Supporting Information

Selective Oxidation of CH_4 to CH_3OH through Plasma Catalysis: Insights from Catalyst Characterization and Chemical kinetics modelling

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1 Thermodynamic equilibrium of CH_4/O_2 conversion

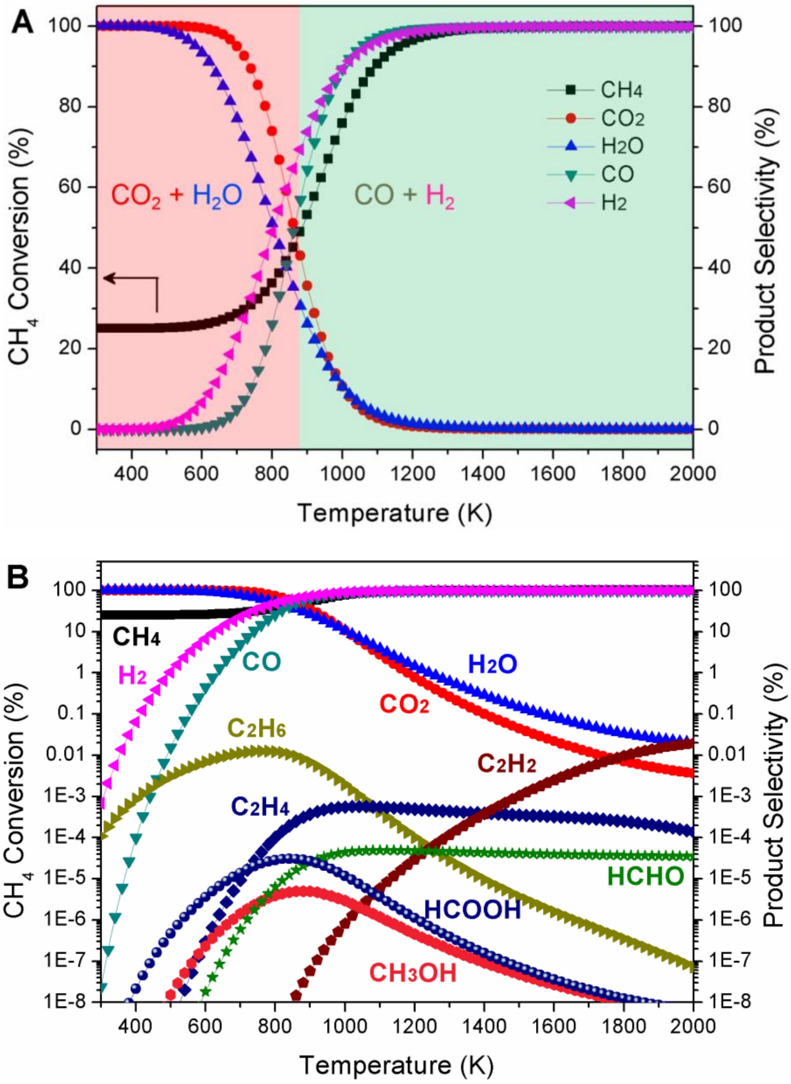
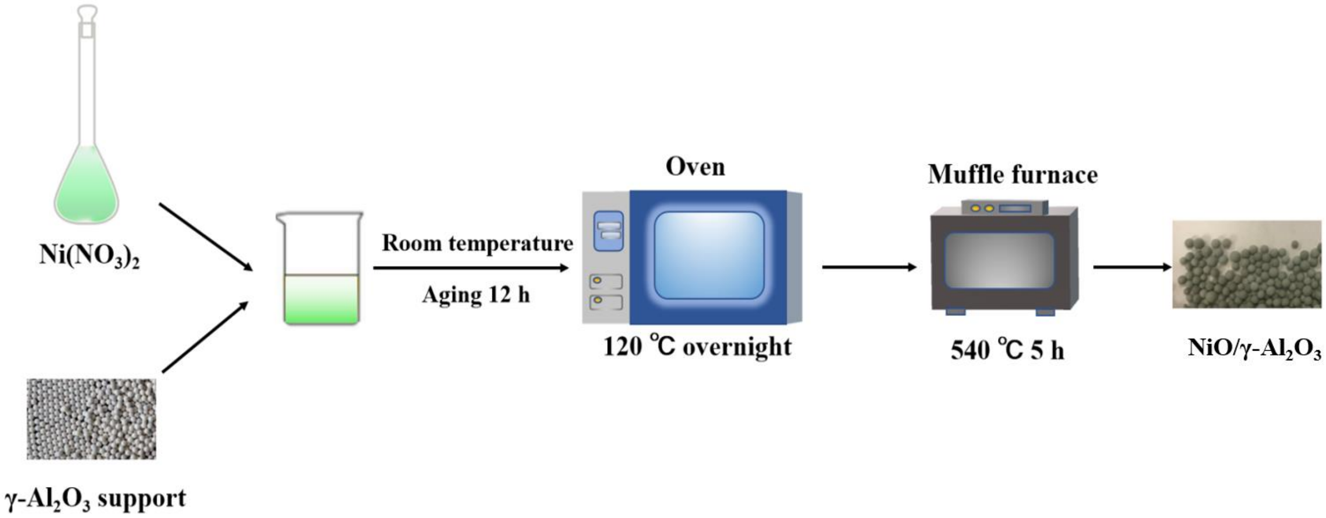


Figure S1. (A) Thermodynamic equilibrium of CH_4 conversion upon oxidation by O_2 (left axis), and product selectivity (right axis), as a function of reaction temperature at atmospheric pressure (mole ratio: CH_4/O_2 = 2/1). **(B)** Product selectivity in logarithmic scale, illustrating the products with lower thermodynamic equilibrium selectivity, including CH_3OH.

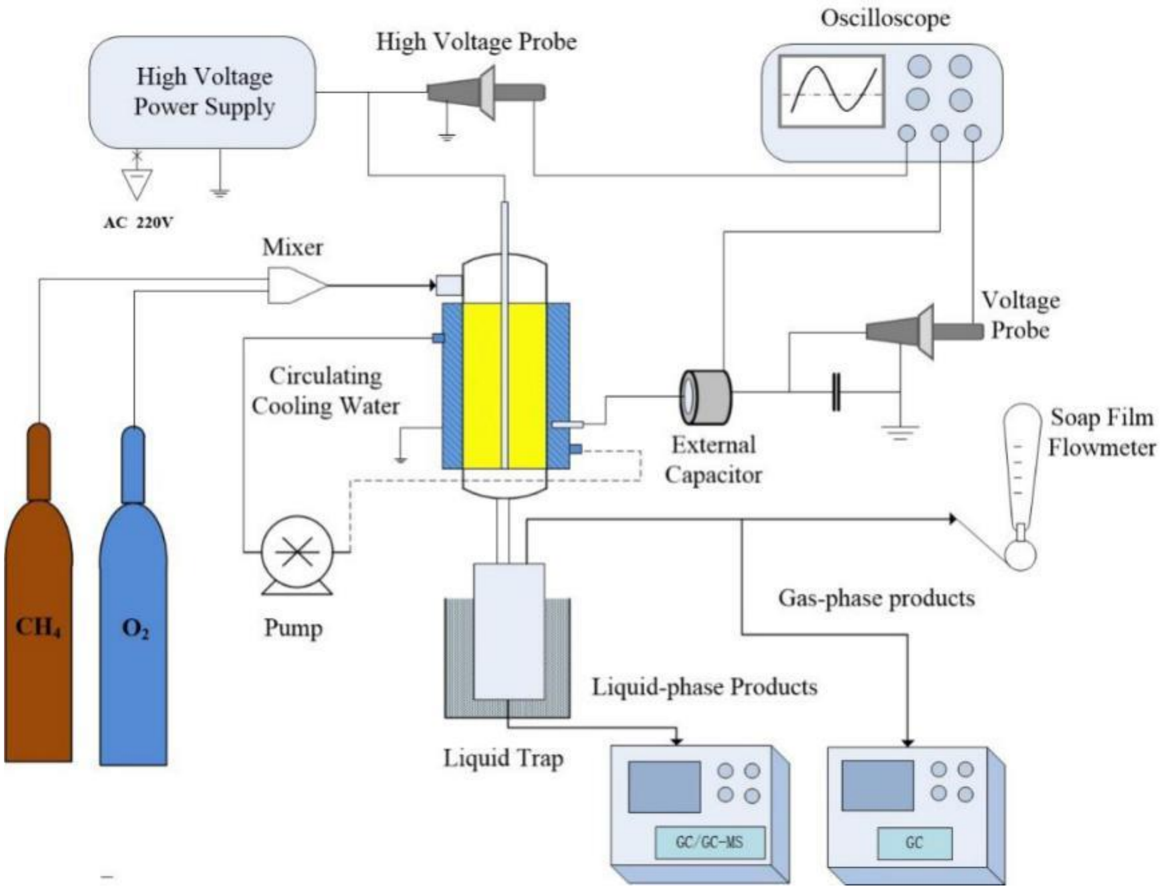
Below 890 K, CO_2 and H_2O are the main products, while above 890 K, CO and H_2 are predominantly formed. The selectivity of the other products are shown in panel (B). The selectivity of H_2 and H_2O are based on the hydrogen balance, while the selectivity of CO, CO_2, CH_3OH, HCHO, HCOOH, C_2H_6, C_2H_4 and C_2H_2 are based on the carbon balance. The equilibrium composition was obtained based on the thermodynamic analysis method,(database system of TheCoufal) adopted from the literature. [1]

2 Catalyst preparation



Scheme S1. Schematic diagram of the Ni catalyst preparation procedure

3 Experimental setup for plasma catalysis



Scheme S2. Schematic diagram of the experimental setup for plasma catalytic SOMTM by molecular oxygen

4 Conversion, product analysis and energy efficiency

Qualitative analysis

In the plasma catalytic SOMTM by O_2, the feed gases (CH_4 and O_2) and gaseous products (CO, CO_2, C_2H_6) were measured by online GC with a thermal conductivity detector (TCD) and a flamable ionized detector (FID). The liquid products, as shown in Figure S2, were collected by a liquid trap and qualitatively analyzed by GC-2014C (Shimadzu, PEG-2000 column) with a flame ionization detector (FID) and GC-MS， ^{1}H-NMR and ATR-FTIR. The GC results (Figure S2A) showed the presence of methanol (CH_3OH), methyl formate ($HCOOCH_3$), ethanol (C_2H_5OH), acetaldehyde (CH_3CHO) and acetic acid (CH_3COOH). The GC-MS results (Figure S2B) showed that CH_3OH, and to a lower extent also formaldehyde (HCHO) and formic acid (HCOOH), were the main products. CH_3OOH and H_2O_2 were also detected by ^{1}H-NMR (Figure S2C). In addition, ATR-FTIR (Attenuated Total Reflection Fourier Transform Infrared Spectroscopy) was performed to identify the characteristic functional groups of the liquid products. As shown in figure S2D, the band at 1050 cm^{-1} can be ascribed to stretching vibration mode of C-O bond from CH_3OH. [2] The band at 1383 cm^{-1} can be ascribed to angular vibration mode of the C-H bond from CH_3OH.[2] The band at 1640 cm^{-1} is assigned to bending mode of the O-H bond from H_2O.[2] The broad band between 3700 and 3000 cm^{-1} can be ascribed to stretching mode of the O-H bond, mainly from H_2O, CH_3OH and HCOOH.[2] The weak band at 2963 cm^{-1} is assigned to the stretching mode of C-H bond from CH_3OH.[2] Note that the relatively strong infrared absorption bands of HCHO coincide with water and methanol absorption. Basically, these qualitative results confirm that the liquid products are H_2O (water), H_2O_2 (hydrogen peroxide), CH_3OH (methanol), HCHO (formaldehyde), HCOOH (formic acid), $HCOOCH_3$ (methyl formate), CH_3CH_2OH (ethanol), CH_3CHO (acetaldehyde) and CH_3COOH (acetic acid).

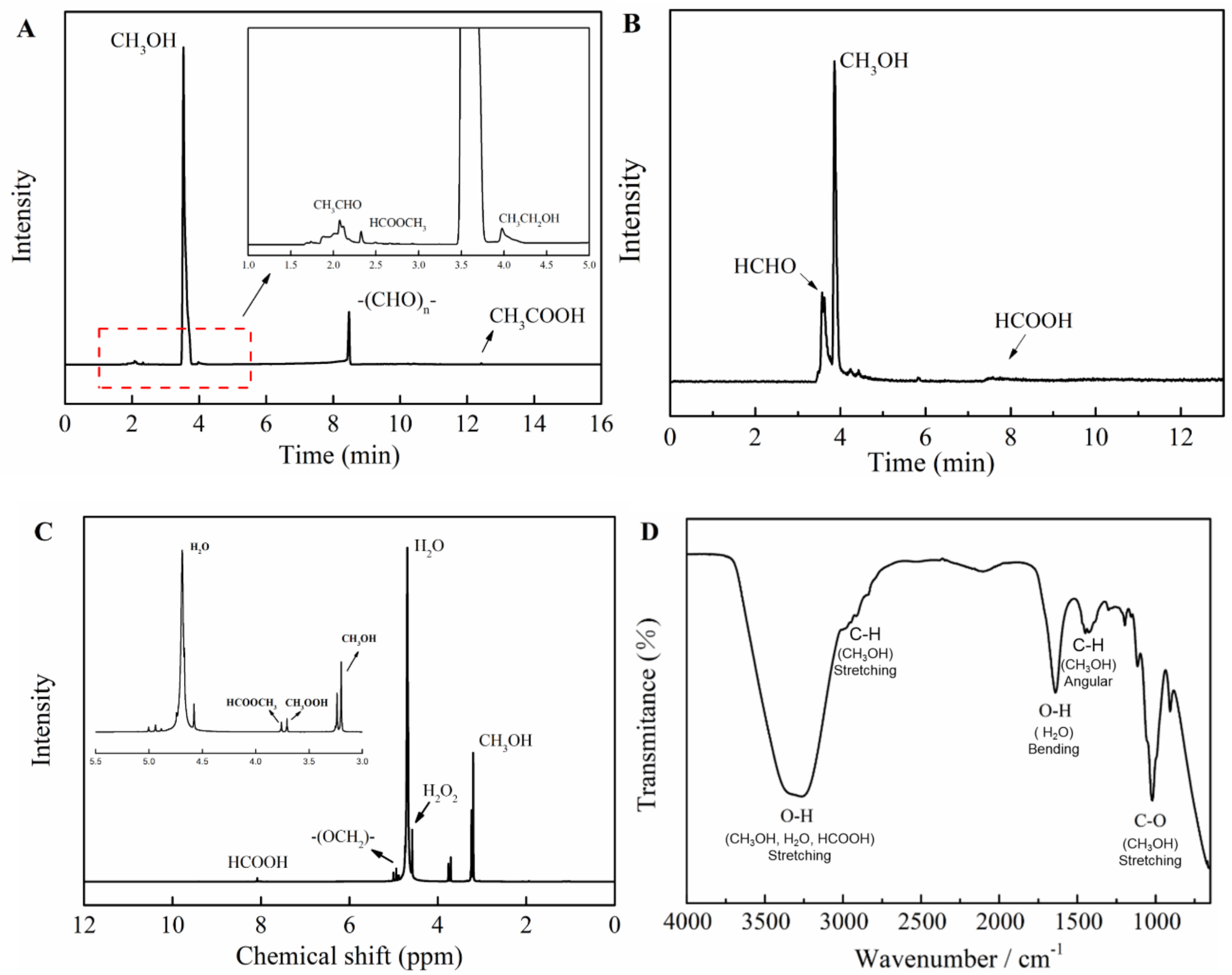


Figure S2. Results of Qualitative analysis of the liquid products. (A). GC spectrum, illustrating the presence of CH_3OH, $HCOOCH_3$, C_2H_5OH, CH_3CHO and CH_3COOH. **(B).** GC-MS spectrum, illustrating the presence of HCHO, CH_3OH and HCOOH. **(C).** H-NMR spectrum, illustrating the presence of H_2O, H_2O_2, CH_3OH, HCOOH, $HCOOCH_3$, CH_3OOH. **(D).**ATR-FTIR spectrum of the total liquid products, illustrating the presence of H_2O, CH_3OH, HCOOH.

