Supporting Information

Numerical simulation study on mechanism of plasma E/N controlling methane selective oxidation reaction

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1. Response Surface Analysis Method

The response surface methodology encompasses various design models, such as Central Composite, Box-Behnken, D-Optimal, and Uniform designs. Each design scheme is suitable for different conditions and requires a different number of experimental runs. Based on the actual experimental conditions and objectives, this study applied the Box-Behnken design principle. To optimize the selectivity of oxygenates under different factor conditions, four main influencing factors—reaction temperature, CH_4/O_2 gas ratio, volume fraction of added water vapor, and reduced electric field—were selected, with oxygenate selectivity as the response value. The process was optimized using the response surface methodology. A four-factor, three-level response surface experiment was designed according to the Box-Behnken combination. A total of 29 experiments were conducted based on the process parameters listed in Table S1, and the experimental results are shown in Table 1.

2. Establishment and Analysis of the Oxygenate Selectivity Model

The reaction temperature, CH_4/O_2 gas ratio, volume fraction of added water vapor, and reduced electric field are denoted as A, B, C, and D, respectively. Using oxygenate selectivity as the response value, multiple regression fitting was performed to obtain the following second-order polynomial regression equation:

$$Y = 61.04 + 1.66A - 1.37B + 1.19C + 2.48D - 4.51AB - 1.99AC - 1.23AD - 0.51BC - 4.7BD - 0.16CD - 11.81A^2 - 6.93B^2 - 6.81C^2 - 14.87D^2$$

As shown in Table S2, the model is highly significant ($P < 0.001$). The coefficient of determination R^2 is 0.9817, indicating excellent model fit and a good ability to intuitively represent the experimental results. The lack-of-fit term is not significant ($P > 0.05$), suggesting minimal model error. The adjusted coefficient of determination R^2Adj is 0.9634. The normal probability plot of the residuals is shown in Fig. S1a; the data points essentially form a straight line, indicating that the residuals follow a normal distribution well, which demonstrates a good fit between the experimental model and the actual data. The plot of residuals versus predicted values is shown in Fig. S1b. The correspondence plot between the

predicted and actual experimental values for oxygenate selectivity is shown in Fig. S1c, the actual experimental values are distributed near the straight line, indicating little discrepancy between actual and predicted values and confirming a good fit of the experimental data results. The regression equation adequately describes the relationship between the various factors and oxygenate selectivity; therefore, this model can be used to analyze and predict oxygenate selectivity.

The magnitude of the F-value is an important indicator for evaluating the degree of influence of each variable on the response value. A larger F-value indicates a greater contribution of the corresponding model component to the response. When the significance test probability $P < 0.05$, it reveals that the variable has a significant influence on the response value, possessing mathematical and statistical significance. Analysis of the influence of each factor on oxygenate selectivity shows that the first-order terms for reaction temperature and reduced electric field have a highly significant effect ($P < 0.01$), while the CH_4/O_2 gas ratio and the volume fraction of added water vapor have a significant effect ($P < 0.05$). The order of influence of the four factors on oxygenate selectivity is D > A > B > C, i.e., reduced electric field > reaction temperature > CH_4/O_2 gas ratio > volume fraction of added water vapor. The second-order terms A^2, B^2, C^2, and D^2 have a highly significant effect on oxygenate selectivity ($P < 0.01$), indicating that these four factors have a non-linear influence on oxygenate selectivity. The interaction terms AB and BD have a highly significant effect ($P < 0.01$), the interaction term AC has a significant effect ($P < 0.05$), while the interaction terms AD, BC, and CD have no significant effect ($P > 0.05$).

3. Interaction Effects of Various Factors

Response surface plots were generated from the experimental results using Design-Expert 10.0 software. In the 3D graphs and contour plots, the colour gradient from blue to red represents an increase in the response value. A steeper gradient indicates a greater slope, meaning the factor has a more pronounced effect on the experimental outcome. The 3D response surface plots provide an intuitive visualization of the interactive effects of the various factors on oxygenate selectivity, facilitating the identification of optimal process parameters and the interactions between them. The response surface analysis results are shown in Figures S2-S6.

4. The numerical simulation of the zero-dimensional

The tool software used in the numerical simulation was the zero-dimensional dynamic solver ZDPlasKin, which is based on the Fortran 90 module and was used to simulate the time evolution of particle density and gas temperature in non-thermal isoplasma with arbitrary complex chemistry. The Boltzmann equation solver (BOLSIG+) was introduced in ZDPlasKin to provide the electron transport coefficient and rate coefficient when the electron energy distribution function is non-Maxwell. All other files that were required for the simulation along with the user manual can be downloaded from: http://www.zdplaskin.laplace.univ-tlse.fr/index.html@page_id=251.html. Renamed the file and added species and chemical reaction equations and rate coefficients published in the literature to the code after downloading. The data used in this paper are shown in Table S3 and Data S1. Reactions with different molecules and radicals. All possible species and elementary reactions in the model referred to the numerical simulation work of atmospheric pressure non-equilibrium plasma zero-dimensional model related to Bolsig+ database and

Professor Bogaerts' research group.

