BaO

MW of Ba^0	137.3270	g/mol
MW of BaO	153.3300	g/mol
wt. of BaO	0.0223	g

Step 3: wt SiO_2

wt. of Support (SiO_2)	4.9777	g

Step 4: wt $BaNO_3$

MW of $Ba(NO_3)_2$	261.3700	g/mol
g of $Ba(NO_3)_2$	0.0381	g
(assay ≥ 99.9% trace metal basis)		
Corrected weight	0.0384	g

Step 5: Volume of SiO_2

From BET surface analysis, total pore volume of SiO_2 is 1.89 ml/g

Volume of SiO_2	9.41	ml

Step 6: Water required

Impregnation volume (100% pore volume)

Water required for BaO	9.41	ml

Table B1 The ingredients of impregnated catalyst.

Catalyst	Loading (wt%)	SiO_2(g)	Metal precursor		Required water (ml)
			$Ba(NO_3)_2$ (g)	$(NH_4)_{10}H_2(W_2O_7)_6$ (g)	
1Ba/SiO_2-I	0.40	4.9777	0.0384	-	9.41
2Ba/SiO_2-I	0.67	4.9626	0.0644	-	9.38
3Ba/SiO_2-I	1.33	4.9256	0.1278	-	9.31
1W/SiO_2-I	0.54	4.9660	-	0.0375	9.40
2W/SiO_2-I	0.89	4.9440	-	0.0618	9.34
3W/SiO_2-I	1.79	4.8871	-	0.1242	9.24

B2 Sol-gel method.

Example 10 g of 1Ba/SiO_2-S catalyst (0.40%wt Ba/SiO_2)

= 10 g (BaO + SiO_2) of 0.40 % (Ba^0 w/w to BaO +SiO_2)

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

Step 1: wt. Ba^0

wt. of Ba^0	0.0400	g

Step 2: wt. BaO

MW of Ba^0	137.3270	g/mol
MW of BaO	153.3300	g/mol
wt. of BaO	0.0447	g

Step 3: wt SiO_2

wt. of SiO_2	9.9553	g
MW of SiO_2	60.0800	g/mol
MW of $Si(OC_2H_5)_4$	208.3300	g/mol
Wt of $Si(OC_2H_5)_4$	34.5206	g

Step 4: wt $BaNO_3$

MW of $Ba(NO_3)_2$	261.3700	g/mol
g of $Ba(NO_3)_2$	0.7610	g

(assay ≥ 99.9% trace metal basis)

(assay ≥ 99.9% trace metal basis)

Corrected weight 0.0769 g

Table B2 The ingredients of sol-gel catalyst.

Catalyst	Loading (wt%)	$Si(OC_2H_5)_4$ (g)	Metal precursor	
			$Ba(NO_3)_2$ (g)	$(NH_4)_{10}H_2(W_2O_7)_6$ (g)
1Ba/SiO_2-S	0.40	34.5206	0.0769	-
2Ba/SiO_2-S	0.67	34.4160	0.1288	-
3Ba/SiO_2-S	1.33	34.1605	0.2557	-
1W/SiO_2-S	0.54	34.4393	-	0.0749
2W/SiO_2-S	0.89	34.2862	-	0.1235
3W/SiO_2-S	1.79	33.8927	-	0.2483

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.