Quantitative analysis

After operating the CH_4/O_2 NTP for 2 hours, the collected liquid sample was dripped with deionized water to 4 ml in the collector, then mixed uniformly and immediately transferred to the refrigerator for further analysis. For quantitative analysis, the concentrations of CH_3OH (methanol), $HCOOCH_3$ (methyl formate), CH_3CH_2OH (ethanol), CH_3CHO (acetaldehyde) and CH_3COOH (acetic) were determined by GC, while the concentration of HCHO (formaldehyde) was measured by GC-MS and the concentration of HCOOH (formic acid) was analyzed by ^{1}H-NMR with DMSO as internal standard in D_2O solvent. The formulas of the standard calibrated concentration curves to calculate the product concentrations are listed in Table S1.

CH_3OH productivity ($mol{\bullet}g_{cat}^{-1}{\bullet}h^{-1}$) can be defined as follow, which can be well compared as a critiaria for the performance of different catalysts on stoichiometric chemical looping using O_2 (Figure 2A). The reaction time was calculated only on duration of methane reaction, without considering the duration of CH_4 activation and CH_3OH extration in the chemical looping.

$$CH_3OH\ \text{Producivity} = \frac{\text{moles of methanol produced (mol/h)}}{\text{catalyst weight (g)}} \tag{1}$$

Table S1. Formulas of the standard concentration curves for each of the products

Products	Analysis Method	Equation	Adj.R-Square
CO	GC	$Y = 7.82324 * 10^{-6} X - 0.00908$	0.998
CO_2	GC	$Y = 8.13251 * 10^{-6} X - 0.03553$	0.999
CH_3OH	GC	$Y = 2.80214 * 10^{-7} X + 0.00689$	0.998
$HCOOCH_3$	GC	$Y = 2.79370 * 10^{-7} X + 0.00357$	0.999
C_2H_5OH	GC	$Y = 1.57550 * 10^{-7} X + 0.00047$	0.998
CH_3CHO	GC	$Y = 1.46516 * 10^{-6} X + 0.00351$	0.998
CH_3COOH	GC	$Y = 2.49203 * 10^{-7} X + 0.00263$	0.999
HCHO	GC-MS	$Y = 5.9647 * 10^{-4} X + 0.01673$	0.999
HCOOH	^{1}H-NMR	$Y = 0.4889 * X + 0.0354$	0.998

Y denotes the concentration of sample, in mol/L; X denotes the peak area of the sample.

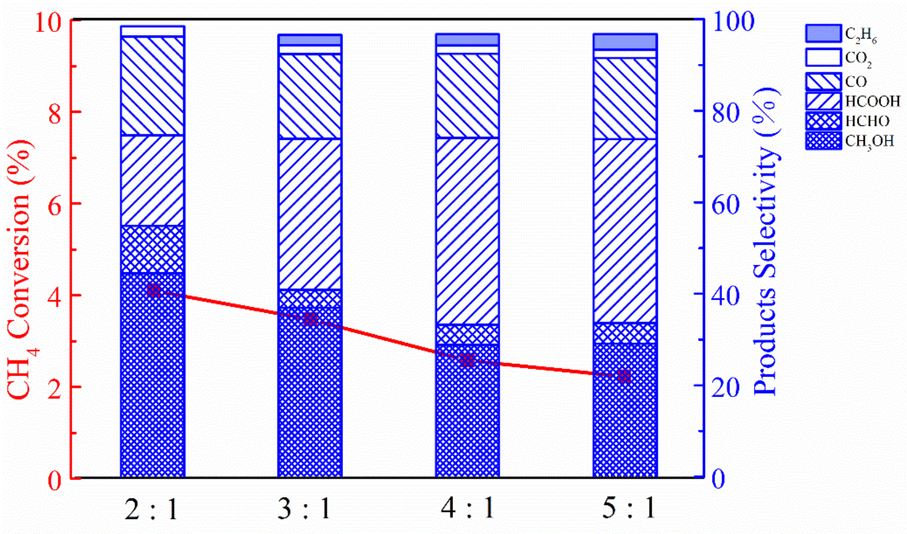


Figure S3. The influence of different CH_4/O_2 molar ratio on CH_4 conversion and product selectivity

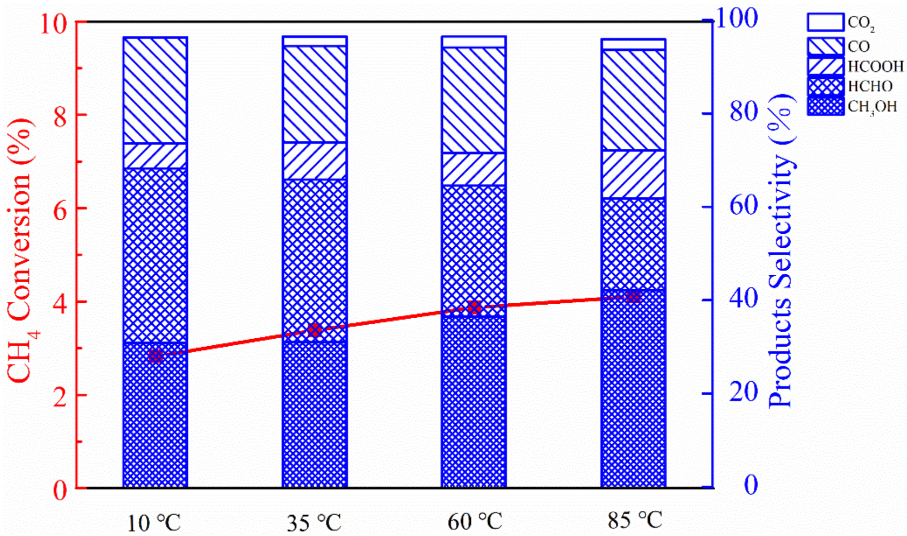


Figure S4. The influence of grounding electrode temperature on CH_4 conversion and product selectivity in CH_4/O_2 plasma

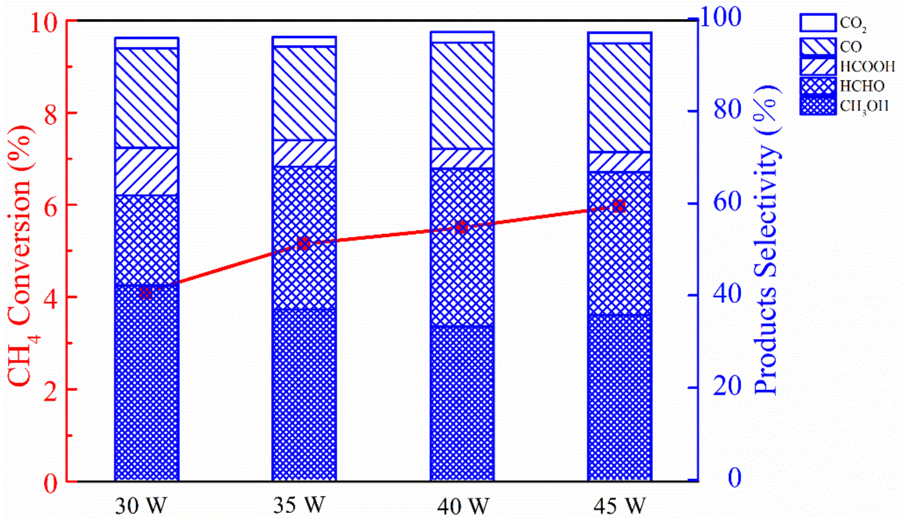


Figure S5. The influence of discharge power on CH_4 conversion and product selectivity in CH_4/O_2 plasma

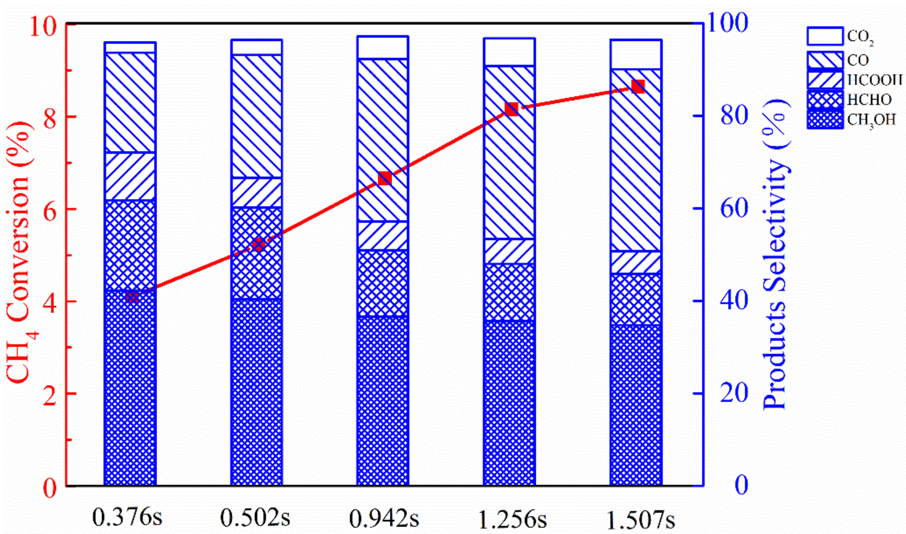


Figure S6. The influence of residence time on CH_4 conversion and product selectivity in CH_4/O_2 plasma

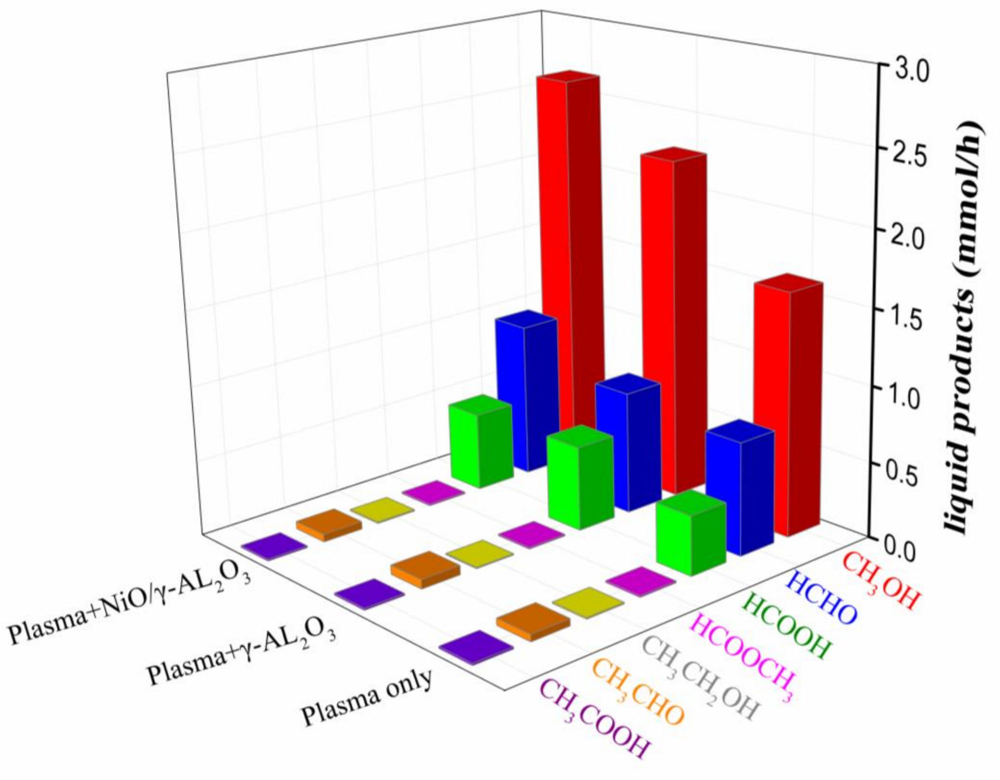


Figure S7. Liquid products distribution after 2-hour CH_4/O_2 NTP operation, for plasma only, plasma + γ-Al_2O_3 beads and plasma + NiO/γ-Al_2O_3 catalyst.