We applied a zero-dimensional (0D) chemical kinetics model using the software ZDPlaskin. 0D model is most suitable for this approach, as it allows to describe the detailed plasma chemistry without too much computational cost. We included 101 electron impact reactions with neutral species and 621 chemical reactions in Table S3.

Non-Maxwellian electron energy distribution functions (EEDFs) was solved in this reaction system. In the BOLSIG+ solver, we constrained the specific parameter constraints including gas type (CH_4+O_2), gas composition ratio (5:1), reaction temperature, and reduced electric field (E/N) range. The solver was first configured to process electron collision cross-section data for the CH_4-O_2 system, with the reduced electric field intensity (E/N) serving as the independent variable to derive corresponding electron distribution characteristics. The E/N values were determined through analysis of oscilloscope-measured Lissajous figures.

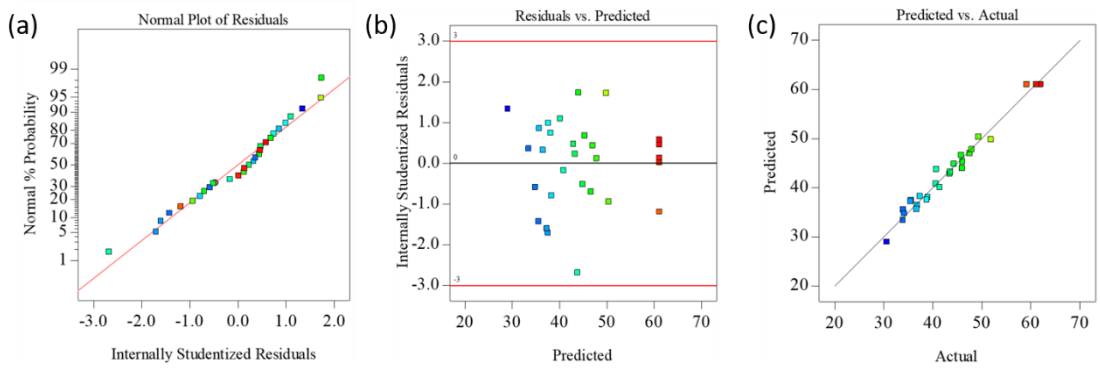

Figure S1. Diagnostic plots for validating the statistical adequacy of the response surface model for C1 oxygenate selectivity. (a) Normal probability plot of the residuals. (b) Plot of internally studentized residuals versus predicted values. (c) Plot of predicted versus actual selectivity values.

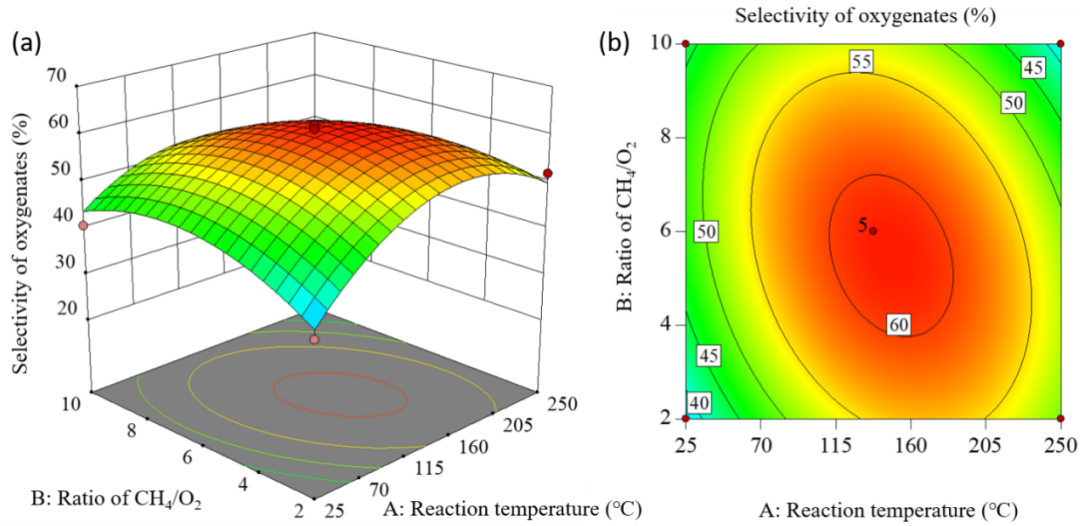

Figure S2. Interactive effect of reaction temperature and CH_4/O_2 molar ratio on oxygenate selectivity. (a) 3D response surface and (b) 2D contour plot reveal the interaction between reaction temperature (A) and reactant ratio (B, CH_4/O_2). The combined effect of high temperature and a high CH_4/O_2 ratio (methane-rich conditions) is conducive to achieving higher oxygenate selectivity.