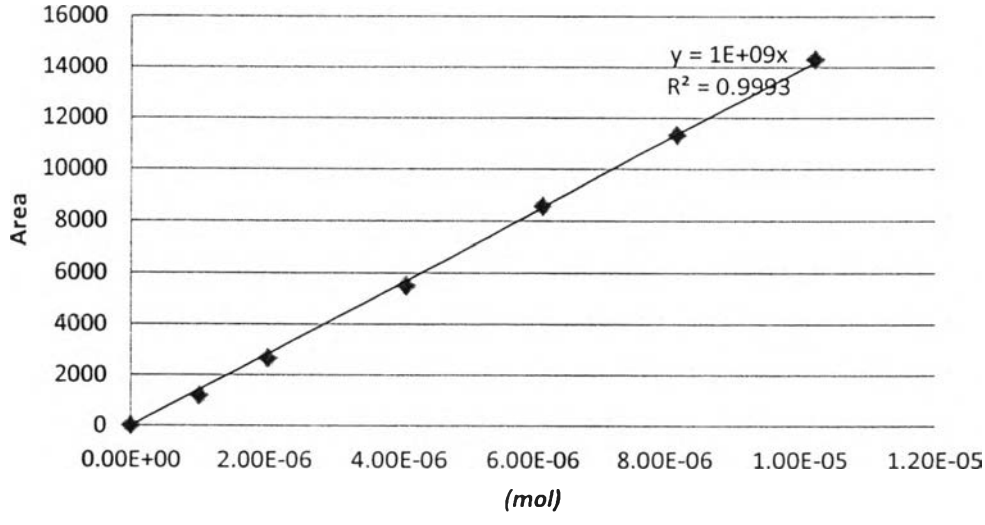

Figure C1 Response factors from GC FID as a function of injection volume of methyl bromide.

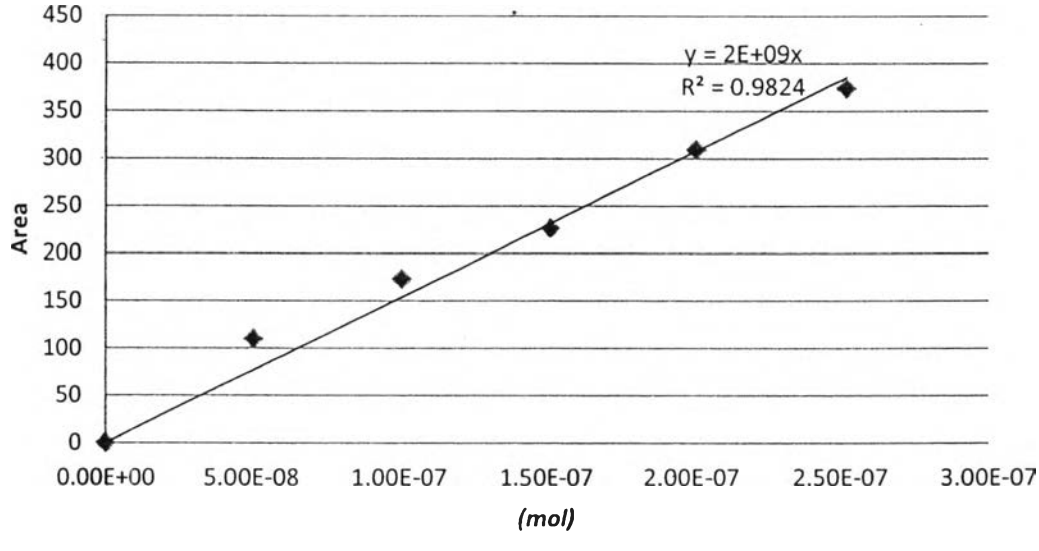

Figure C2 Response factors from GC FID as a function of injection volume of dibromomethanes.

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,

TOS		FID					TCD	%CH_4 Conversion	% Selectivity					%CH_3Br Yield
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	13618	7.8	88.4	1200	157.1	1888	21.86	0.11	1.27	50.32	3.29	45.01	11.00
64	1.1	14597	8.5	124.7	1503	175.1	1844	22.76	0.11	1.59	55.99	3.26	39.05	12.75
98	1.6	14113	9.2	129	1511	188	1803.5	23.33	0.12	1.65	56.43	3.51	38.29	13.16
132	2.2	14275	8.5	127.9	1427.1	172.2	1757.5	22.34	0.11	1.71	55.77	3.36	39.05	12.46
166	2.8	14457	8.3	133.5	1357.4	155.9	1785.5	21.73	0.11	1.82	54.32	3.12	40.62	11.80
200	3.3	14374	7.8	124.6	1394.6	158	1653.6	21.54	0.11	1.73	56.71	3.21	38.23	12.22
234	3.9	14515	7.8	126.8	1459.2	155.8	1855	22.56	0.10	1.64	55.32	2.95	39.98	12.48
268	4.5	14344	6.7	144.6	1481.1	161.7	1499.2	21.67	0.09	2.00	60.06	3.28	34.56	13.01
302	5.0	14427	6.2	108.6	1506.8	162.9	1421	21.28	0.09	1.52	61.87	3.34	33.17	13.16
336	5.6	14367	6.3	113.4	1455.9	152.9	1460.8	21.14	0.09	1.61	60.57	3.18	34.55	12.81
370	6.2	14431.5	5.6	104.6	1453.8	149.5	1364.5	20.63	0.08	1.53	62.08	3.19	33.12	12.80
404	6.7	14467.7	5.4	102.2	1461.8	146.8	1337.3	20.51	0.08	1.50	62.68	3.15	32.60	12.86
438	7.3	14439.1	4	82.3	1546.8	150.2	1210.5	20.54	0.06	1.20	66.11	3.21	29.42	13.58
472	7.9	14483.1	3.8	78.5	1538.2	148.4	1174.8	20.27	0.06	1.16	66.63	3.21	28.93	13.51

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 commercial SiO_2.