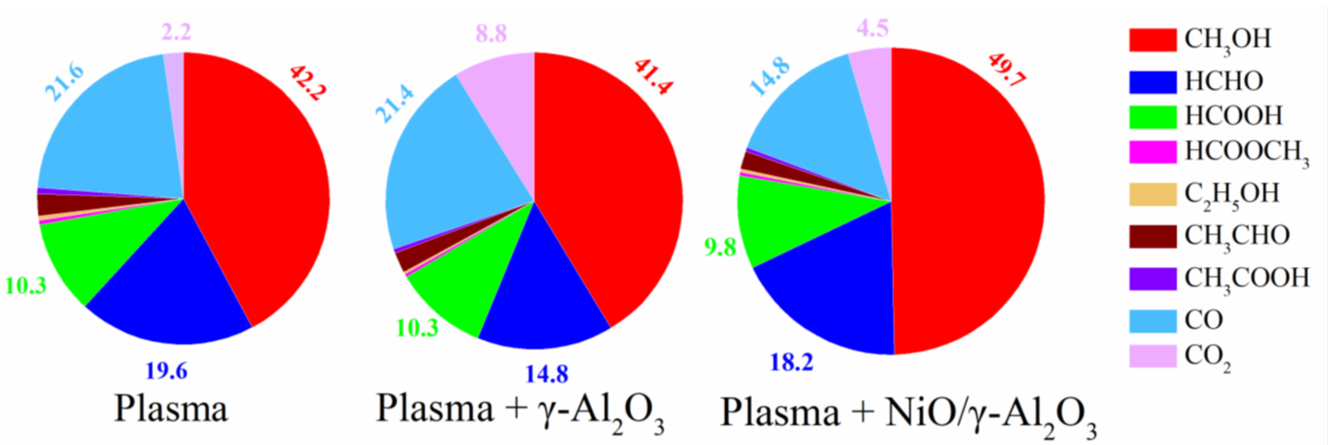


Figure S8. Products selectivity distribution of SOMTM (Carbon based), for all gas and liquid products, in the case of only plasma, plasma with γ-Al_2O_3 beads, and plasma with (10 wt%) NiO/γ-Al_2O_3 catalyst

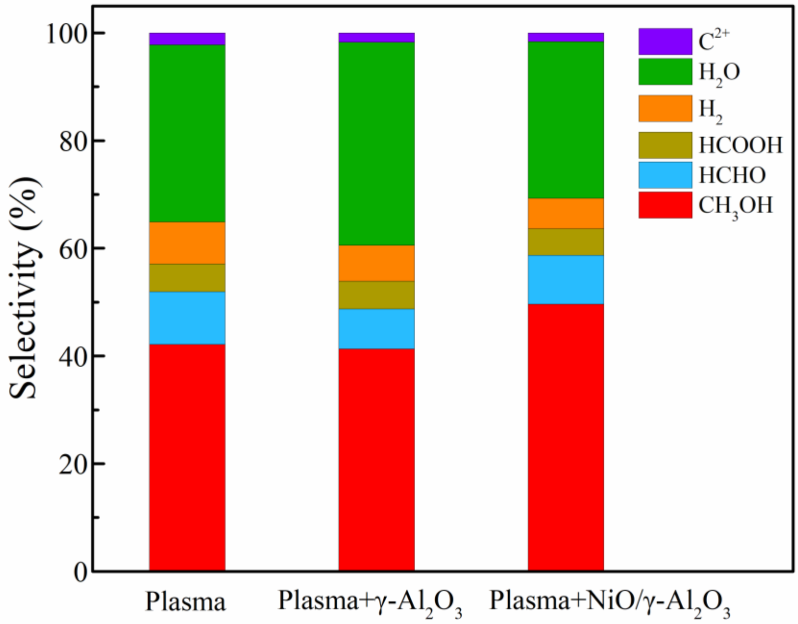


Figure S9. Products selectivity of SOMTM (hydrogen based) using only plasma, plasma with γ-Al_2O_3 beads, and plasma with (10 wt.%) NiO/γ-Al_2O_3 catalyst (400 ml/min CH_4, 200 ml/min O_2, 85°C circulating water, 1.25g NiO/γ-Al_2O_3 catalyst, 30W discharge power and 0.375 s residence time).

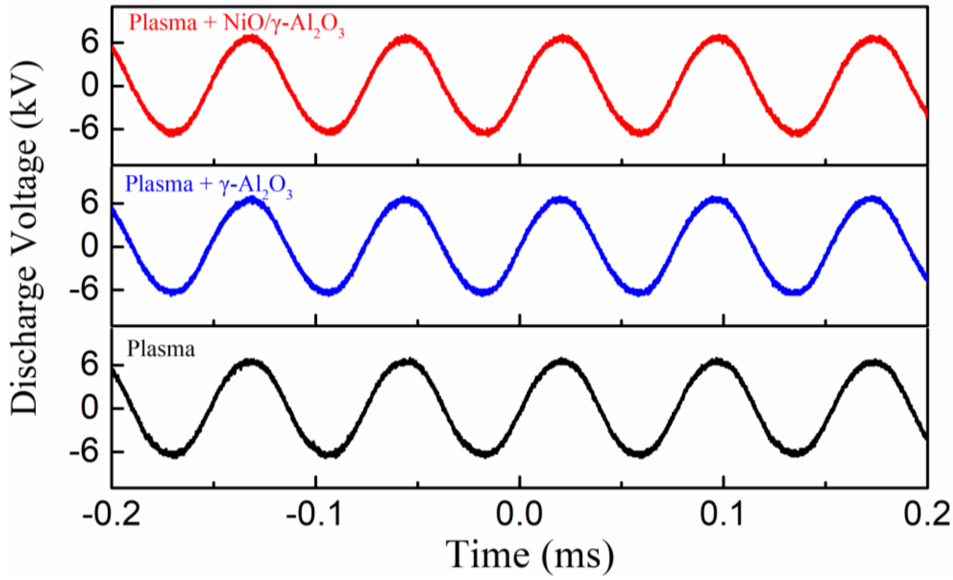


Figure S10. Discharge voltage in the case of plasma, plasma+γ-Al_2O_3, and plasma + NiO/γ-Al_2O_3

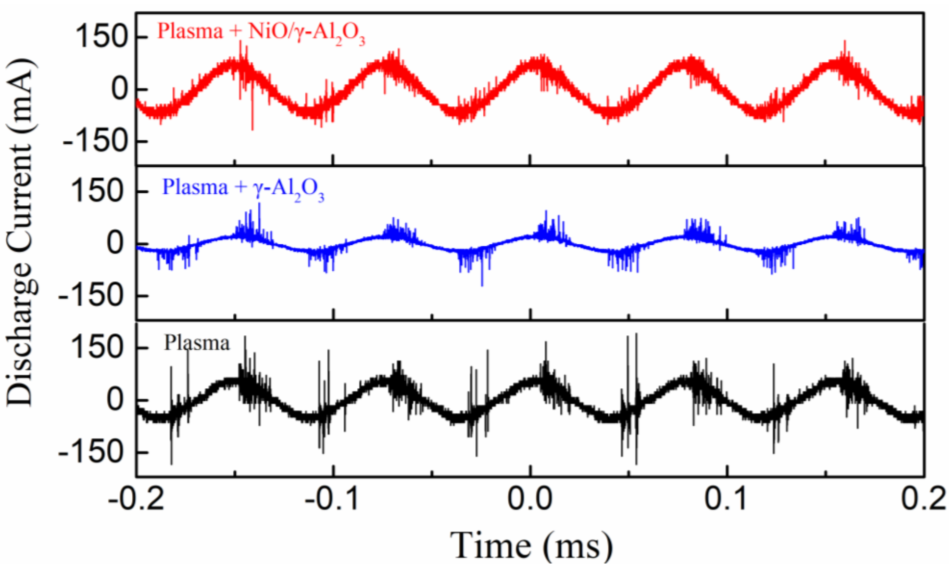


Figure S11. Discharge current in the case of plasma, plasma+γ-Al_2O_3, and plasma + NiO/γ-Al_2O_3

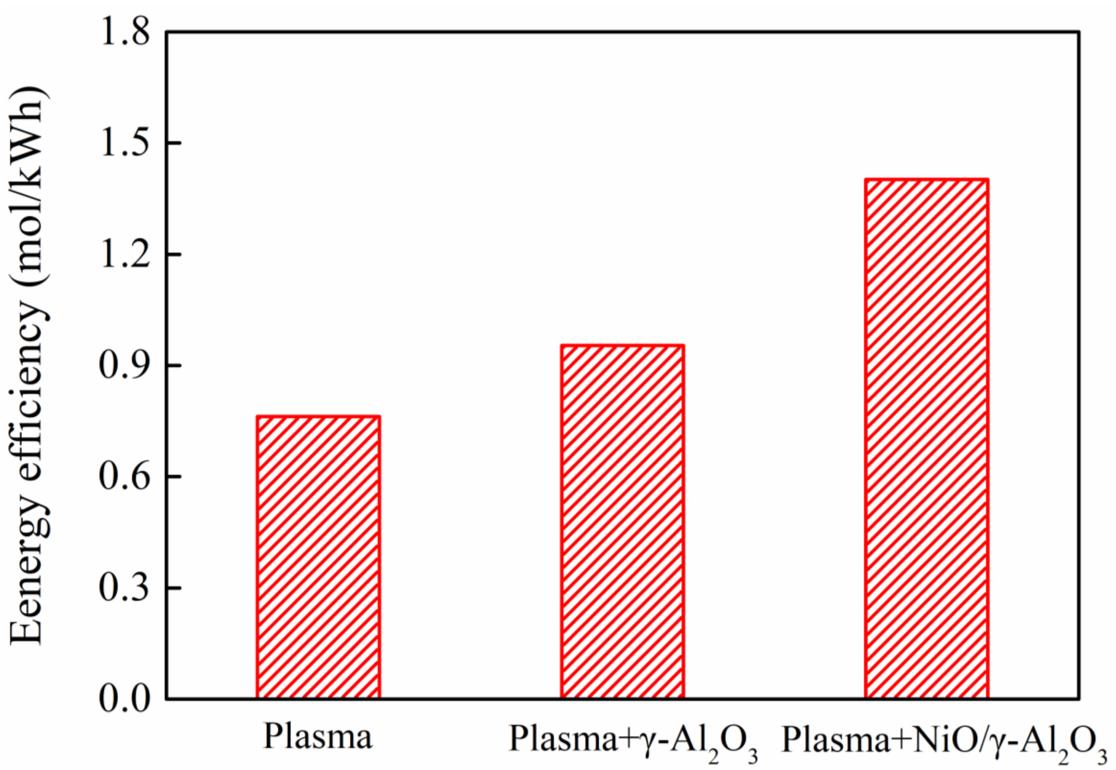


Figure S12. Energy efficiency in the case of plasma, plasma + γ-Al_2O_3 and plasma + NiO/γ-Al_2O_3

5 Chemical Kinetics Modeling

Description of the Modeling Approach

We applied a zero-dimensional (0D) chemical kinetics model using the software ZDplaskin.[3-4] A 0D model is most suitable for this approach, as it allows to describe the detailed plasma chemistry without too much computational cost. We included 70 electron impact reactions with neutral species, 138 ion impact (electron-ion, ion-neutral and ion-ion) reactions and 374 neutral-neutral reactions. All simulated species are shown in Table S2. The other data used in the model are summarized in Table S3, S4 and S5.

Physical Model

The time evolution of the species densities, $N_{i=1\ldots i\max}$, can be written as equation F1. The source terms Q_{ij} describe the contribution from various chemical reactions, j =1…jmax.

$$\frac{d[Ni]}{dt} = \sum_{j=1}^{jmax} Q_{ij}(t) \qquad \text{F1}$$

For example, for the reaction R1, the reaction rate is calculated by equation F2, and the source terms are expressed as equations F3, F4 and F5.

$$a\mathrm{A} + b\mathrm{B} \rightarrow a'\mathrm{A} + c\mathrm{C} \qquad \text{R1}$$

$$R_j = k_j [\mathrm{A}]^a[\mathrm{B}]^b \qquad \text{F2}$$

$$Q_\mathrm{A} = (a' - a)R_j \qquad \text{F3}$$

$$Q_\mathrm{B} = -bR_j \qquad \text{F4}$$

$$Q_\mathrm{C} = cR_j \qquad \text{F5}$$

For the neutral-neutral chemical reactions, the rate coefficients (k_j) are a function of the gas temperature (see below). Hence, the latter is calculated by equation F6.

$$\frac{N_{gas}}{\gamma-1}\frac{dT_{gas}}{dt} = \sum_{j=1}^{jmax} \pm\delta\varepsilon j \cdot R_j + P_{elast} \cdot [N_e] \qquad \text{F6}$$

Here γ is the specific gas heat ratio, $\delta\varepsilon_j$ is the energy needed (minus-sign) or released (plus-sign) for the various chemical reactions, and $P_{elast}\cdot[N_e]$ represents the Joule heating caused by the discharge current. .

The rate coefficients for the neutral-neutral, electron-ion, ion-neutral and ion-ion reactions can then be obtained from the three-parameter Arrhenius form F7.

$$k_j(\mathrm{T}) = A_j\, T^{B_j} \exp\left(- E_j \cdot R T^{-1}\right) \qquad \text{F7}$$

The unit of k_j is in m^3/s for two-body reactions. T is the gas temperature in Kelvin. The three parameters, A_j, B_j and E_j represent the pre-exponential factor, the temperature factor, and the activation energy, respectively, and they are adopted from the NIST database. [5]

For the electron-impact reactions, we solved the Boltzmann Equation F8 for a range of reduced electric field values (E/n, where E is the electric field and n is the gas density), in order to obtain the electron energy distribution function (F) and the mean electron temperature. The rate constants for the electron-impact reactions can then be calculated by equation F9, from the EEDF and the energy-dependent cross sections.

$$\frac{\partial f}{\partial t} + v \cdot \nabla f - \frac{e}{m} E \cdot \nabla v f = C[f] \qquad \text{F8}$$

$$k = G \int_0^{\infty} \varepsilon \sigma_k F d\varepsilon \qquad \text{F9}$$

Where σ_k is the cross-section of the target particle, F represents the EEDF, ε is the electron energy in eV, and $G = \sqrt{2e/m}$.