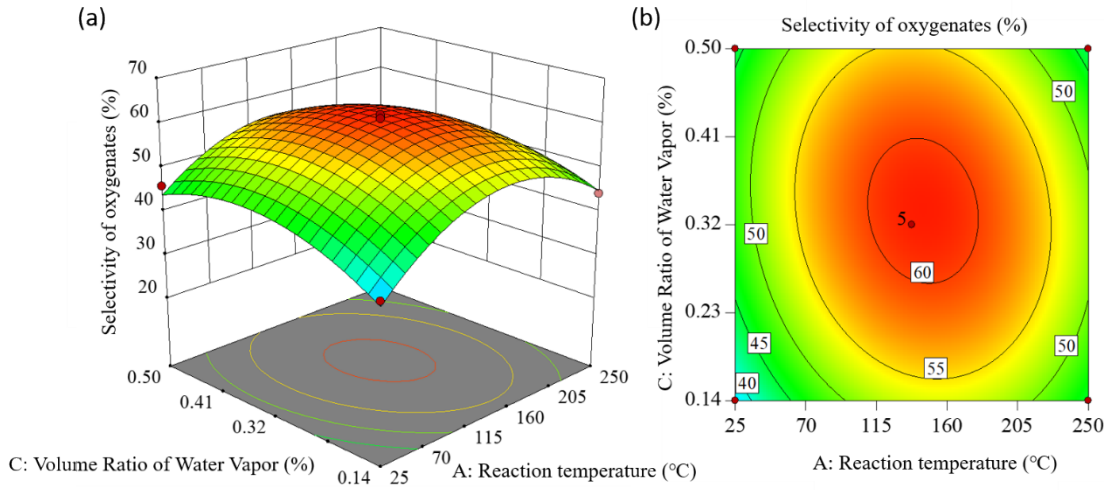

Figure S3. Interactive effect of reaction temperature and water vapor volume ratio on oxygenate selectivity. (a) 3D surface plot and (b) its 2D projection illustrate how reaction temperature (A) and water vapor addition (C) jointly influence the product distribution.

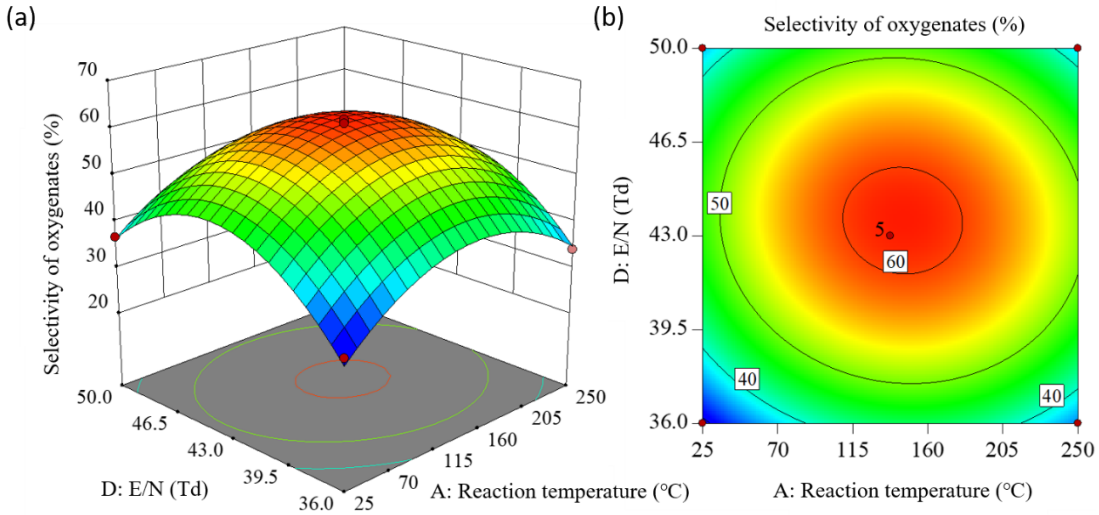

Figure S4. Interactive effect of reaction temperature and reduced electric field on oxygenate selectivity. (a) 3D surface plot and (b) its 2D contour plot visually represents the combined effect of reaction temperature (A) and reduced electric field (D, E/N) on selectivity. The colour gradient and contour lines indicate that the region of highest selectivity (red, ~60%) occurs in the parameter space combining low-to-moderate temperature with higher E/N.