TOS		FID					TCD	%CH_4 Conversion	% Selectivity					%CH_3Br Yield
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	13333	4	16	178	0	3608	20.95	0.06	0.24	7.95	0.00	91.75	1.67
64	1.1	13161	2	23	1163	48	3325	27.04	0.02	0.25	37.68	0.78	61.26	10.19
98	1.6	13533	0	21	1251	53	3350	27.12	0.00	0.23	39.23	0.83	59.71	10.64
132	2.2	13810	0	16	1109	45	3380	25.93	0.00	0.18	36.24	0.74	62.79	9.40
166	2.8	13797	0	15	1225	67	3169	25.99	0.00	0.17	39.95	1.09	58.74	10.38
200	3.3	14147	0	13	1129	48	3007	24.25	0.00	0.15	39.35	0.83	59.61	9.54
234	3.9	14533	0	11	1125	39	2814	23.00	0.00	0.13	40.91	0.71	58.20	9.41
268	4.5	14804	0	10	1042	34	2660	21.54	0.00	0.13	40.46	0.66	58.72	8.72
302	5.0	14799	0	8	1011	30	2514	20.78	0.00	0.12	41.12	0.61	58.13	8.54
336	5.6	14957	0	8	1023	25	2577	20.90	0.00	0.11	40.85	0.50	58.51	8.54
370	6.2	14229	0	9	1026	33	2692	22.23	0.00	0.11	39.82	0.64	59.39	8.85
404	6.7	14316	0	8	1069	35	2742	22.60	0.00	0.10	40.36	0.65	58.85	9.12
438	7.3	13962	3	7	992	43	2562	21.84	0.03	0.09	40.11	0.87	58.89	8.76
472	7.9	14100	4	4	1023	23	2572	21.85	0.05	0.05	40.93	0.46	58.51	8.94

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 sol-gel SiO_2.

TOS		FID					TCD	%CH_4 Conversion	% Selectivity					%CH_3Br Yield
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	12988	-	-	432	35	356	7.33	0	0	66.22	2.69	31.08	4.85
64	1.1	15130	-	-	647	44	638	9.70	0	0	62.70	2.14	35.16	6.08
98	1.6	14956	-	-	708	42	881	11.47	0	0	57.56	1.70	40.74	6.60
132	2.2	15035	-	-	768	39	999	12.44	0	0	56.63	1.44	41.93	7.04
166	2.8	14938	-	-	666	32	1185	12.51	0	0	49.11	1.19	49.70	6.14
200	3.3	14522	-	-	519	20	1245	11.83	0	0	41.95	0.81	57.24	4.96
234	3.9	15106	-	-	552	22	1294	11.93	0	0	42.50	0.84	56.66	5.07
268	4.5	15176	-	-	521	23	1252	11.44	0	0	41.85	0.94	57.22	4.79
302	5.0	15266	-	-	542	26	1178	11.22	0	0	44.24	1.04	54.72	4.96
336	5.6	15328	-	-	521	30	1139	10.85	0	0	44.05	1.25	54.70	4.78
370	6.2	15443	-	-	512	14	1246	11.13	0	0	41.72	0.56	57.72	4.64
404	6.7	15434	-	-	456	17	1254	10.73	0	0	38.72	0.72	60.56	4.15
438	7.3	15450	-	-	537	23	1166	11.00	0	0	44.30	0.97	54.73	4.87
472	7.9	15540	-	-	511	16	1234	11.02	0	0	41.86	0.67	57.47	4.61

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 of $1Ba/SiO_2$-I.