Data for the 0D modeling of CH_4/O_2 DBD plasma

Table S2. 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		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			

Table S3. Electron-impact reactions with different molecules and radicals. All cross sections used to calculate the rate coefficients were adopted from the Urquijo database,[6] and the rate coefficients were calculated by a Boltzmann solver ,[7] except for the reaction with OH and OH- (last two rows), where a rate coefficient of 8.44×10^{-9} $cm^3 s^{-1}$ and 1.95×10^{-8} $cm^3 s^{-1}$ was used, respectively. [8]

Reactions	Reaction type/Rate constants (cm^3s^{-1})
$e + CH_4 \rightarrow e + e + CH_4^+$	Ionization
$e + CH_4 \rightarrow e + e + CH_3^+ + H$	Ionization
$e + CH_4 \rightarrow e + CH_3 + H$	Dissociation
$e + CH_4 \rightarrow e + CH_2 + H_2$	Dissociation
$e + CH_4 \rightarrow e + CH + H_2 + H$	Dissociation
$e + CH_4 \rightarrow e + C + H_2 + H_2$	Dissociation
$e + CH_4 \rightarrow CH_3 + H^-$	Dissociation
$e + CH_4 \rightarrow H_2 + CH_2^-$	Dissociation
$e + CH_3 \rightarrow e + CH_2 + H$	Dissociation
$e + CH_2 \rightarrow e + CH + H$	Dissociation

$e + O_2 \rightarrow O^- + O$	Ionization
$e + O_2 \rightarrow O_2^-$	Dissociation
$e + O_2 \rightarrow e + O + O$	Dissociation
$e + O_2 \rightarrow e + O_2(a1)$	Electronic excitation
$e + O_2 \rightarrow e + O_2(b1)$	Electronic excitation
$e + O_2(a1) \rightarrow e + O_2$	Electronic deexcitation
$e + O \rightarrow e + O(1D)$	Electronic excitation
$e + O \rightarrow e + O(1S)$	Electronic excitation
$e + CO \rightarrow e + C + O$	Dissociation
$e + CO \rightarrow e + e + CO^+$	Ionization
$e + CO_2 \rightarrow e + e + CO_2^+$	Ionization
$e + CO_2(E1) \rightarrow e + e + CO_2^+$	Ionization
$e + CO_2(E2) \rightarrow e + e + CO_2^+$	Ionization
$e + CO_2 \rightarrow O^- + CO$	Dissociation
$e + CO_2 \rightarrow e + CO + O$	Dissociation
$e + CO_2(E1) \rightarrow e + CO + O$	Dissociation
$e + CO_2(E2) \rightarrow e + CO + O$	Dissociation
$e + CO_2 \rightarrow e + CO_2(E1)$	Electronic excitation
$e + CO_2 \rightarrow e + CO_2(E2)$	Electronic excitation
$e + C_2H_6 \rightarrow e + e + C_2H_6^+$	Ionization
$e + C_2H_6 \rightarrow e + C_2H_5 + H$	Dissociation
$e + C_2H_6 \rightarrow e + C_2H_4 + H_2$	Dissociation
$e + C_2H_5 \rightarrow e + C_2H_4 + H$	Dissociation
$e + C_2H_5 \rightarrow e + C_2H_3 + H_2$	Dissociation
$e + C_2H_4 \rightarrow e + e + C_2H_4^+$	Ionization
$e + C_2H_4 \rightarrow e + C_2H_3 + H$	Dissociation
$e + C_2H_4 \rightarrow e + C_2H_2 + H_2$	Dissociation
$e + C_2H_3 \rightarrow e + C_2H_2 + H$	Dissociation
$e + C_2H_2 \rightarrow e + e + C_2H_2^+$	Ionization
$e + C_2H_2 \rightarrow e + C_2H + H$	Dissociation
$e + C_3H_8 \rightarrow e + C_3H_7 + H$	Dissociation
$e + C_3H_8 \rightarrow e + C_3H_6 + H_2$	Dissociation
$e + C_3H_8 \rightarrow e + C_2H_4 + CH_4$	Dissociation
$e + C_3H_7 \rightarrow e + C_3H_6 + H$	Dissociation
$e + C_3H_7 \rightarrow e + C_2H_4 + CH_3$	Dissociation
$e + C_3H_7 \rightarrow e + C_2H_3 + CH_4$	Dissociation
$e + C_3H_6 \rightarrow e + C_2H_2 + CH_4$	Dissociation

$e + H_2 \rightarrow e + H_2(B3\sum g+)$	Electronic excitation
$e + H_2 \rightarrow e + H_2(V1)$	Vibrational excitation
$e + H_2 \rightarrow e + H_2(V2)$	Vibrational excitation
$e + H_2 \rightarrow e + H_2(V3)$	Vibrational excitation
$e + H_2 \rightarrow e + H + H$	Dissociation
$e + H_2 \rightarrow e + e + H_2^+$	Ionization
$e + H_2(B3\sum g+) \rightarrow e + H_2$	Electronic deexcitation
$e + H_2(B3\sum g+) \rightarrow e + e + H_2^+$	Ionization
$e + H \rightarrow e + H(2P)$	Electronic excitation
$e + H \rightarrow e + H(2S)$	Electronic excitation
$e + H \rightarrow e + e + H^+$	Ionization
$e + H(2P) \rightarrow e + H$	Electronic deexcitation
$e + H(2P) \rightarrow e + H(2S)$	Electronic excitation
$e + H(2P) \rightarrow e + e + H^+$	Ionization
$e + H^- \rightarrow e + e + H$	Ionization
$e + H_2O \rightarrow O^- + H_2$	Dissociation
$e + H_2O \rightarrow OH^- + H$	Dissociation
$e + H_2O \rightarrow H^- + OH$	Dissociation
$e + H_2O \rightarrow e + OH + H$	Dissociation
$e + H_2O \rightarrow e + OH + H$	Dissociation
$e + OH^- \rightarrow e + OH + e$	Ionization
$e + OH \rightarrow e + H + O$	8.44×10^{-9}
$e + OH^- \rightarrow e + e + H + O$	1.95×10^{-8}

Table S4. Electron-ion, ion-neutral and ion-ion reactions included in this model. The rate coefficients were adopted from literature.[3, 9, 10] M denotes any molecule in the plasma (mainly CH_4 and O_2).

Reactions	Rate coefficients (cm^3s^{-1})
$e + CH_5^+ \rightarrow CH_3 + H + H$	$2.57 \times 10^{-7} \times (300/T_e)^{0.3}$
$e + CH_5^+ \rightarrow CH_2 + H_2 + H$	$6.61 \times 10^{-8} \times (300/T_e)^{0.3}$
$e + C_2H_5^+ \rightarrow C_2H_4 + H$	$7.70 \times 10^{-9} \times (300/T_e)^{0.71}$
$e + C_2H_5^+ \rightarrow C_2H_3 + H + H$	$1.92 \times 10^{-8} \times (300/T_e)^{0.71}$
$e + C_2H_5^+ \rightarrow C_2H_2 + H_2 + H$	$1.60 \times 10^{-8} \times (300/T_e)^{0.71}$
$e + C_2H_5^+ \rightarrow C_2H_2 + H + H + H$	$8.98 \times 10^{-9} \times (300/T_e)^{0.71}$
$e + C_2H_5^+ \rightarrow CH_3 + CH_2$	$9.62 \times 10^{-9} \times (300/T_e)^{0.71}$
$e + C_2H_4^+ \rightarrow C_2H_2 + H + H$	$3.43 \times 10^{-8} \times (300/T_e)^{0.71}$
$e + C_2O_2^+ \rightarrow CO + CO$	$9.64 \times 10^{-6} \times T_e^{-0.34}$
$e + H_3O^+ \rightarrow H_2O + H$	$7.09 \times 10^{-8} \times (T_e/300)^{-0.5}$
$e + H_3O^+ \rightarrow OH + H_2$	$5.37 \times 10^{-8} \times (T_e/300)^{-0.5}$
$e + H_3O^+ \rightarrow OH + H + H$	$3.05 \times 10^{-7} \times (T_e/300)^{-0.5}$
$e + CH_4^+ \rightarrow CH_3 + H$	1.18×10^{-8}
$e + CH_4^+ \rightarrow CH_2 + 2H$	2.42×10^{-8}
$e + CH_4^+ \rightarrow CH + H_2 + H$	1.41×10^{-8}
$e + CH_3^+ \rightarrow CH_2 + H$	2.25×10^{-8}
$e + CH_3^+ \rightarrow CH + H_2$	7.88×10^{-9}
$e + CH_3^+ \rightarrow CH + 2H$	9.00×10^{-9}
$e + CH_3^+ \rightarrow C + H + H_2$	1.69×10^{-8}
$e + CH_2^+ \rightarrow CH + H$	1.00×10^{-8}
$e + CH_2^+ \rightarrow C + H_2$	4.82×10^{-9}
$e + CH_2^+ \rightarrow C + 2H$	2.53×10^{-8}
$e + CH^+ \rightarrow C + H$	3.23×10^{-8}
$CO_2 + CO^+ \rightarrow CO_2^+ + CO$	1.00×10^{-9}
$CO_2 + O^- + M \rightarrow CO_3^- + M$	9.00×10^{-29}
$CO_2 + O_2^- + M \rightarrow CO_4^- + M$	1.00×10^{-29}
$CO_2 + O_3^- \rightarrow O_2 + CO_3^-$	5.50×10^{-10}
$CO_2 + CO_2^+ + M \rightarrow C_2O_4^+ + M$	3.00×10^{-28}
$CO + O^- \rightarrow CO_2 + e$	5.50×10^{-10}
$CO + CO_3^- \rightarrow CO_2 + CO_2 + e$	5.50×10^{-17}
$O + CO_3^- \rightarrow CO_2 + O_2^-$	8.00×10^{-11}
$O + CO_4^- \rightarrow CO_3^- + O_2$	1.10×10^{-10}
$O + CO_4^- \rightarrow CO_2 + O_2 + O^-$	0.14×10^{-10}
$O + CO_4^- \rightarrow CO_2 + O_3^-$	0.14×10^{-10}

$CO + C_2O_3^+ + M \rightarrow C_2O_2^+ + CO_2 + M$	2.60×10^{-26}
$CO + C_2O_4^+ + M \rightarrow C_2O_3^+ + CO_2 + M$	4.20×10^{-26}
$CH_5^+ + CO \rightarrow HCO^+ + CH_4$	9.90×10^{-10}
$CH_5^+ + C_2H_6 \rightarrow C_2H_5^+ + H_2 + CH_4$	0.23×10^{-9}
$CH_5^+ + C_2H_4 \rightarrow C_2H_5^+ + CH_4$	0.15×10^{-8}
$CH_5^+ + C_2H_2 \rightarrow C_2H_3^+ + CH_4$	0.16×10^{-8}
$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3$	0.15×10^{-8}
$CH_4^+ + C_2H_6 \rightarrow C_2H_4^+ + CH_4 + H_2$	0.19×10^{-8}
$CH_3^+ + CH_4 \rightarrow CH_4^+ + CH_3$	0.17×10^{-9}
$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2$	0.12×10^{-8}
$C_2H_4^+ + H \rightarrow C_2H_3^+ + H_2$	3.00×10^{-10}
$C_2H_3^+ + C_2H_4 \rightarrow C_2H_5^+ + C_2H_2$	8.90×10^{-10}
$H_2^+ + CH_4 \rightarrow CH_3^+ + H_2 + H$	2.30×10^{-9}
$H^+ + CH_4 \rightarrow CH_4^+ + H$	1.50×10^{-9}
$H^- + H \rightarrow H_2 + e$	1.30×10^{-9}
$CH_5^+ + H_2O \rightarrow H_3O^+ + CH_4$	$0.37 \times 10^{-8} \times (300/T_{gas})^{0.5}$
$CH_4^+ + H_2O \rightarrow H_3O^+ + CH_3$	$0.26 \times 10^{-8} \times (300/T_{gas})^{0.5}$
$C_2H_6^+ + H_2O \rightarrow H_3O^+ + C_2H_5$	$0.30 \times 10^{-8} \times (300/T_{gas})^{0.5}$
$C_2H_5^+ + H_2O \rightarrow H_3O^+ + C_2H_4$	$0.14 \times 10^{-8} \times (300/T_{gas})^{0.5}$
$C_2H_3^+ + H_2O \rightarrow H_3O^+ + C_2H_2$	$0.11 \times 10^{-8} \times (300/T_{gas})^{0.5}$
$H^- + H_2O \rightarrow OH^- + H_2$	3.80×10^{-9}
$O^- + CH_4 \rightarrow OH^- + CH_3$	1.00×10^{-10}
$O^- + H_2 \rightarrow H_2O + e$	7.00×10^{-10}
$CO_2^+ + CH_4 \rightarrow CH_4^+ + CO_2$	5.50×10^{-10}
$CO^+ + CH_4 \rightarrow CH_4^+ + CO$	7.93×10^{-10}
$OH^- + H \rightarrow H_2O + e$	1.40×10^{-9}
$O_3^- + M \rightarrow O_3 + M + e$	2.30×10^{-11}
$CH_4^+ + CO_2 \rightarrow HCOO^+ + CH_3$	9.50×10^{-10}
$CH_4^+ + CO \rightarrow HCO^+ + CH_3$	7.00×10^{-10}
$CH_4^+ + CO \rightarrow CH_3CO^+ + H$	6.00×10^{-10}
$CH_4^+ + C_2H_6 \rightarrow C_2H_4^+ + CH_4 + H_2$	1.91×10^{-9}
$CH_4^+ + C_2H_4 \rightarrow C_2H_5^+ + CH_3$	4.23×10^{-10}
$CH_4^+ + C_2H_4 \rightarrow C_2H_4^+ + CH_4$	1.38×10^{-9}
$CH_4^+ + C_2H_2 \rightarrow C_2H_3^+ + CH_3$	1.23×10^{-9}
$CH_4^+ + C_2H_2 \rightarrow C_2H_2^+ + CH_4$	1.13×10^{-9}
$CH_4^+ + H \rightarrow CH_3^+ + H_2$	1.00×10^{-11}
$CH_4^+ + O \rightarrow CH_3^+ + OH$	1.00×10^{-9}