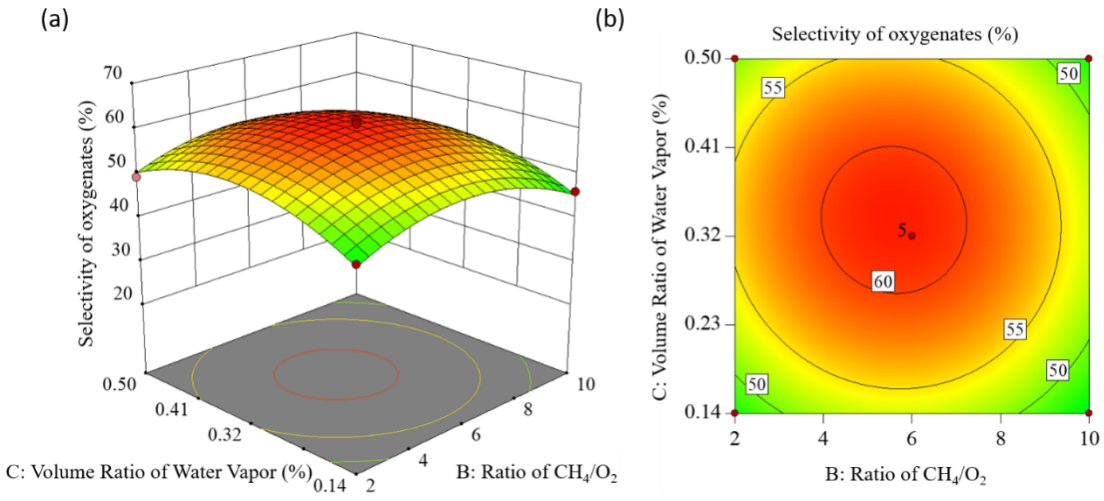

Figure S5. Interactive effect of CH_4/O_2 molar ratio and water vapor volume ratio on oxygenate selectivity. (a) 3D response surface and (b) 2D contour plot delineate the complex interaction between reactant composition (B, CH_4/O_2) and the third component, water vapor (C).

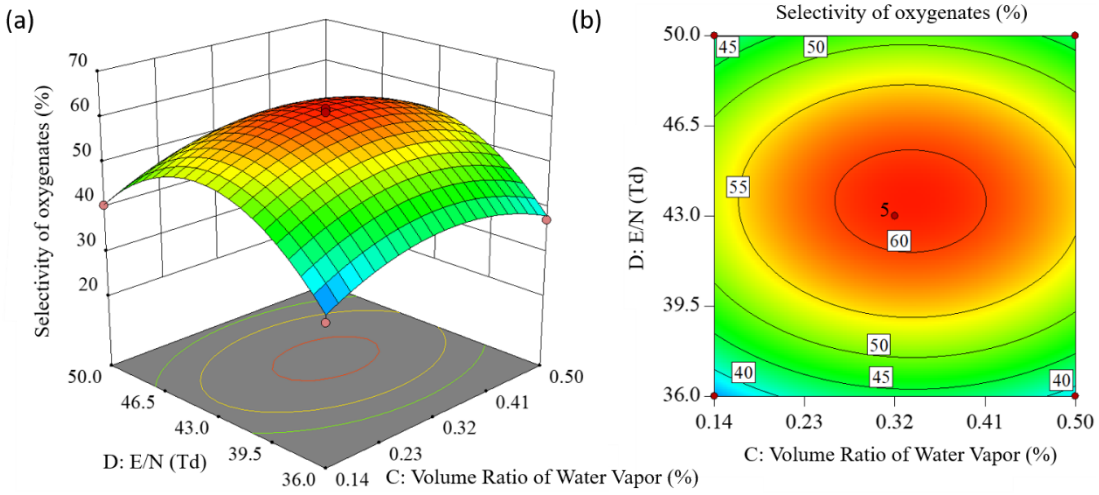

Figure S6. Interactive effect of water vapor volume ratio and reduced electric field on oxygenate selectivity. (a) 3D response surface plot and (b) 2D contour plot jointly illustrate the synergistic effect of two key parameters—water vapor addition (C) and reduced electric field strength (E/N, D)—on the selectivity of C1 oxygenates.