TOS		FID					TCD	%CH_4 Conversion	% Selectivity					%CH_3Br Yield
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	14051	5	43	13	367	3864	21.39	0.06	0.61	0.55	7.61	91.16	0.12
64	1.1	13600	-	-	81	7	4561	23.68	0.00	0.00	3.01	0.13	96.85	0.71
98	1.6	14821	-	-	329	-	4859	24.74	0.00	0.00	10.65	0.00	89.35	2.64
132	2.2	14832	-	-	716	-	4863	27.00	0.00	0.00	20.57	0.00	79.43	5.55
166	2.8	14754	-	-	956	-	4699	27.93	0.00	0.00	26.35	0.00	73.65	7.36
200	3.3	14575	-	-	1077	-	4696	28.83	0.00	0.00	28.75	0.00	71.25	8.29
234	3.9	14471	-	-	1119	-	4506	28.62	0.00	0.00	30.41	0.00	69.59	8.70
268	4.5	14499	18	22	1163	-	4246	28.15	0.17	0.21	32.38	0.00	67.24	9.11
302	5.0	14249	2	30	1169	-	4148	28.19	0.02	0.29	33.04	0.00	66.65	9.32
336	5.6	14350	2	34	1142	-	4215	28.12	0.02	0.33	32.17	0.00	67.49	9.05
370	6.2	14296	2	32	1139	-	4415	28.82	0.02	0.30	31.12	0.00	68.57	8.97
404	6.7	14353	2	35	1169	-	4406	28.88	0.02	0.32	31.72	0.00	67.94	9.16
438	7.3	14306	2	36	1142	-	4435	28.90	0.02	0.33	31.07	0.00	68.58	8.98
472	7.9	14323	2	35	1139	-	4404	28.75	0.02	0.33	31.17	0.00	68.49	8.96

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 660 °C, and 2 g of $2Ba/SiO_2$-I.

TOS		FID					TCD	%CH_4 Conversion	% Selectivity					%CH_3Br Yield
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	8626	1.6	3	356		2895	26.81	0.03	0.05	17.76	0.00	82.17	4.76
64	1.1	10724		6	580	23	3319	26.75	0.00	0.08	23.37	0.46	76.03	6.25
98	1.6	10700		8	792	36	3163	27.82	0.00	0.10	30.31	0.69	68.84	8.43
132	2.2	10714		10	861	42	3161	28.35	0.00	0.12	32.08	0.78	66.95	9.09
166	2.8	10661		12	1047	56	3087	29.58	0.00	0.14	36.91	0.99	61.89	10.92
200	3.3	10602		13	1101	52	3066	30.00	0.00	0.15	38.27	0.91	60.59	11.48
234	3.9	10493		15	1240	74	2992	31.00	0.00	0.17	41.53	1.24	57.00	12.88
268	4.5	10581		17	1164	72	2998	30.31	0.00	0.20	39.96	1.23	58.54	12.11
302	5.0	10596		18	1200	96	2930	30.35	0.00	0.21	41.07	1.63	57.01	12.46
336	5.6	10566		20	1254	99	2887	30.65	0.00	0.23	42.45	1.68	55.57	13.01
370	6.2	10599		19	1301	166	2788	30.74	0.00	0.22	43.70	2.79	53.24	13.43
404	6.7	10575		19	1376	114	2805	31.20	0.00	0.21	45.32	1.87	52.53	14.14
438	7.3	10472		20	1414	133	2670	31.21	0.00	0.23	47.02	2.21	50.48	14.68
472	7.9	10472		20	1414	133	2670	31.21	0.00	0.23	47.02	2.21	50.48	14.68

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 660 °C, and 2g of $3Ba/SiO_2$-I.

TOS		FID					TCD	%CH_4 Conversion	% Selectivity					%CH_3Br Yield
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	9596.4	-	-	826	69	2778	28.61	0	0	33.85	1.41	64.73	9.68
64	1.1	10793	-	-	750	43	3157	27.26	0	0	29.22	0.84	69.94	7.97
98	1.6	10636	-	-	849	48	3128	28.20	0	0	32.02	0.91	67.07	9.03
132	2.2	10467	-	-	964	54	3102	29.31	0	0	35.00	0.98	64.02	10.26
166	2.8	10428	-	-	1069	74	3072	30.12	0	0	37.48	1.30	61.23	11.29
200	3.3	10418	-	-	986	59	3064	29.43	0	0	35.76	1.07	63.17	10.52
234	3.9	10351	-	-	1049	68	3025	29.91	0	0	37.43	1.21	61.36	11.19
268	4.5	10358	-	-	1055	64	3026	29.93	0	0	37.58	1.14	61.28	11.25
302	5.0	10325	-	-	1000	58	3021	29.54	0	0	36.41	1.06	62.53	10.75
336	5.6	10411	-	-	1023	61	3014	29.52	0	0	36.97	1.10	61.93	10.91
370	6.2	10354	-	-	1045	63	3019	29.83	0	0	37.42	1.13	61.46	11.16
404	6.7	10420	-	-	1036	63	3033	29.69	0	0	37.11	1.13	61.76	11.02
438	7.3	10394	-	-	1046	60	3015	29.73	0	0	37.49	1.08	61.44	11.14
472	7.9	10357	-	-	1066	67	3064	30.18	0	0	37.52	1.18	61.31	11.32

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 660 °C, and 2 g of $1Ba/SiO_2$-S.