$CH_4^+ + O_2 \rightarrow O_2^+ + CH_4$	3.90×10^{-10}
$CH_3^+ + CH_4 \rightarrow CH_4^+ + CH_3$	1.36×10^{-10}
$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2$	1.20×10^{-9}
$CH_3^+ + CH_2 \rightarrow C_2H_3^+ + H_2$	9.90×10^{-10}
$CH_3^+ + CH \rightarrow C_2H_2^+ + H_2$	7.10×10^{-10}
$CH_3^+ + C_2H_6 \rightarrow C_2H_5^+ + CH_4$	1.48×10^{-9}
$CH_3^+ + C_2H_4 \rightarrow C_2H_3^+ + CH_4$	3.50×10^{-10}
$CH_3^+ + C_2H_3 \rightarrow C_2H_3^+ + CH_3$	3.00×10^{-10}
$CH_2^+ + CH_4 \rightarrow CH_3^+ + CH_3$	1.38×10^{-10}
$CH_2^+ + CH_4 \rightarrow C_2H_5^+ + H$	3.90×10^{-10}
$CH_2^+ + CH_4 \rightarrow C_2H_4^+ + H_2$	8.40×10^{-10}
$CH_2^+ + CH_4 \rightarrow C_2H_3^+ + H_2 + H$	2.31×10^{-10}
$CH_2^+ + CH_4 \rightarrow C_2H_2^+ + 2H_2$	3.97×10^{-10}
$CH_2^+ + H_2 \rightarrow CH_3^+ + H$	1.90×10^{-9}
$CH^+ + CH_4 \rightarrow C_2H_4^+ + H$	6.50×10^{-11}
$CH^+ + CH_4 \rightarrow C_2H_3^+ + H_2$	1.09×10^{-9}
$CH^+ + CH_4 \rightarrow C_2H_2^+ + H + H_2$	1.43×10^{-10}
$CH^+ + H_2 \rightarrow CH_2^+ + H$	1.20×10^{-9}
$C_2H_6^+ + C_2H_4 \rightarrow C_2H_4^+ + C_2H_6$	1.15×10^{-9}
$C_2H_6^+ + C_2H_2 \rightarrow C_2H_5^+ + C_2H_3$	2.47×10^{-10}
$C_2H_6^+ + H \rightarrow C_2H_5^+ + H_2$	1.00×10^{-10}
$C_2H_5^+ + H \rightarrow C_2H_4^+ + H_2$	1.00×10^{-10}
$C_2H_4^+ + C_2H_3 \rightarrow C_2H_5^+ + C_2H_2$	5.00×10^{-10}
$C_2H_4^+ + C_2H_3 \rightarrow C_2H_3^+ + C_2H_4$	5.00×10^{-10}
$C_2H_4^+ + H \rightarrow C_2H_3^+ + H_2$	3.00×10^{-10}
$C_2H_4^+ + O \rightarrow CH_3^+ + HCO$	1.08×10^{-10}
$C_2H_3^+ + C_2H_6 \rightarrow C_2H_5^+ + C_2H_4$	2.91×10^{-10}
$C_2H_3^+ + C_2H_4 \rightarrow C_2H_5^+ + C_2H_2$	8.90×10^{-10}
$C_2H_3^+ + C_2H_3 \rightarrow C_2H_5^+ + C_2H$	5.00×10^{-10}
$C_2H_3^+ + C_2H \rightarrow C_2H_2^+ + C_2H_2$	3.30×10^{-10}
$C_2H_3^+ + H \rightarrow C_2H_2^+ + H_2$	6.80×10^{-11}
$C_2H_2^+ + CH_4 \rightarrow C_2H_3^+ + CH_3$	4.10×10^{-9}
$C_2H_2^+ + C_2H_6 \rightarrow C_2H_5^+ + C_2H_3$	1.31×10^{-10}
$C_2H_2^+ + C_2H_6 \rightarrow C_2H_4^+ + C_2H_4$	2.48×10^{-10}
$C_2H_2^+ + C_2H_4 \rightarrow C_2H_4^+ + C_2H_2$	4.14×10^{-10}
$C_2H_2^+ + C_2H_3 \rightarrow C_2H_3^+ + C_2H_2$	3.30×10^{-10}
$C_2H_2^+ + H_2 \rightarrow C_2H_3^+ + H$	1.00×10^{-11}

$O_2^+ + CH_2 \rightarrow CH_2^+ + O_2$	4.30×10^{-10}
$O_2^+ + CH \rightarrow CH^+ + O_2$	3.10×10^{-10}
$O_2^+ + C_2H_4 \rightarrow C_2H_4^+ + O_2$	6.80×10^{-10}
$O_2^+ + C_2H_2 \rightarrow C_2H_2^+ + O_2$	1.11×10^{-9}
$O_2^+ + O^- \rightarrow O + O_2$	2.90×10^{-8}
$O_2^+ + O^- \rightarrow 3O$	2.90×10^{-8}
$O^- + CH_4 \rightarrow OH^- + CH_3$	1.00×10^{-10}
$O^- + C \rightarrow e + CO$	5.00×10^{-10}
$O^- + H_2 \rightarrow e + H_2O$	7.00×10^{-10}
$O^- + H_2 \rightarrow OH^- + H$	3.00×10^{-11}
$O^- + H \rightarrow e + OH$	5.00×10^{-10}
$O^- + O \rightarrow e + O_2$	2.30×10^{-11}
$O^- + CO \rightarrow e + CO_2$	6.50×10^{-10}
$CO_2^+ + H_2O \rightarrow H_2O^+ + CO_2$	1.70×10^{-9}
$CO_2^+ + H_2O \rightarrow HCOO^+ + OH$	5.00×10^{-10}
$CO_2^+ + CH_4 \rightarrow CH_4^+ + CO_2$	5.50×10^{-10}
$CO_2^+ + C_2H_4 \rightarrow C_2H_4^+ + CO_2$	1.50×10^{-10}
$CO_2^+ + C_2H_2 \rightarrow C_2H_2^+ + CO_2$	7.30×10^{-10}
$CO_2^+ + O_2 \rightarrow O_2^+ + CO_2$	5.30×10^{-11}
$CO_2^+ + O \rightarrow O_2^+ + CO$	1.64×10^{-10}
$OH^- + CH_3 \rightarrow e + CH_3OH$	1.00×10^{-9}
$OH^- + CH \rightarrow e + CH_2O$	5.00×10^{-10}
$OH^- + C \rightarrow e + HCO$	5.00×10^{-10}
$OH^- + H \rightarrow e + H_2O$	1.40×10^{-9}
$H_3O^+ + CO_3^- \rightarrow H_2O + H + CO_2 + O$	1.00×10^{-7}
$H_3O^+ + CO_4^- \rightarrow H_2O + H + CO_2 + O_2$	1.00×10^{-7}
$CO_3^- + CO_2^+ \rightarrow CO_2 + CO_2 + O$	5.00×10^{-7}
$CO_4^- + CO_2^+ \rightarrow CO_2 + CO_2 + O_2$	5.00×10^{-7}
$CO_3^- + C_2O_2^+ \rightarrow CO_2 + CO + CO + O$	5.00×10^{-7}
$CO_4^- + C_2O_2^+ \rightarrow CO_2 + CO + CO + O_2$	5.00×10^{-7}

Table S5. Neutral-neutral reactions included in the model, with the corresponding rate coefficients adopted from literature [3, 9, 10] and NIST database. [5,] M denotes any molecule in the plasma (mainly CH_4 and O_2).

Reactions:	Rate coefficients (cm^3s^{-1} for two-body reactions and cm^6s^{-1} for three-body reactions)
$CH_4 + CH \rightarrow C_2H_4 + H$	9.97×10^{-11}
$CH_3 + CH_3 + M \rightarrow C_2H_6 + M$	$1.68 \times 10^{-24} \times (T_{gas}/298)^{-7} \times e^{(-1390.4/Tgas)}$
$CH_3 + CH_2 \rightarrow C_2H_4 + H$	7.01×10^{-11}
$CH_3 + C_2H_5 + M \rightarrow C_3H_8 + M$	$1.00 \times 10^{-28} \times 0.5$
$CH_3 + H + M \rightarrow CH_4 + M$	$3.01 \times 10^{-28} \times (T_{gas}/298)^{-1.80}$
$CH_2 + CH_2 \rightarrow C_2H_2 + H + H$	$3.32 \times 10^{-10} \times e^{(-5530.43/Tgas)}$
$CH_2 + CH_2 \rightarrow C_2H_2 + H_2$	$9.98 \times 10^{-12} \times T_{gas}^{0.59}$
$CH_2 + C_2H_5 \rightarrow C_2H_4 + CH_3$	3.01×10^{-11}
$CH_2 + C_2H_3 \rightarrow C_2H_2 + CH_3$	3.01×10^{-11}
$CH_2 + H \rightarrow CH + H_2$	$1.00 \times 10^{-11} \times e^{(899.69/Tgas)}$
$CH + C_2H_6 + M \rightarrow C_3H_7 + M$	1.14×10^{-29}
$CH + H \rightarrow C + H_2$	$1.31 \times 10^{-10} \times e^{(-805.87/Tgas)}$
$C + H_2 \rightarrow CH + H$	1.50×10^{-10}
$C_2H_5 + C_2H_5 \rightarrow C_2H_6 + C_2H_4$	2.41×10^{-12}
$C_2H_5 + C_3H_7 \rightarrow C_3H_8 + C_2H_4$	1.91×10^{-12}
$C_2H_5 + C_3H_7 \rightarrow C_3H_6 + C_2H_6$	2.41×10^{-12}
$C_2H_5 + H \rightarrow CH_3 + CH_3$	5.99×10^{-11}
$C_2H_5 + H \rightarrow C_2H_4 + H_2$	3.01×10^{-12}
$C_2H_5 + H \rightarrow C_2H_6$	6.00×10^{-11}
$C_2H_4 + H + M \rightarrow C_2H_5 + M$	$7.69 \times 10^{-30}\ e^{(-380.08/Tgas)}$
$C_2H_3 + H \rightarrow C_2H_2 + H_2$	2.01×10^{-11}
$C_2H_3 + H + M \rightarrow C_2H_4 + M$	8.26×10^{-30}
$C_2H_2 + H + M \rightarrow C_2H_3 + M$	$1.08 \times 10^{-25} \times (T_{gas}/298)^{-7.27} \times e^{(-3630.02/Tgas)}$
$C_3H_7 + H \rightarrow C_3H_8$	$9.67 \times 10^{-11} \times (T_{gas}/298)^{0.22}$
$C_2H_6 + CH_2 \rightarrow C_3H_8$	4.80×10^{-12}
$H + H + M \rightarrow H_2 + M$	6.00×10^{-33}
$O + O + M \rightarrow O_2 + M$	$1.27 \times 10^{-32} \times ((T_{gas}/298)^{-1.00}) \times e^{(-170.0/Tgas)}$
$O(1S) + O \rightarrow O(1D) + O$	$5.00 \times 10^{-11} \times e^{(-300.0/Tgas)}$
$H_2(V1) + H_2 \rightarrow H_2 + H_2$	1.00×10^{-13}
$H_2(B3\sum g+) + H_2 \rightarrow H_2 + H_2$	1.00×10^{-13}
$O_2(b1) + M \rightarrow O_2 + M$	$6.0\ 0\times 10^{-11}$
$H + CH_2OH \rightarrow CH_3OH$	$2.89 \times 10^{-10} \times (T_{gas}/298)^{0.04}$
$CH_2OH + H + M \rightarrow CH_3OH + M$	1.18×10^{-29}
$CH_2OH + H_2O_2 \rightarrow CH_3OH + HO_2$	$5.00 \times 10^{-15} \times e^{(-1300.0/Tgas)}$
$CH_2OH + HCO \rightarrow CH_3OH + CO$	2.01×10^{-10}
$CH_2OH + CH_2OH \rightarrow CH_2O + CH_3OH$	8.00×10^{-12}

$CH_3 + OH \rightarrow CH_3OH$	1.45×10^{-10}
$CH_3 + OH + M \rightarrow CH_3OH + M$	7.17×10^{-27}
$CH_3O + H_2O \rightarrow CH_3OH + OH$	$1.46 \times 10^{-15} \times (T_{gas}/298)^{3.8} \times e^{(-5780.0/Tgas)}$
$CH_3O + CH_3CO \rightarrow CH_3OH + CH_2CO$	1.00×10^{-11}
$CH_3O + HCO \rightarrow CH_3OH + CO$	1.50×10^{-10}
$CH_3O + CH_2OH \rightarrow CH_2O + CH_3OH$	4.00×10^{-11}
$CH_3O + CH_3O \rightarrow CH_2O + CH_3OH$	1.00×10^{-10}
$C_3H_7 + CH_2OH \rightarrow CH_3OH + C_3H_6$	8.00×10^{-13}
$CH_3OO + OH \rightarrow CH_3OH + O_2$	1.00×10^{-10}
$C_2H_5 + CH_2OH \rightarrow CH_3OH + C_2H_4$	4.00×10^{-12}
$H_2 + CH_2OH \rightarrow CH_3OH + H$	$8.60 \times 10^{-15} \times (T_{gas}/298)^{3.5} \times e^{(-5271/Tgas)}$
$C_3H_8 + CH_2OH \rightarrow CH_3OH + C_3H_7$	$1.99 \times 10^{-15} \times (T_{gas}/298)^{2.95} \times e^{(-6032/Tgas)}$
$C_3H_8 + CH_3O \rightarrow CH_3OH + C_3H_7$	$7.21 \times 10^{-13} \times e^{(-3251/Tgas)}$
$C_2H_6 + CH_2OH \rightarrow CH_3OH + C_2H_5$	$8.73 \times 10^{-15} (T_{gas}/298)^{3.0} \times e^{(-7032/Tgas)}$
$C_2H_6 + CH_3O \rightarrow CH_3OH + C_2H_5$	$4.00 \times 10^{-13} \times e^{(-3571/Tgas)}$
$CH_4 + CH_2OH \rightarrow CH_3OH + CH_3$	$5.03 \times 10^{-13} \times (T_{gas}/298)^{5.0} \times e^{(-7477/Tgas)}$
$CH_4 + CH_3O \rightarrow CH_3OH + CH_3$	$2.42 \times 10^{-15} \times (T_{gas}/298)^{5.0} \times e^{(-2810/Tgas)}$
$CH_2O + CH_2OH \rightarrow CH_3OH + HCO$	$7.72 \times 10^{-14} \times (T_{gas}/298)^{2.8} \times e^{(-2951/Tgas)}$
$CH_2O + CH_3O \rightarrow CH_3OH + HCO$	$1.69 \times 10^{-13} \times e^{(-1500.0/TGAS)}$
$CH_2OH + H_2O \rightarrow CH_3OH + OH$	$4.12 \times 10^{-14} \times (T_{gas}/298)^{3} \times e^{(-10439/Tgas)}$
$CH_3O + H \rightarrow CH_3OH$	$3.39 \times 10^{-10} \times (T_{gas}/298)^{0.33}$
$CH_3O + H + M \rightarrow CH_3OH + M$	$1.68 \times 10^{-26} \times (T_{gas}/298)^{0.33}$
$H_2 + CH_3O \rightarrow CH_3OH + H$	$1.66 \times 10^{-15} \times (T_{gas}/298)^{4} \times e^{(-2471/Tgas)}$
$C_3H_6 + CH_2OH \rightarrow CH_3OH + C_3H_5$	$1.99 \times 10^{-15} \times (T_{gas}/298)^{2.95} \times e^{(-6031/Tgas)}$
$C_3H_6 + CH_3O \rightarrow CH_3OH + C_3H_5$	$2.97 \times 10^{-15} \times (T_{gas}/298)^{2.95} \times e^{(-6031/Tgas)}$
$CH_3CHO + CH_3O \rightarrow CH_3OH + CH_3CO$	8.30×10^{-15}
$CH_2O + H_2 \rightarrow CH_3OH$	$2.29 \times 10^{-11} \times (T_{gas}/298) \times e^{(-35128/Tgas)}$
$O(1D) + CH_4 \rightarrow CH_3OH$	4.98×10^{-11}
$CH_3OH + CH_2 \rightarrow CH_3 + CH_2OH$	$4.38 \times 10^{-15} \times (T_{gas}/298)^{3.2} \times e^{(-3609/Tgas)}$
$CH_3OH + CH_2 \rightarrow CH_3O + CH_3$	$1.12 \times 10^{-15} \times (T_{gas}/298)^{3.1} \times e^{(-3489/Tgas)}$
$CH_3OH + O \rightarrow CH_2OH + OH$	7.99×10^{-15}
$CH_3OH + H \rightarrow H_2 + CH_2OH$	$2.42 \times 10^{-12} \times (T_{gas}/298)^{2.0} \times e^{(-2274/Tgas)}$
$CH_3OH + H \rightarrow H_2 + CH_3O$	$2.93 \times 10^{-14} \times (T_{gas}/298)^{3.4} \times e^{(-3645/Tgas)}$
$CH_3OH + OH \rightarrow CH_2OH + H_2O$	1.92×10^{-14}
$CH_3OH + OH \rightarrow CH_3O + H_2O$	4.80×10^{-20}
$CH_3OH + CH_3CO \rightarrow CH_3CHO + CH_2OH$	$2.13 \times 10^{-13} \times (T_{gas}/298)^{3.0} \times e^{(-6207/Tgas)}$
$CH_3OH + HCO \rightarrow CH_2O + CH_2OH$	$2.41 \times 10^{-13} \times (T_{gas}/298)^{2.9} \times e^{(-6604/Tgas)}$