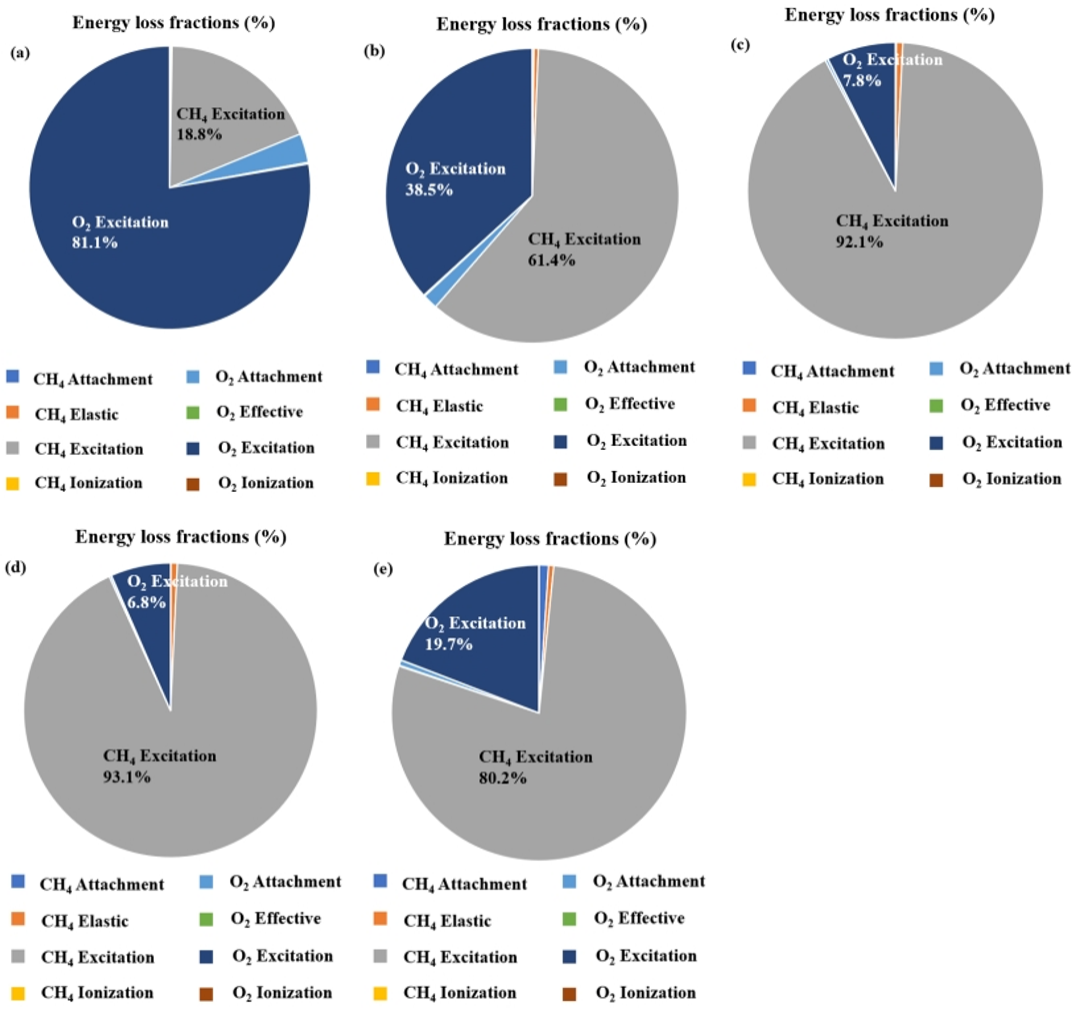

Figure S7. Energy loss fractions : (a)T_{gas}=423K, n(CH_4)/n(O_2)=1:5, E/N=43.7Td (b) T_{gas}=423K, n(CH_4)/n(O_2)=1:1, E/N=43.7Td (c) T_{gas}=423K, n(CH_4)/n(O_2)=5:1, E/N=43.7Td (d) T_{gas}=298K, n(CH_4)/n(O_2)= 5:1, E/N=43.7Td (e) T_{gas}=423K, n(CH_4)/n(O_2)= 5:1, E/N=79.4Td.