TOS		FID					TCD	%CH_4 Conversion	% Selectivity					%CH_3Br Yield
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	10242	-	-	353.7	-	3388	25.97	0	0	15.51	0.00	84.49	4.03
64	1.1	11327	-	-	549.9	-	3247	25.00	0	0	22.95	0.00	77.05	5.74
98	1.6	11171	-	-	797	-	3011	26.14	0	0	31.77	0.00	68.23	8.30
132	2.2	10992	-	-	1010	76	2845	27.65	0	0	37.89	1.43	60.68	10.48
166	2.8	10893	-	-	1205	89	2720	28.80	0	0	43.10	1.59	55.31	12.41
200	3.3	10828	-	-	1209	91	2615	28.52	0	0	44.10	1.66	54.24	12.58
234	3.9	10804	-	-	1246	64	2555	28.48	0	0	45.63	1.17	53.20	13.00
268	4.5	10726	-	-	1350	99	2513	29.35	0	0	47.73	1.75	50.52	14.01
302	5.0	10663	-	-	1445	99	2451	29.91	0	0	50.03	1.71	48.25	14.97
336	5.6	10663	-	-	1445	99	2451	29.91	0	0	50.03	1.71	48.25	14.97
370	6.2	10663	-	-	1345	99	2451	29.18	0	0	48.24	1.78	49.98	14.08
404	6.7	10663	-	-	1445	99	2451	29.91	0	0	50.03	1.71	48.25	14.97
438	7.3	10663	-	-	1400	99	2451	29.59	0	0	49.24	1.74	49.01	14.57
472	7.9	10663	-	-	1445	99	2451	29.91	0	0	50.03	1.71	48.25	14.97

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, 2 g of $2Ba/SiO_2$-S.

TOS		FID					TCD	%CH_4 Conversion	% Selectivity					%CH_3Br Yield
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	9961	-	49	629	25	2765	26.29	0	0.74	28.16	0.56	70.35	7.41
64	1.1	10784	-	46	961	37	2919	28.14	0	0.60	36.12	0.70	62.40	10.17
98	1.6	10679	-	41	1106	47	2879	29.27	0	0.51	39.69	0.85	58.78	11.62
132	2.2	10728	-	47	1106	53	2824	28.99	0	0.58	40.08	0.97	58.20	11.62
166	2.8	10672	-	48	1131	56	2821	29.30	0	0.59	40.62	1.00	57.59	11.90
200	3.3	10660	-	42	1170	65	2803	29.52	0	0.51	41.58	1.15	56.62	12.27
234	3.9	10656	-	12	1184	61	2817	29.54	0	0.15	41.91	1.08	56.69	12.38
268	4.5	10568	-	40	1280	67	2762	30.33	0	0.47	44.11	1.15	54.12	13.38
302	5.0	10551	-	41	1278	69	2748	30.31	0	0.48	44.17	1.19	54.00	13.39
336	5.6	10519	-	38	1370	72	2749	31.04	0	0.43	45.87	1.21	52.33	14.24
370	6.2	10589	-	41	1289	82	2759	30.41	0	0.48	44.18	1.41	53.76	13.44
404	6.7	10506	-	38	1429	77	2696	31.28	0	0.43	47.36	1.28	50.79	14.81
438	7.3	10531	-	43	1262	69	2735	30.20	0	0.51	43.95	1.20	54.15	13.27
472	7.9	10521	-	42	1283	71	2711	30.29	0	0.50	44.55	1.23	53.52	13.49

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 660 °C, 2g of $3Ba/SiO_2$-S