$CH_3OH + CH_3OO \rightarrow CH_2OH + CH_3OOH$	$3.01 \times 10^{-12} \times e^{(-6905/Tgas)}$
$CH_3OH + C_2H \rightarrow C_2H_2 + CH_2OH$	1.00×10^{-11}
$CH_3OH + C_2H \rightarrow C_2H_2 + CH_3O$	2.01×10^{-12}
$CH_3OH + C_2H_3 \rightarrow C_2H_4 + CH_2OH$	$4.38 \times 10^{-15} \times (T_{gas}/298)^{3.2} \times e^{(-3611/Tgas)}$
$CH_3OH + C_2H_3 \rightarrow C_2H_4 + CH_3O$	$1.12 \times 10^{-15} \times (T_{gas}/298)^{3.1} \times e^{(-3491/Tgas)}$
$CH_3OH + C_2H_5 \rightarrow C_2H_6 + CH_2OH$	$4.38 \times 10^{-15} \times (T_{gas}/298)^{3.2} \times e^{(-4607/Tgas)}$
$CH_3OH + C_2H_5 \rightarrow C_2H_6 + CH_3O$	$1.12 \times 10^{-15} \times (T_{gas}/298)^{3.1} \times e^{(-4499/Tgas)}$
$CH_3OH + C_3H_5 \rightarrow C_3H_6 + CH_2OH$	$4.33 \times 10^{-13} \times (T_{gas}/298)^{2.9} \times e^{(-10302/Tgas)}$
$CH_3OH + C_3H_7 \rightarrow C_3H_8 + CH_2OH$	$7.57 \times 10^{-14} \times (T_{gas}/298)^{3.7} \times e^{(-5305/Tgas)}$
$CH_3OH + C_3H_7 \rightarrow C_3H_8 + CH_3O$	$1.12 \times 10^{-15} \times (T_{gas}/298)^{3.1} \times e^{(-5197/Tgas)}$
$CH_3OH + H \rightarrow CH_3 + H_2O$	1.91×10^{-28}
$CH_3OH + O_2 \rightarrow CH_2OH + HO_2$	$3.40 \times 10^{-11} \times e^{(-22616/Tgas)}$
$CH_3OH + HO_2 \rightarrow CH_2OH + H_2O_2$	$1.60 \times 10^{-11} \times e^{(-6328/Tgas)}$
$CH_3OH + CH_2OH \rightarrow CH_3OH + CH_3O$	$1.30 \times 10^{-14} \times e^{(-6075/Tgas)}$
$CH_3OH + CH_3 \rightarrow CH_4 + CH_2OH$	$1.35 \times 10^{-15} \times (T_{gas}/298)^{4.9} \times e^{(-3380/Tgas)}$
$CH_3OH + CH_3 \rightarrow CH_4 + CH_3O$	$2.62 \times 10^{-16} \times (T_{gas}/298)^{4.7} \times e^{(-2911/Tgas)}$
$CH_3OH + CH_3O \rightarrow CH_3OH + CH_2OH$	$5.00 \times 10^{-13} \times e^{(-2045/Tgas)}$
$CH_3OH \rightarrow H_2 + CH_2O$	$2.12 \times 10^{-13} \times (T_{gas}/298)^{1.22} \times e^{(-43548.6/Tgas)}$
$CH_3OH \rightarrow CH_2 + H_2O$	$2.61 \times 10^{-15} \times (T_{gas}/298)^{1.6} \times e^{(-46556/Tgas)}$
$O_2 + CH_2 \rightarrow CH_2O + O$	6.64×10^{-14}
$CH_2 + OH \rightarrow CH_2O + H$	3.00×10^{-11}
$HCO + H_2O \rightarrow CH_2O + OH$	$8.54 \times 10^{-13} \times (T_{gas}/298)^{1.35} \times e^{(-13112/Tgas)}$
$HCO + H_2O_2 \rightarrow CH_2O + HO_2$	$1.69 \times 10^{-13} \times e^{(-3491/Tgas)}$
$HCO + HCO \rightarrow CH_2O + CO$	4.48×10^{-11}
$CH_2OH + O \rightarrow CH_2O + OH$	1.50×10^{-10}
$H + CH_2OH \rightarrow CH_2O + H_2$	1.00×10^{-11}
$CH_2OH + O_2 \rightarrow CH_2O + HO_2$	9.60×10^{-12}
$CH_2OH + OH \rightarrow CH_2O + H_2O$	4.00×10^{-11}
$CH_2OH + HO_2 \rightarrow CH_2O + H_2O_2$	2.01×10^{-11}
$CH_2OH + HCO \rightarrow CH_2O + CH_2O$	3.01×10^{-10}
$CH_3 + CH_2OH \rightarrow CH_2O + CH_4$	1.41×10^{-10}
$CH_3O + CH_2 \rightarrow CH_2O + CH_3$	3.01×10^{-11}
$CH_3O + O \rightarrow CH_2O + OH$	1.00×10^{-11}
$CH_3O + H \rightarrow CH_2O + H_2$	$3.14 \times 10^{-10} \times (T_{gas}/298)^{-0.58} \times e^{(-855/Tgas)}$
$CH_3O + O_2 \rightarrow CH_2O + HO_2$	$7.82 \times 10^{-14} \times e^{(-1150/Tgas)}$
$CH_3O + OH \rightarrow CH_2O + H_2O$	3.01×10^{-11}
$CH_3O + HO_2 \rightarrow CH_2O + H_2O_2$	5.00×10^{-13}

$CH_3O + CH_3 \rightarrow CH_2O + CH_4$	4.00×10^{-11}
$CH_3OO + CH_2 \rightarrow CH_2O + CH_3O$	3.01×10^{-11}
$CH_3OO + CH_3O \rightarrow CH_2O + CH_3OOH$	5.00×10^{-13}
$H_2 + HCO \rightarrow CH_2O + H$	$2.66 \times 10^{-13} \times (T_{gas}/298)^{2.0} \times e^{(-8972/Tgas)}$
$C_2H_2 + CH_2OH \rightarrow CH_2O + C_2H_3$	$1.20 \times 10^{-12} \times e^{(-4530/Tgas)}$
$CH_4 + HCO \rightarrow CH_2O + CH_3$	$2.39 \times 10^{-15} \times (T_{gas}/298)^{3.78} \times e^{(-10746/Tgas)}$
$O(1D) + CH_4 \rightarrow CH_2O + H_2$	7.51×10^{-12}
$CH_2 + OH \rightarrow CH_2O + H$	$9.55 \times 10^{-11} \times (TGAS/298)^{0.12} \times e^{(81.8/Tgas)}$
$CH + H_2O \rightarrow CH_2O + H$	$2.82 \times 10^{-11} \times (TGAS/298)^{-1.22} \times e^{(-12/Tgas)}$
$CH_2OH + CH_2 \rightarrow CH_2O + CH_3$	2.01×10^{-12}
$CH_2OH \rightarrow CH_2O + H$	$4.88 \times 10^{-5} \times (TGAS/298)^{-2.5} \times e^{(-7203/Tgas)}$
$CH_2 + CO_2 \rightarrow CH_2O + CO$	3.90×10^{-14}
$CH_3 + O \rightarrow CH_2O + H$	$1.25 \times 10^{-10} \times (TGAS/298)^{-0.03} \times e^{(-18/Tgas)}$
$CH_3 + O_2 \rightarrow CH_2O + OH$	$2.81\times 10^{-13} \times e^{(-4981/Tgas)}$
$CH_3 + OH \rightarrow H_2 + CH_2O$	$9.10 \times 10^{-11} \times e^{(-1500/Tgas)}$
$CH_3O \rightarrow CH_2O + H$	7.36×10^{-06}
$CH_3OO + HO_2 \rightarrow CH_2O + H_2O + O_2$	$1.60 \times 10^{-15} \times e^{(-1730/Tgas)}$
$C_2H + CH_2OH \rightarrow CH_2O + C_2H_2$	5.98×10^{-11}
$C_2H + CH_3O \rightarrow CH_2O + C_2H_2$	4.00×10^{-11}
$C_2H_3 + O_2 \rightarrow CH_2O + HCO$	$4.62 \times 10^{-12} \times e^{(-170/Tgas)}$
$C_2H_3 + CH_2OH \rightarrow C_2H_4 + CH_2O$	5.00×10^{-11}
$C_2H_3 + CH_3O \rightarrow C_2H_4 + CH_2O$	4.00×10^{-11}
$C_2H_4 + O \rightarrow CH_2O + CH_2$	$8.30 \times 10^{-12} \times e^{(-754.3/Tgas)}$
$C_2H_4 + O_3 \rightarrow CH_2O + HCOOH$	1.35×10^{-18}
$C_2H_5 + O \rightarrow CH_2O + CH_3$	2.67×10^{-11}
$C_2H_5 + CH_2OH \rightarrow C_2H_6 + CH_2O$	4.00×10^{-12}
$C_2H_5 + CH_3O \rightarrow C_2H_6 + CH_2O$	4.00×10^{-11}
$C_2H_6 + HCO \rightarrow CH_2O + C_2H_5$	$4.18 \times 10^{-13} \times (T_{gas}/298)^{2.72} \times e^{(-9182/Tgas)}$
$C_3H_5 + CH_2OH \rightarrow CH_2O + C_3H_6$	3.01×10^{-11}
$C_3H_5 + CH_3O \rightarrow CH_2O + C_3H_6$	5.00×10^{-11}
$C_3H_7 + CH_3O \rightarrow CH_2O + C_3H_8$	4.00×10^{-11}
$C_3H_7 + CH_2OH \rightarrow CH_2O + C_3H_8$	1.60×10^{-12}
$HOCH_2OH \rightarrow CH_2O + H_2O$	$4.15 \times 10^{13} \times e^{(-22731.4/Tgas)}$
$CH_2O + CH_2 \rightarrow CH_3 + HCO$	1.00×10^{-14}
$CH_2O + H \rightarrow CH_3O$	$4.34 \times 10^{-12} \times (T_{gas}/298)^{1.66} \times e^{(-865/Tgas)}$
$CH_2O + H \rightarrow H_2 + HCO$	$1.44 \times 10^{-11} \times e^{(-1744/Tgas)}$
$CH_2O + O_2 \rightarrow HCO + HO_2$	$9.14 \times 10^{-12} \times (T_{gas}/298)^{2.05} \times e^{(-19128/Tgas)}$

$CH_2O + OH \rightarrow HCO + H_2O$	$4.73 \times 10^{-12} \times (T_{gas}/298)^{1.18} \times e^{(225/Tgas)}$
$CH_2O + CH \rightarrow CH_2CHO$	$1.57 \times 10^{-10} \times e^{(260/Tgas)}$
$CH_2O + HO_2 \rightarrow HOCH_2OO$	$9.70 \times 10^{-15} \times e^{(626/Tgas)}$
$CH_2O + HO_2 \rightarrow HCO + H_2O_2$	$1.50 \times 10^{-13} \times (T_{gas}/298)^{2.7} \times e^{(-5798/Tgas)}$
$CH_2O + C_2H_3 \rightarrow C_2H_4 + HCO$	$3.21 \times 10^{-15} \times (T_{gas}/298)^{4.21} \times e^{(-818/Tgas)}$
$CH_2O + CH_3 \rightarrow CH_3CH_2O$	$4.98\times 10^{-13} \times e^{(-3188.0/Tgas)}$
$CH_2O + CH_3 \rightarrow CH_4 + HCO$	$2.04 \times 10^{-15} \times (T_{gas}/298)^{3.92} \times e^{(-2322/Tgas)}$
$CH_2O + C_3H_7 \rightarrow C_3H_8 + HCO$	$7.49 \times 10^{-14} \times (T_{gas}/298)^{2.9} \times e^{(-2947/Tgas)}$
$CH_2O + CH_3OO \rightarrow HCO + CH_3OOH$	$3.30 \times 10^{-12} \times e^{(-5870/Tgas)}$
$CH_2O + C_2H_5 \rightarrow C_2H_6 + HCO$	$8.19 \times 10^{-14} \times (T_{gas}/298)^{2.81} \times e^{(-2947/Tgas)}$
$CH_2O + C_3H_5 \rightarrow C_3H_6 + HCO$	$1.05 \times 10^{-11} \times (T_{gas}/298)^{1.9} \times e^{(-9155/Tgas)}$
$CH_2O \rightarrow CO + H_2$	$1.51 \times 10^{14} \times e^{(-50886/Tgas)}$
$O_2 + HOCH_2O \rightarrow HCOOH + HO_2$	3.50×10^{-14}
$HOCH_2O \rightarrow HCOOH + H$	$1.00 \times 10^{14} \times e^{(-7507/Tgas)}$
$CH_2OO \rightarrow HCOOH$	1.20×10^{-12}
$HOCH_2OO + HOCH_2OO \rightarrow HCOOH + HOCH_2OH + O_2$	$5.65 \times 10^{-14} \times e^{(750/Tgas)}$
$HCO + OH \rightarrow HCOOH$	2.01×10^{-11}
$HCOOH + OH \rightarrow H_2O + HCOO$	$1.07 \times 10^{-16} \times (T_{gas}/298)^{4.93} \times e^{(2549.7/Tgas)}$
$HCOOH + OH \rightarrow COOH + H_2O$	$9.85 \times 10^{-13} \times e^{(-1036.0/Tgas)}$
$HCOOH \rightarrow CO_2 + H_2$	$4.46 \times 10^{13} \times e^{(-34397.9/Tgas)}$
$HCOOH \rightarrow CO + H_2O$	$7.49 \times 10^{14} \times e^{(-34518.1/Tgas)}$
$CH_3 + CH_2OH \rightarrow CH_3CH_2OH$	$9.44 \times 10^{-11} \times (T_{gas}/298)^{-0.19} \times e^{(-22.9/Tgas)}$
$CH_3 + CH_2OH + M \rightarrow CH_3CH_2OH + M$	$2.17 \times 10^{-27} \times (T_{gas}/298)^{0.19} \times e^{(-22.9/Tgas)}$
$C_2H_5 + OH \rightarrow CH_3CH_2OH$	$8.25 \times 10^{-11} \times (T_{gas}/298)^{-0.61} \times e^{(38.5/Tgas)}$
$C_2H_5 + OH + M \rightarrow CH_3CH_2OH + M$	$1.90 \times 10^{-27} \times (T_{gas}/298)^{-0.61} \times e^{(38.5/Tgas)}$
$O(1D) + C_2H_6 \rightarrow CH_3CH_2OH$	9.96×10^{-10}
$CH_3CH_2OO + CH_3CH_2OO \rightarrow CH_3CH_2OH + CH_3CHO + O_2$	2.31×10^{-14}
$CH_2CH_2OH + H \rightarrow CH_3CH_2OH$	8.30×10^{-11}
$CH_3CHOH + H \rightarrow CH_3CH_2OH$	8.30×10^{-11}
$CH_2CH_2OH + H + M \rightarrow CH_3CH_2OH + M$	9.30×10^{-26}
$HCO + CH_3CO \rightarrow CH_3CHO + CO$	1.50×10^{-11}
$CH_3 + HCO \rightarrow CH_3CHO$	4.42×10^{-11}
$CH_3 + HCO + M \rightarrow CH_3CHO + M$	1.02×10^{-27}
$C_2H_5 + O \rightarrow CH_3CHO + H$	1.33×10^{-10}
$C_2H_5 + O_2 \rightarrow CH_3CHO + OH$	$2.14 \times 10^{-13} \times (T_{gas}/298)^{-1.03} \times e^{(-4861.0/Tgas)}$
$C_2H_4 + HO_2 \rightarrow CH_3CHO + OH$	$1.00 \times 10^{-14} \times e^{(-4001.0/TGAS)}$
$C_2H_6 + CH_3CO \rightarrow CH_3CHO + C_2H_5$	$1.91 \times 10^{-13} \times (T_{gas}/298)^{2.75} \times e^{(-8822.0/Tgas)}$