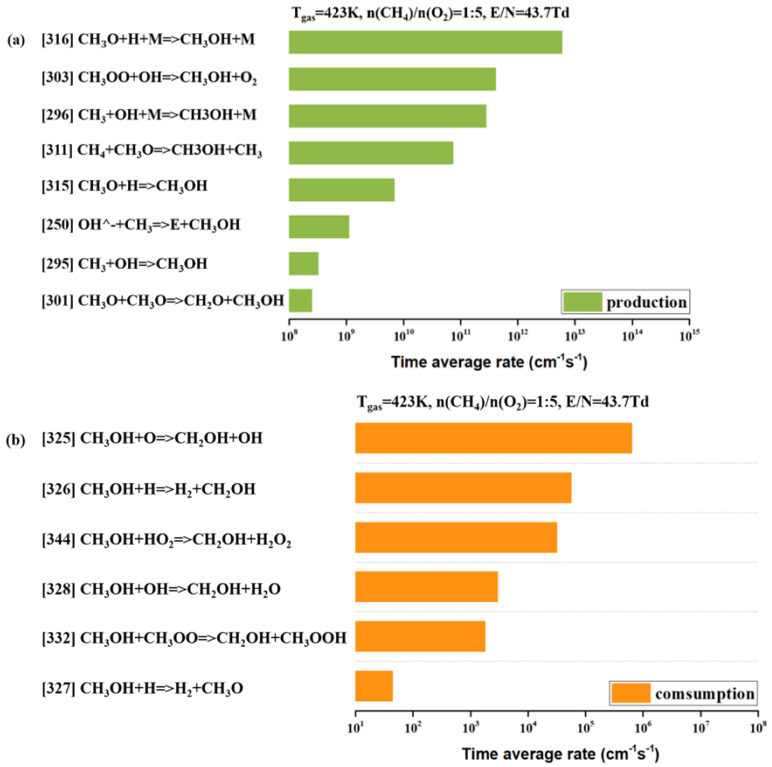

Figure S8. Time-averaged net reaction rates for the major formation and consumption pathways contributing to the net production of methanol under T_{gas}=423 K, n(CH_4)/n(O_2) =1:5, E/N=43.7 Td.

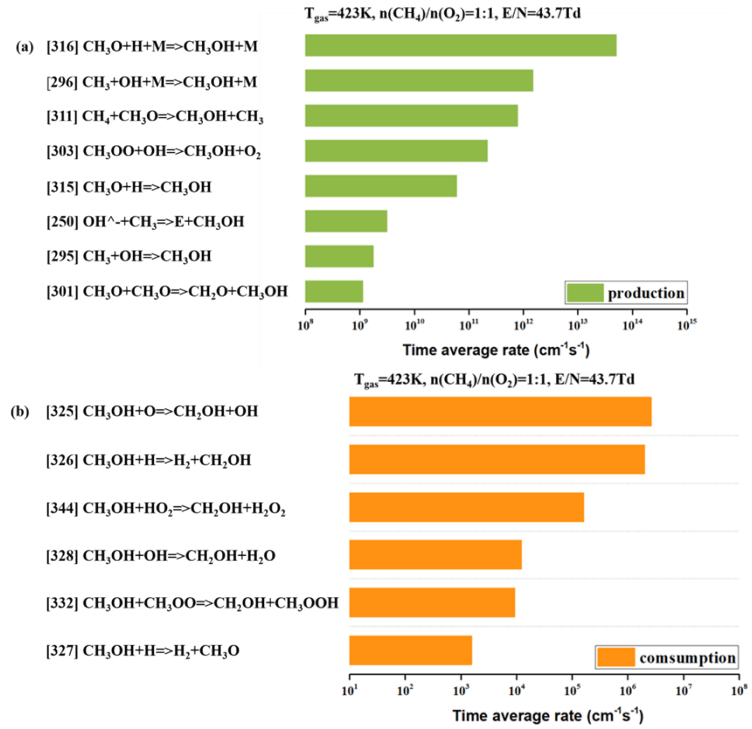

Figure S9. Time-averaged net reaction rates for the major formation and consumption pathways contributing to the net production of methanol under T_{gas}=423 K, n(CH_4)/n(O_2) =1:1, E/N=43.7 Td.