TOS		FID					TCD	%CH_4 Conversion	% Selectivity					%CH_3Br Yield
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	10099	-	-	262	188	2894	23.80	0.00	0.00	13.10	4.69	82.20	3.12
64	1.1	10956	-	-	476	21	3242	25.10	0.00	0.00	20.43	0.45	79.12	5.13
98	1.6	10844	-	-	782	46	3104	27.19	0.00	0.00	30.43	0.90	68.68	8.27
132	2.2	10731	-	-	938	68	3019	28.30	0.00	0.00	34.88	1.26	63.85	9.87
166	2.8	10657	-	-	903	76	2995	28.11	0.00	0.00	34.16	1.44	64.41	9.60
200	3.3	10751	-	-	863	77	3008	27.68	0.00	0.00	33.04	1.47	65.48	9.15
234	3.9	10714	-	-	902	89	2994	28.04	0.00	0.00	34.05	1.68	64.27	9.55
268	4.5	10787	-	-	893	83	3012	27.89	0.00	0.00	33.74	1.57	64.69	9.41
302	5.0	10777	-	-	904	84	2995	27.92	0.00	0.00	34.13	1.59	64.29	9.53
336	5.6	10789	-	-	889	79	2987	27.73	0.00	0.00	33.84	1.50	64.65	9.38
370	6.2	10750	-	-	897	82	3012	27.98	0.00	0.00	33.84	1.55	64.61	9.47
404	6.7	10800	-	-	871	94	3110	28.16	0.00	0.00	32.43	1.75	65.82	9.13
438	7.3	10888	-	-	903	86	2991	27.70	0.00	0.00	34.12	1.62	64.25	9.45
472	7.9	10699	-	-	911	88	2941	27.90	0.00	0.00	34.68	1.67	63.65	9.67

Table D10 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, 2 of $1W/SiO_2$-I

TOS		FID					TCD	%CH_4 Conversion	% Selectivity					%CH_3Br Yield
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	12316	-	15	438	-	3769	24.90	0	0.20	16.95	0	82.85	4.22
64	1.1	14301	-	22	961	-	4264	27.25	0	0.22	28.32	0	71.46	7.72
98	1.6	14179	2	26	1188	58	3917	27.79	0.02	0.26	34.40	0.84	64.49	9.56
132	2.2	14216	2	27	1212	60	3585	26.79	0.02	0.28	36.84	0.91	61.94	9.87
166	2.8	14224	2	30	1235	60	3552	26.81	0.02	0.31	37.48	0.91	61.29	10.05
200	3.3	14130	3	31	1254	59	3449	26.71	0.03	0.33	38.50	0.91	60.23	10.28
234	3.9	14166	3	32	1198	56	3265	25.68	0.03	0.35	38.72	0.90	60.00	9.94
268	4.5	14191	3	29	1207	56	3046	24.92	0.03	0.34	40.54	0.94	58.15	10.10
302	5.0	14245	3	27	1149	52	3012	24.34	0.03	0.32	39.65	0.89	59.10	9.65
336	5.6	14305	3	26	1129	50	2889	23.68	0.04	0.31	40.23	0.89	58.53	9.53
370	6.2	14394	3	24	1094	47	2884	23.31	0.03	0.30	39.55	0.84	59.27	9.22
404	6.7	14355	3	24	1132	49	2860	23.52	0.03	0.29	40.55	0.87	58.25	9.54
438	7.3	14251	3	23	1122	47	2783	23.28	0.03	0.29	40.99	0.86	57.83	9.54
472	7.9	14999	6	23	1100	49	2722	22.04	0.07	0.29	41.02	0.92	57.70	9.04

Table D11 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, 2 g of $2W/SiO_2$-I

TOS		FID					TCD	%CH_4 Conversion	% Selectivity					%CH_3Br Yield
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	8237	-	27	204	-	2391	23.23	0.00	0.59	12.97	0.00	86.44	3.01
64	1.1	10698	-	12	775	58	2601	25.23	0.00	0.18	33.89	1.27	64.66	8.55
98	1.6	10899	-	10	830	63	2025	22.60	0.00	0.17	41.17	1.56	57.10	9.30
132	2.2	10988	-	11	799	61	2018	22.15	0.00	0.19	40.34	1.54	57.93	8.94
166	2.8	11036	-	-	780	-	1846	20.71	0.00	0.00	42.63	0.00	57.37	8.83
200	3.3	11036	-	-	780	-	1846	20.71	0.00	0.00	42.63	0.00	57.37	8.83
234	3.9	11036	-	-	800	-	1846	20.89	0.00	0.00	43.25	0.00	56.75	9.04
268	4.5	11036	-	-	780	-	1846	20.71	0.00	0.00	42.63	0.00	57.37	8.83
302	5.0	11036	-	-	780	-	1846	20.71	0.00	0.00	42.63	0.00	57.37	8.83
336	5.6	11036	-	-	790	-	1846	20.80	0.00	0.00	42.95	0.00	57.05	8.93
370	6.2	11036	-	-	780	-	1846	20.71	0.00	0.00	42.63	0.00	57.37	8.83
404	6.7	11036	-	-	810	-	1846	20.98	0.00	0.00	43.56	0.00	56.44	9.14
438	7.3	11036	-	-	780	-	1846	20.71	0.00	0.00	42.63	0.00	57.37	8.83
472	7.9	11036	-	-	823	-	1846	21.10	0.00	0.00	43.95	0.00	56.05	9.27