$CH_4 + CH_3CO \rightarrow CH_3CHO + CH_3$	$4.82 \times 10^{-14} \times (T_{gas}/298)^{2.88} \times e^{(-10802.0/Tgas)}$
$CH_2O + CH_3CO \rightarrow CH_3CHO + HCO$	$3.01 \times 10^{-13} \times e^{(-6501/Tgas}$
$C_3H_5 + O_2 \rightarrow CH_3CHO + HCO$	7.21×10^{-12}
$CH_3CO + H_2O_2 \rightarrow CH_3CHO + HO_2$	$3.01 \times 10^{-13} \times e^{(-4138/Tgas)}$
$CH_3CO + CH_3CO \rightarrow CH_3CHO + CH_2CO$	1.49×10^{-11}
$CH_3CH_2OO \rightarrow CH_3CHO + OH$	1.02×10^{-18}
$C_2H_3 + OH \rightarrow CH_3CHO$	5.00×10^{-11}
$C_2H_3 + OH + M \rightarrow CH_3CHO + M$	1.15×10^{-27}
$CH_3CHOH + O \rightarrow CH_3CHO + OH$	3.16×10^{-10}
$CH_3CHOH + H \rightarrow CH_3CHO + H_2$	3.32×10^{-11}
$CH_3CHOH + O_2 \rightarrow CH_3CHO + HO_2$	$7.76 \times 10^{-11} \times (T_{gas}/298)^{-1.64} \times e^{(-422.0/Tgas)}$
$CH_3CH_2O + O_2 \rightarrow CH_3CHO + HO_2$	9.48×10^{-15}
$CH_3O + CH_3CO \rightarrow CH_2O + CH_3CHO$	5.68×10^{-11}
$C_3H_7 + O \rightarrow CH_3CHO + CH_3$	8.00×10^{-11}
$C_3H_7 + HO_2 \rightarrow CH_3CHO + CH_3 + OH$	4.00×10^{-11}
$C_3H_7 + CH_3OO \rightarrow CH_3CHO + CH_3O + CH_3$	4.00×10^{-11}
$H_2 + CH_3CO \rightarrow CH_3CHO + H$	$2.18 \times 10^{-13} \times (T_{gas}/298)^{1.82} \times e^{(-8866.0/Tgas)}$
$C_3H_6 + CH_3CO \rightarrow CH_3CHO + C_3H_5$	$7.82 \times 10^{-13} \times (T_{gas}/298)^{2.0} \times e^{(-8168.0/Tgas)}$
$C_3H_8 + CH_3CO \rightarrow CH_3CHO + C_3H_7$	$7.82 \times 10^{-13} \times (T_{gas}/298)^{2.0} \times e^{(-8168.0/Tgas)}$
$CH_4 + CH_3CO \rightarrow CH_3CHO + CH_3$	$4.82 \times 10^{-14} \times (T_{gas}/298)^{2.88} \times e^{(-10803.0/Tgas)}$
$CH_2CHO + H_2 \rightarrow CH_3CHO + H$	3.00×10^{-10}
$CH_3CHO + H \rightarrow CH_3CHOH$	2.49×10^{-18}
$CH_3CHO + OH \rightarrow CH_3CO + H_2O$	8.48×10^{-13}
$CH_3 + COOH \rightarrow CH_3COOH$	5.81×10^{-11}
$CH_3 + COOH + M \rightarrow CH_3COOH + M$	5.0×10^{-27}
$CH_3CO + OH \rightarrow CH_3COOH$	7.01×10^{-11}
$CH_3CO + OH + M \rightarrow CH_3COOH + M$	5.00×10^{-27}
$CH_2OO \rightarrow CO + H_2O$	6.00×10^{4}
$HCOO \rightarrow CO + OH$	1.45×10^{-11}
$CH_3CO \rightarrow CO + CH_3$	$3.87 \times 10^{-13} \times (T_{gas}/298)^{0.63} \times e^{(-8505.0/Tgas)}$
$O_2 + CH_2 \rightarrow CO + H_2O$	4.00×10^{-13}
$C + O_2 \rightarrow CO + O$	1.60×10^{-11}
$OH + C \rightarrow CO + H$	1.15×10^{-10}
$CH + O \rightarrow CO + H$	6.59×10^{-11}
$CH + O_2 \rightarrow CO + OH$	8.30×10^{-11}
$HCO + CH_2 \rightarrow CO + CH_3$	3.01×10^{-11}
$HCO + H \rightarrow CO + H_2$	1.83×10^{-11}

$HCO + OH \rightarrow CO + H_2O$	1.69×10^{-10}
$HCO + C_2H_3 \rightarrow C_2H_4 + CO$	1.50×10^{-10}
$HCO \rightarrow CO + H$	1.16×10^{-14}
$COOH \rightarrow CO + OH$	5.42×10^{-26}
$CH_3 + HCO \rightarrow CH_4 + CO$	4.40×10^{-11}
$C_3H_7 + HCO \rightarrow C_3H_8 + CO$	1.00×10^{-10}
$C_2H + O \rightarrow CO + CH$	$2.41 \times 10^{-13} \times e^{(-230.0/Tgas)}$
$C_2H + O_2 \rightarrow CO + HCO$	4.00×10^{-12}
$C_2H + OH \rightarrow CO + CH_2$	3.01×10^{-11}
$C_2H + HCO \rightarrow C_2H_2 + CO$	1.00×10^{-10}
$C_2H_5 + HCO \rightarrow C_2H_6 + CO$	2.01×10^{-10}
$C_3H_5 + HCO \rightarrow C_3H_6 + CO$	1.00×10^{-10}
$CH_2CO + CH_2 \rightarrow C_2H_4 + CO$	2.09×10^{-10}
$CH_2CO + H \rightarrow CO + CH_3$	4.56×10^{-14}
$CO_2 + H \rightarrow CO + OH$	$2.51 \times 10^{-10} \times e^{(-13353.0/Tgas)}$
$C_2H_2 + O \rightarrow CO + CH_2$	$3.49 \times 10^{-12} \times (T_{gas}/298)^{1.5} \times e^{(-850.0/Tgas)}$
$CH_3 + O \rightarrow CO + H_2 + H$	5.68×10^{-11}
$CH_2 + O \rightarrow CO + H_2$	5.53×10^{-11}
$CH_2 + O \rightarrow CO + H + H$	8.29×10^{-11}
$C_2H_3 + O \rightarrow CO + CH_3$	1.25×10^{-11}
$CH + CO_2 \rightarrow HCO + CO$	9.68×10^{-13}
$CH + CO_2 \rightarrow CO + CO + H$	9.68×10^{-13}
$H + C_2HO \rightarrow CH_2 + CO$	2.50×10^{-10}
$OH + CH_2CO \rightarrow CO + CH_2OH$	1.70×10^{-11}
$HCOO \rightarrow CO_2 + H$	6.42×10^{-12}
$CH_3COO \rightarrow CO_2 + CH_3$	$1.17 \times 10^{-12} \times (T_{gas}/298)^{0.29} \times e^{(-2310.0/Tgas)}$
$CH_3CO + O \rightarrow CO_2 + CH_3$	1.60×10^{-11}
$CH_3CO + O_2 \rightarrow CO_2 + CH_3O$	$7.37 \times 10^{-14} \times e^{(542.0/Tgas)}$
$HCO + O_3 \rightarrow CO_2 + O_2 + H$	8.30×10^{-13}
$COOH + O_2 \rightarrow CO_2 + HO_2$	2.09×10^{-12}
$COOH \rightarrow CO_2 + H$	1.52×10^{-24}
$C_2H + O_2 \rightarrow CH + CO_2$	$7.70 \times 10^{-17} \times (T_{gas}/298)^{4.4} \times e^{(1150.0/Tgas)}$
$CO + O_3 \rightarrow CO_2 + O_2$	4.00×10^{-25}
$CO + OH \rightarrow CO_2 + H$	1.49×10^{-13}
$CO + HO_2 \rightarrow CO_2 + OH$	2.01×10^{-17}
$CO + COOH \rightarrow CO_2 + HCO$	1.00×10^{-14}
$CO + CH_3O \rightarrow CO_2 + CH_3$	$2.61 \times 10^{-11} \times e^{(-5943.0/Tgas)}$

$CO + CH_3OO \rightarrow CO_2 + CH_3O$	7.01×10^{-18}
$C_2H_2 + COOH \rightarrow CO_2 + C_2H_3$	3.01×10^{-14}
$C_2H_4 + COOH \rightarrow CO_2 + C_2H_5$	1.00×10^{-14}
$O(1D) + CO \rightarrow CO_2$	8.00×10^{-11}
$O + CH_2CO \rightarrow CH_2 + CO_2$	2.29×10^{-13}
$HO_2 + CH_3CO \rightarrow CH_3 + CO_2 + OH$	5.00×10^{-11}
$CH_3 + OH \rightarrow CH_2OH + H$	$3.18 \times 10^{-12} \times (T_{gas}/298) \times e^{(-1606.0/Tgas)}$
$CH + H_2O \rightarrow CH_2OH$	$9.48 \times 10^{-12} \times (T_{gas}/298)^{3.0} \times e^{(380.0/Tgas)}$
$O(1D) + CH_4 \rightarrow CH_2OH + H$	$1.50 \times 10^{10} \times 0.046$
$CH_3 + O_3 \rightarrow CH_3O + O_2$	2.61×10^{-12}
$CH_3 + OH \rightarrow CH_3O + H$	$6.45 \times 10^{-13} \times (T_{gas}/298)^{1.01} \times e^{(-6015.0/Tgas)}$
$CH_3 + HO_2 \rightarrow CH_3O + OH$	$7.68 \times 10^{-12} \times (T_{gas}/298)^{0.27} \times e^{(346.5/Tgas)}$
$CH_3OO + O \rightarrow CH_3O + O_2$	4.30×10^{-11}
$CH_3OO + H \rightarrow CH_3O + OH$	1.60×10^{-10}
$CH_3OO + O_3 \rightarrow CH_3O + O_2 + O_2$	1.52×10^{-17}
$CH_3OO + CH_3 \rightarrow CH_3O + CH_3O$	$8.40 \times 10^{-12} \times e^{(710.0/Tgas)}$
$C_2H_5 + CH_3OO \rightarrow CH_3O + CH_3CH_2O$	4.00×10^{-11}
$CH_3OO + CH_3OO \rightarrow CH_3O + CH_3O + O_2$	$7.40 \times 10^{-13} \times e^{(-520.0/Tgas)}$
$CH_3 + O \rightarrow CH_3O$	$1.22 \times 10^{-10} \times (T_{gas}/298)^{0.05} \times e^{(68.6/Tgas)}$
$CH_3 + O_2 \rightarrow CH_3O + O$	$2.19 \times 10^{-10} \times e^{(-15759.0/Tgas)}$
$O(1D) + CH_4 \rightarrow CH_3O + H$	6.44×10^{-04}
$CH_3OOH + H \rightarrow H_2 + CH_3OO$	$0.52 \times e^{(-936.0/Tgas)}$
$CH_3OOH + OH \rightarrow H_2O + CH_2OOH$	1.89×10^{-12}
$CH_3OOH + OH \rightarrow CH_3OO + H_2O$	$1.90 \times 10^{-12} \times e^{(190/Tgas)}$
$CH_3 + O_2 \rightarrow CH_3OO$	$1.79 \times 10^{-12} \times (T_{gas}/298)^{1.66}$
$CH_3OO \rightarrow CH_2OOH$	$1.79 \times 10^{-12} \times (T_{gas}/298)^{1.5} \times e^{(-21293.0/Tgas)}$
$CH_2O + OH \rightarrow HOCH_2O$	$1.13 \times 10^{-13} \times (T_{gas}/298)^{1.63} \times e^{(-2157.0/Tgas)}$
$CH_3OO + H_2O_2 \rightarrow CH_3OOH + HO_2$	$4.00 \times 10^{-12} \times e^{(-5000.8/Tgas)}$
$CH_3OO + HO_2 \rightarrow CH_3OOH + O_2$	$3.50 \times 10^{-14} \times e^{(1831.0/Tgas)}$
$H_2 + CH_3OO \rightarrow CH_3OOH + H$	$5.00 \times 10^{-11} \times e^{(-13112.7/Tgas)}$
$C_3H_6 + CH_3OO \rightarrow C_3H_5 + CH_3OOH$	$3.30 \times 10^{-12} \times e^{(-8582.0/Tgas)}$
$C_3H_8 + CH_3OO \rightarrow C_3H_7 + CH_3OOH$	$1.00 \times 10^{-11} \times e^{(-9752.7/Tgas)}$
$C_2H_6 + CH_3OO \rightarrow C_2H_5 + CH_3OOH$	$6.54 \times 10^{-13} \times (T_{gas}/298)^{2.69} \times e^{(-10016.0/Tgas)}$
$CH_4 + CH_3OO \rightarrow CH_3 + CH_3OOH$	$3.01 \times 10^{-13} \times e^{(-9302/Tgas)}$
$CH_2O + HOCH_2O \rightarrow HOCH_2OH + HCO$	1.00×10^{-15}
$O + CH_2 \rightarrow HCO + H$	5.01×10^{-11}
$CH + O_2 \rightarrow HCO + O$	1.66×10^{-11}