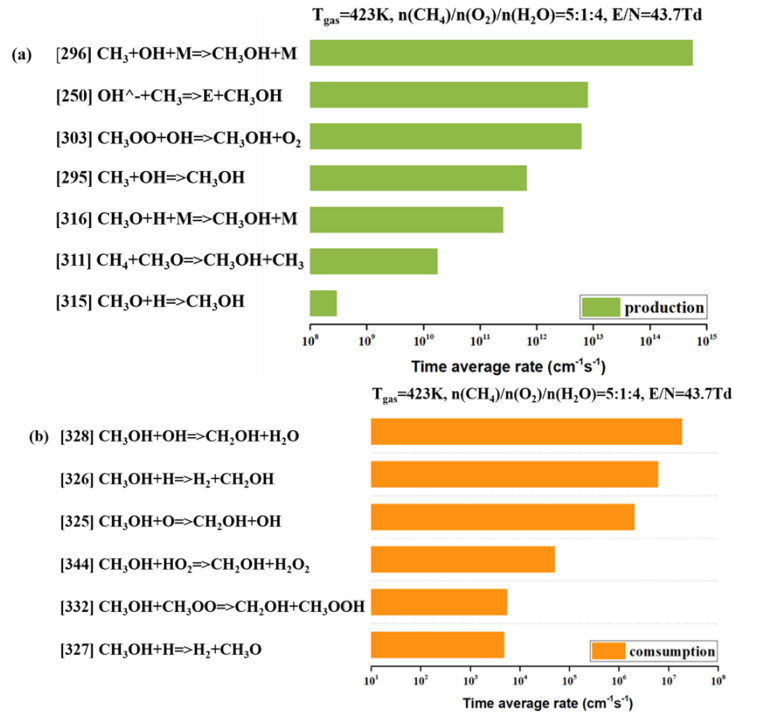

Figure S10. Time-averaged net reaction rates for the major formation and consumption pathways contributing to the net production of methanol under T_{gas}=423 K, n(CH_4)/n(O_2)/n(H_2O) =5:1:4, E/N=43.7 Td.

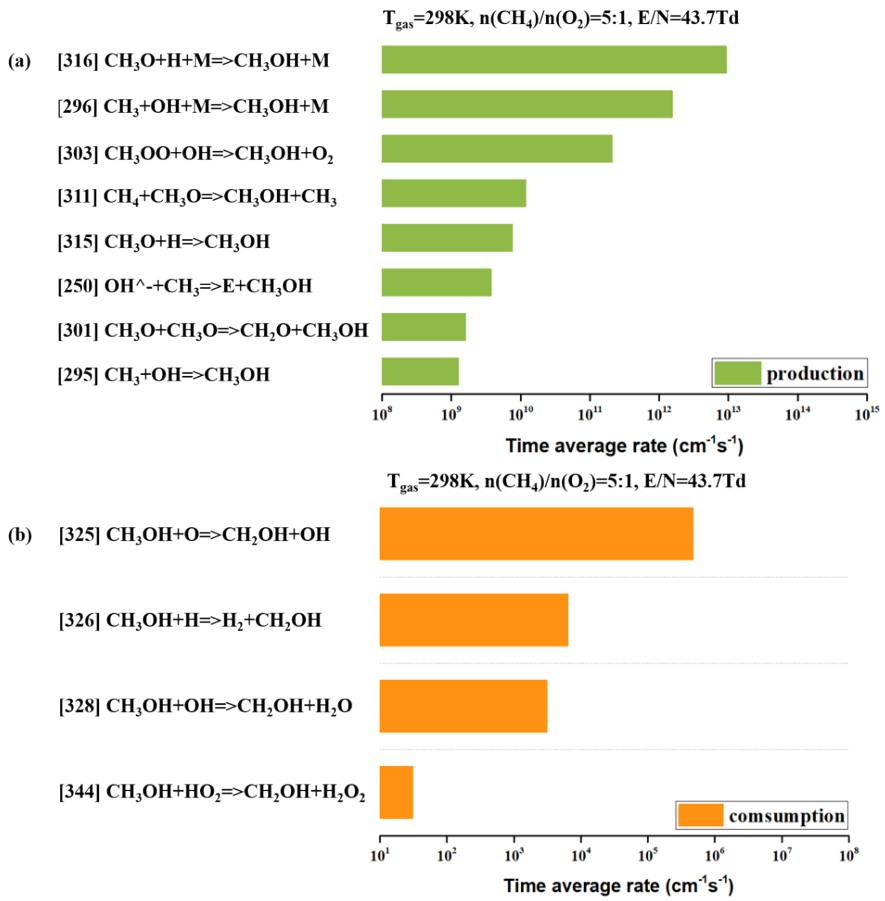

Figure S11. Time-averaged net reaction rates for the major formation and consumption pathways contributing to the net production of methanol under T_{gas}=298 K, n(CH_4)/n(O_2) =5:1, E/N=43.7 Td.