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 660 °C, 2g of $3W/SiO_2$-I

TOS		FID					TCD	%CH_4 Conversion	% Selectivity					%CH_3Br Yield
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	10931	-	-	157	-	3696	24.56	0.00	0.00	6.95	0.00	93.05	1.71
64	1.1	10843	-	-	261	-	3723	25.68	0.00	0.00	10.98	0.00	89.02	2.82
98	1.6	10544	-	-	660	30	3489	28.44	0.00	0.00	24.82	0.56	74.61	7.06
132	2.2	10452	-	-	1069	73	2830	29.04	0.00	0.00	39.38	1.34	59.27	11.44
166	2.8	10413	-	-	1122	99	2371	27.60	0.00	0.00	44.53	1.96	53.50	12.29
200	3.3	10528	-	-	1159	115	2188	26.92	0.00	0.00	47.11	2.34	50.56	12.68
234	3.9	10566	-	-	1184	124	1921	25.86	0.00	0.00	50.64	2.65	46.71	13.09
268	4.5	10624	-	-	1146	121	1815	24.93	0.00	0.00	51.20	2.70	46.10	12.76
302	5.0	10727	-	-	1132	120	1746	24.30	0.00	0.00	51.82	2.75	45.44	12.59
336	5.6	10688	-	-	1142	118	1696	24.20	0.00	0.00	52.74	2.72	44.53	12.76
370	6.2	10655	-	-	1171	114	1690	24.46	0.00	0.00	53.50	2.60	43.90	13.08
404	6.7	10650	-	-	1144	111	1559	23.58	0.00	0.00	54.85	2.66	42.49	12.94
438	7.3	10651	-	-	1165	120	1610	24.05	0.00	0.00	54.43	2.80	42.77	13.09
472	7.9	10646	-	-	1167	123	1630	24.19	0.00	0.00	54.15	2.85	43.00	13.10

Table D13 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, 2 g of $1W/SiO_2$-S

TOS		FID					TCD	%CH_4 Conversion	% Selectivity					%CH_3Br Yield
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	9927	-	-	609	17	2879	26.35	0.00	0.00	27.01	0.38	72.61	7.12
64	1.1	11214	-	-	1221	43	3006	29.32	0.00	0.00	41.37	0.73	57.90	12.13
98	1.6	11140	-	-	1321	53	2899	29.76	0.00	0.00	44.10	0.88	55.02	13.12
132	2.2	11672	-	-	1280	17	2904	28.41	0.00	0.00	43.54	0.29	56.17	12.37
166	2.8	11149	-	-	1278	60	2835	29.21	0.00	0.00	43.77	1.03	55.20	12.79
200	3.3	11224	-	-	1280	60	2835	29.09	0.00	0.00	43.81	1.03	55.16	12.74
234	3.9	11343	-	-	1199	54	2916	28.60	0.00	0.00	41.58	0.94	57.49	11.89
268	4.5	11298	-	-	1185	50	2995	28.89	0.00	0.00	40.68	0.86	58.46	11.75
302	5.0	11263	-	-	1271	60	2841	28.98	0.00	0.00	43.58	1.03	55.39	12.63
336	5.6	11203	-	-	1289	62	2759	28.89	0.00	0.00	44.62	1.07	54.30	12.89
370	6.2	11240	-	-	1289	63	2744	28.77	0.00	0.00	44.75	1.09	54.16	12.87
404	6.7	11260	-	-	1206	62	2805	28.38	0.00	0.00	42.59	1.09	56.32	12.09
438	7.3	11328	-	-	1105	57	2833	27.63	0.00	0.00	40.27	1.04	58.69	11.13
472	7.9	11275	-	-	1184	57	2829	28.28	0.00	0.00	41.97	1.01	57.02	11.87