Table S1. Experimental Design and Results of Selectivity Optimization of Oxide Compounds by Response Surface Methodology

No.	A- Temperature (℃)	B- Ratio of CH_4/O_2	C- Volume Ratio of Water Vapor (%)	D- E/N (Td)	Oxygenates Selectivity (%)
1	25	2	0.32	43	35.53
2	250	2	0.32	43	51.83
3	25	10	0.32	43	40.68
4	250	10	0.32	43	38.94
5	137.5	6	0.14	36	33.89
6	137.5	6	0.5	36	37.33
7	137.5	6	0.14	50	40.62
8	137.5	6	0.5	50	43.42
9	25	6	0.32	36	30.54
10	250	6	0.32	36	34.11
11	25	6	0.32	50	36.79
12	250	6	0.32	50	35.42
13	137.5	2	0.14	43	47.48
14	137.5	10	0.14	43	46.03
15	137.5	2	0.5	43	49.28
16	137.5	10	0.5	43	45.81
17	25	6	0.14	43	38.72
18	250	6	0.14	43	44.29
19	25	6	0.5	43	45.95
20	250	6	0.5	43	43.55
21	137.5	2	0.32	36	33.86
22	137.5	10	0.32	36	41.36
23	137.5	2	0.32	50	47.93
24	137.5	10	0.32	50	36.65
25	137.5	6	0.32	43	61.26

26	137.5	6	0.32	43	61.78
27	137.5	6	0.32	43	61.97
28	137.5	6	0.32	43	59.14
29	137.5	6	0.32	43	61.07

Table S2. Regression Analysis Results of Selectivity Model and Regression Coefficients for Oxidative Compounds

Source	Sum of Squares Deviation	Degrees of Freedom	Mean Square	F Value	P Value Significance	Source
Model	2401.18	14	171.51	53.62	< 0.0001	**
A - Reaction temperature	33.10	1	33.10	10.35	0.0062	**
B - Gas ratio of CH_4/O_2	22.52	1	22.52	7.04	0.0189	*
C - Volume fraction of water vapor added	17.06	1	17.06	5.34	0.0367	*
D - Reduced electric field	73.71	1	73.71	23.04	0.0003	**
AB	81.36	1	81.36	25.44	0.0002	**
AC	15.88	1	15.88	4.96	0.0428	*
AD	6.10	1	6.10	1.91	0.1889	
BC	1.02	1	1.02	0.32	0.5812	
BD	88.17	1	88.17	27.57	0.0001	**
CD	0.10	1	0.10	0.032	0.8606	
A^2	905.02	1	905.02	282.95	< 0.0001	**
B^2	311.81	1	311.81	97.48	< 0.0001	**
C^2	300.77	1	300.77	94.04	< 0.0001	**
D^2	1433.45	1	1433.45	448.16	< 0.0001	**
Residual	44.78	14	3.20			
Overfitting term	39.71	10	3.97	3.13	0.1413	ns
Pure error	5.07	4	1.27			
Total sum	2445.96	28				
	R^2=0.9817	Adj R^2=0.9634		PreR^2=0.9033		

P < 0.01 is considered extremely significant, represented by **. P < 0.05 is significant, represented by *. P > 0.05 is not significant, represented by ns.

Table S3. Species included in the 0D model.

Category	Molecules	Excited species	Radicals	Ions
CxHy species	C_3H_8, C_3H_6, C_2H_6, C_2H_4, C_2H_2, CH_4, C	CH_4(V1), CH_4(V2)	C_3H_7, C_3H_5,C_2H_5, C_2H_3,C_2H, CH_3, CH_2, CH	$C_2H_6^+$, $C_2H_5^+$, $C_2H_4^+$, $C_2H_3^+$, $C_2H_2^+$, CH_5^+, CH_4^+, CH_3^+, CH_2^-, CH_2^+, CH^+
H species	H_2	H_2(V1), H_2(V2), H_2(V3), H_2(B3∑g+)	H, H(2P), H(2S)	H^+, H_2^+, H^-
CO species	CO_2, CO	CO_2(E1), CO_2(E2),		CO_2^+, CO^+, CO_3^- , CO_4^-, $C_2O_2^+$, $C_2O_3^+$, $C_2O_4^+$
O species	O_3, O_2,	O(1D), O(1S), O_2(a1), O_2(b1),	O	O_2^+, O_3^- ,O_2^-, O^-
CxHyOz species	HCOOH, $HOCH_2OH$, $HOCH_2O$, HCHO, CH_3OH, CH_3OOH, CH_3CH_2OH, CH_3CHO, CH_2CHO, CH_3COOH, CH_3CH_2OOH		HCO,HCOO, $HOCH_2OO$, CH_2OH, CH_3O, CH_3OO, CH_2OOH, COOH, CH_2OO, CH_3CH_2O, CH_2CH_2OH, CH_3CHOH, CH_3CO, CH_2COOH, CH_3COO, CH_2CO, C_2HO, CH_3CH_2OO	$HCOO^+$, HCO^+, CH_3CO^+
OH species	H_2O, H_2O_2		HO_2, OH	H_2O^+, H_3O^+, OH^-
Electrons	e			