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 660 °C, 2 g of $2W/SiO_2$-S

TOS		FID					TCD	%CH_4 Conversion	% Selectivity					%CH_3Br Yield
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	10071	-	-	1138.1	57	2811.4	30.20	0.00	0.00	41.16	1.03	57.81	12.43
64	1.1	10553	-	-	1304	76	2829	30.58	0.00	0.00	44.20	1.29	54.51	13.52
98	1.6	10486	-	-	1417	80	2853	31.63	0.00	0.00	46.02	1.30	52.68	14.56
132	2.2	10433	-	-	1468	92	2716	31.60	0.00	0.00	48.00	1.50	50.49	15.17
166	2.8	10473	-	-	1392	102	2679	30.86	0.00	0.00	46.93	1.72	51.35	14.48
200	3.3	10487	-	-	1408	89	2478	30.07	0.00	0.00	49.21	1.56	49.24	14.80
234	3.9	10653	-	-	1423	95	2723	30.87	0.00	0.00	47.14	1.57	51.29	14.55
268	4.5	10668	-	-	1523	105	2630	31.21	0.00	0.00	49.60	1.71	48.69	15.48
302	5.0	10648	-	-	1520	110	2573	31.02	0.00	0.00	50.04	1.81	48.15	15.52
336	5.6	10662	-	-	1561	110	2573	31.27	0.00	0.00	50.70	1.79	47.51	15.86
370	6.2	10598	-	-	1692	122	2395	31.65	0.00	0.00	54.32	1.96	43.72	17.20
404	6.7	10695	-	-	1560	119	2443	30.71	0.00	0.00	51.85	1.98	46.17	15.93
438	7.3	10652	-	-	1626	118	2493	31.46	0.00	0.00	52.41	1.90	45.69	16.49
472	7.9	10652	-	-	1626	118	2493	31.46	0.00	0.00	52.41	1.90	45.69	16.49

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 660 °C, 2g of $3W/SiO_2$-S

TOS		FID					TCD	%CH_4 Conversion	% Selectivity					%CH_3Br Yield
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	10366	-	-	744	64	2393	24.52	0.00	0.00	34.82	1.50	63.68	8.54
64	1.1	10863	-	-	1119	109	2263	26.30	0.00	0.00	45.49	2.22	52.30	11.96
98	1.6	10720	-	-	1364	138	1942	27.16	0.00	0.00	53.76	2.72	43.52	14.60
132	2.2	10628	-	-	1444	145	1865	27.65	0.00	0.00	56.04	2.81	41.15	15.49
166	2.8	10639	-	-	1481	161	1726	27.36	0.00	0.00	58.24	3.17	38.59	15.94
200	3.3	10594	-	-	1492	167	1783	27.81	0.00	0.00	57.62	3.22	39.15	16.02
234	3.9	10540	-	-	1533	178	1642	27.65	0.00	0.00	59.99	3.48	36.53	16.58
268	4.5	10576	-	-	1448	166	1762	27.40	0.00	0.00	57.17	3.28	39.55	15.66
302	5.0	10522	-	-	1496	175	1689	27.59	0.00	0.00	58.81	3.44	37.75	16.22
336	5.6	10510	-	-	1458	170	1687	27.28	0.00	0.00	58.27	3.40	38.33	15.90
370	6.2	10536	-	-	1487	167	1678	27.41	0.00	0.00	58.90	3.31	37.79	16.14
404	6.7	10556	-	-	1469	164	1647	27.08	0.00	0.00	59.06	3.30	37.65	15.99
438	7.3	10598	-	-	1456	173	1678	27.07	0.00	0.00	58.32	3.46	38.21	15.79
472	7.9	10597	-	-	1532	176	1750	28.00	0.00	0.00	58.59	3.37	38.05	16.40

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Proceedings:

1. Somjit, K.; and Kitiyanan, B. (2015, April 21) Oxidative Bromination of Methane by Ba/SiO2 and W/SiO2 Catalysts: Effect of Catalysts Preparation. Proceedings of The 6th Research Symposium on Petroleum, Petrochemicals, and Advanced Materials and The 21th PPC Symposium on Petroleum, Petrochemicals, and Polymers, Bangkok, Thailand.