$C_2H_3 + O_2 \rightarrow CH_2O + HCO$	2.62×10^{-12}
$CO + H \rightarrow HCO$	$1.96\times 10^{-13} \times e^{(-1370/Tgas)}$
$CO + CH_3O \rightarrow CH_2O + HCO$	3.26×10^{-33}
$CH_2CO + OH \rightarrow CH_2O + HCO$	4.65×10^{-11}
$C_2H_2 + CO \rightarrow C_2H + HCO$	$8.00 \times 10^{-10} \times e^{(-53653.8/Tgas)}$
$C_2H_4 + O \rightarrow CH_3 + HCO$	$1.50 \times 10^{-12} \times (T_{gas}/298)^{1.55} \times e^{(-215.0/Tgas)}$
$C_2H_4 + O \rightarrow HCO + CH_3$	4.51×10^{-13}
$C_2H_4 + CO \rightarrow HCO + C_2H_3$	$2.51\times 10^{-10} \times e^{(-45593.7/Tgas)}$
$C_2H_3 + O \rightarrow HCO + CH_2$	1.25×10^{-11}
$H + CO + M \rightarrow HCO + M$	$1.90 \times 10^{-33} \times e^{(-841.95/Tgas)}$
$C_2H_4 + O_3 \rightarrow CH_2O + CH_2OO$	1.35×10^{-18}
$OH + CO \rightarrow COOH$	1.00×10^{-14}
$C_2H_3 + O \rightarrow CH_2CHO$	$5.50 \times 10^{-11} \times (T_{gas}/298)^{0.2} \times e^{(215/Tgas)}$
$C_2H_3 + O_2 \rightarrow CH_2CHO + O$	$1.79 \times 10^{-11} \times (T_{gas}/298)^{-0.61} \times e^{(-2648/Tgas)}$
$CO + CH_3 \rightarrow CH_3CO$	1.06×10^{-17}
$CH_2CO + H \rightarrow CH_3CO$	$3.68 \times 10^{-12} \times (T_{gas}/298)^{1.61} \times e^{(-1322/Tgas)}$
$CH_2CO + H \rightarrow CH_2CHO$	4.16×10^{-16}
$C_2H_4 + O \rightarrow CH_2CHO + H$	6.24×10^{-13}
$CH_3CO + CH_2 \rightarrow CH_2CO + CH_3$	3.01×10^{-11}
$O + CH_3CO \rightarrow OH + CH_2CO$	8.75×10^{-11}
$CH_3CO + OH \rightarrow CH_2CO + H_2O$	2.01×10^{-11}
$C_2H_3 + O \rightarrow CH_2CO + H$	1.60×10^{-10}
$CH_3 + CH_3CO \rightarrow CH_4 + CH_2CO$	1.01×10^{-11}
$CO + CH_2 \rightarrow CH_2CO$	1.00×10^{-15}
$C_2H_2 + O \rightarrow CH_2CO$	2.16×10^{-13}
$C_2H_2 + OH \rightarrow CH_2CO + H$	1.00×10^{-13}
$C_2H_2 + HO_2 \rightarrow CH_2CO + OH$	$1.00 \times 10^{-14} \times e^{(-4001/Tgas)}$
$C_2H_4 + O \rightarrow CH_2CO + H_2$	3.82×10^{-14}
$CH_3CH_2OO + O_3 \rightarrow CH_3CH_2O + O_2 + O_2$	9.27×10^{-18}
$CH_3CH_2OO + CH_3CH_2OO \rightarrow CH_3CH_2O + CH_3CH_2O + O_2$	4.00×10^{-14}
$CH_3CH_2OO \rightarrow CH_3CH_2O + O$	1.19×10^{-30}
$C_2H_5 + O \rightarrow CH_3CH_2O$	1.23×10^{-10}
$C_2H_5 + O_3 \rightarrow CH_3CH_2O + O_2$	3.32×10^{-14}
$C_2H_5 + O_2 \rightarrow CH_3CH_2O + O$	1.74×10^{-32}
$C_2H_5 + HO_2 \rightarrow CH_3CH_2O + OH$	4.98×10^{-11}
$C_2H_4 + OH \rightarrow CH_2CH_2OH$	8.23×10^{-12}
$C_2H_5 + O \rightarrow C_2H_4 + OH$	4.40×10^{-11}

$C_2H_3 + O \rightarrow C_2H_2 + OH$	1.25×10^{-11}
$C_2H_2 + O \rightarrow C_2HO + H$	$1.53 \times 10^{-13} \times (T_{gas}/298)^{2.8} \times e^{(-250.2/Tgas)}$
$H + O + M \rightarrow OH + M$	$4.36 \times 10^{-32} \times (T_{gas}/298)^{-1.00}$
$H + O_2 + M \rightarrow HO_2 + M$	$4.11 \times 10^{-32} \times (T_{gas}/298)^{-1.10}$
$H + O_3 \rightarrow OH + O_2$	2.86×10^{-11}
$CH_4 + OH \rightarrow CH_3 + H_2O$	$1.36 \times 10^{-13} \times (T_{gas}/298)^{3.04} \times e^{(-920.1/Tgas)}$
$CH + CO + M \rightarrow C_2HO + M$	$4.15 \times 10^{-30} \times (T_{gas}/298)^{-1.90}$
$C_2H_6 + OH \rightarrow C_2H_5 + H_2O$	$1.06 \times 10^{-12} \times (T_{gas}/298)^{3.0} \times e^{(-435.0/Tgas)}$
$C_2H_5 + OH \rightarrow C_2H_4 + H_2O$	4.00×10^{-11}
$C_2H_3 + OH \rightarrow C_2H_2 + H_2O$	5.00×10^{-11}
$H + OH + M \rightarrow H_2O + M$	$4.33 \times 10^{-30} \times (T_{gas}/298)^{-2.0}$
$H + HO_2 \rightarrow H_2O + O$	$8.30 \times 10^{-11} \times e^{(-502.77/Tgas)}$
$H + HO_2 \rightarrow OH + OH$	$2.81 \times 10^{-10} \times e^{(-440.22/Tgas)}$
$H + HO_2 \rightarrow H_2 + O_2$	$4.15 \times 10^{-11} \times e^{(-248.81/Tgas)}$
$H + CH_3O \rightarrow CH_3 + OH$	9.93×10^{-12}
$O + OH \rightarrow H + O_2$	$4.55 \times 10^{-12} \times (T_{gas}/298)^{0.40} \times e^{(371.66/Tgas)}$
$O + HO_2 \rightarrow O_2 + OH$	$1.36 \times 10^{-11} \times (T_{gas}/298)^{0.75}$
$O + CH_3O \rightarrow CH_3 + O_2$	$3.55 \times 10^{-11} \times e^{(-239.25/Tgas)}$
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	$2.20 \times 10^{-13} \times e^{(600/Tgas)}$
$HO_2 + HO_2 + M \rightarrow H_2O_2 + O_2 + M$	$1.90 \times 10^{-33} \times e^{(980/Tgas)}$
$HO_2 + CH_3CH_2OO \rightarrow CH_3CH_2OOH + O_2$	$3.80 \times 10^{-13} \times e^{(899.69/Tgas)}$
$CH_3CH_2OO + CH_3CH_2OO \rightarrow CH_3CH_2O + CH_3CH_2O + O_2$	3.97×10^{-14}
$CH_2 + CH_3CO \rightarrow CH_2CO + CH_3$	3.00×10^{-11}
$H + CH_2OH \rightarrow CH_3 + OH$	1.60×10^{-10}
$OH + CH_3CH_2OOH \rightarrow H_2O + CH_3CH_2OO$	$3.00 \times 10^{-12} \times e^{(190/Tgas)}$
$C_2H_5 + O_2 \rightarrow CH_3CH_2OO$	5.00×10^{-12}
$O(1D) + CH_4 \rightarrow CH_3 + OH$	3.11×10^{-10}
$O(1D) + CO \rightarrow CO + O$	5.00×10^{-11}
$O_2(b1) + O_3 \rightarrow O_2 + O_2 + O$	2.20×10^{-11}
$O(1S) + O_2(a1) \rightarrow O(1D) + O_2(b1)$	2.90×10^{-11}
$O(1S) + O_2(a1) \rightarrow O + O + O$	3.20×10^{-11}
$O(1D) + H_2O \rightarrow OH + OH$	2.20×10^{-10}
$CO_2(E1) + M \rightarrow CO_2 + M$	1.00×10^{-11}
$CO_2(E2) + M \rightarrow CO_2 + M$	1.00×10^{-11}
$C_2H + H + M \rightarrow C_2H_2 + M$	1.23×10^{-29}
$CH_4 + C_2H \rightarrow C_2H_2 + CH_3$	$3.01 \times 10^{-12} \times e^{(-250.18/Tgas)}$
$C_2H_4 + C_2H \rightarrow C_2H_2 + C_2H_3$	1.40×10^{-10}

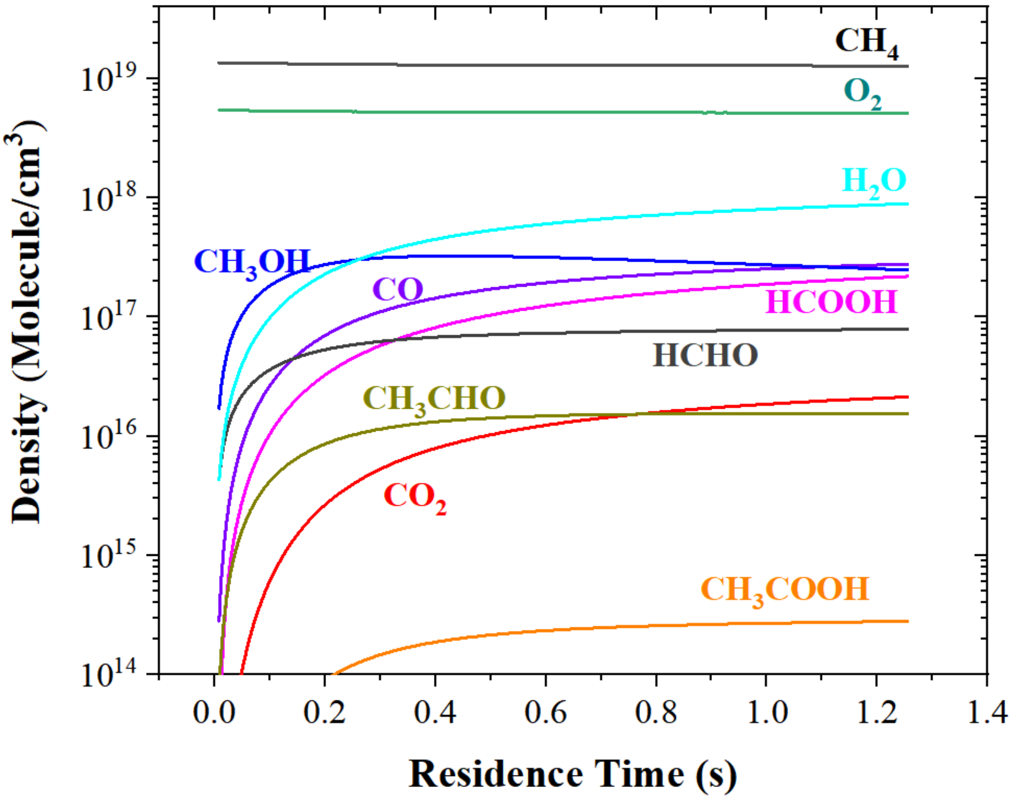


Figure S13. Species densities in the CH_4/O_2 plasma, obtained by the chemical kinetics modeling, as a function of residence time

6 Catalyst characterization

6.1 XRD

The structural properties of the Ni catalysts with varying metal loading (2, 6, 10, 15, 20, and 25 wt%) were investigated by X-ray diffraction (XRD), conducted using a SmartLab 9kW diffractometer with Cu Kα radiation (240 kV, 50 mA). The samples were scanned from 5° to 80° at a step of 0.01° with scanning speed of 10 °/min. As shown in Figure 4 A, peaks were observed at 2θ of 37.48°, 39.46°, 45.85°, 60.82°, and 67.07°, and identified as γ-Al_2O_3. [11] For a metal loading below 10 wt. %, there was no evident NiO peak, which indicates a high dispersion of NiO particles on γ-Al_2O_3. When the metal loading increased to more than 10 wt.%, a group of NiO (JCPDS 65-5745) diffraction peaks at 2θ of 37.3°, 43.3°, 62.9° and 75.4° gradually appeared, corresponding to the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes of NiO.

Table S6. Physical parameters of the supports and Ni catalysts

Catalysts	NiO loading by XRF	Particle size by XRD (nm)	BET surface area (m^2/g)	Average pore size (nm)	Pore volume (cm^3/g)
γ-Al_2O_3	/	/	216.5	9.2	0.500
2wt.% NiO/γ-Al_2O_3	2.7	/	197.8	9.9	0.490
6wt.% NiO/γ-Al_2O_3	7.3	/	185.4	10.1	0.469
10wt.% NiO/γ-Al_2O_3	12.0	/	170.8	10.4	0.443
10wt.% NiO/γ-Al_2O_3-Spent	/	/	161.2	10.4	0.417
15wt.% NiO/γ-Al_2O_3	18.5	10.3	146.2	10.7	0.391
20wt.% NiO/γ-Al_2O_3	23.2	13.0	143.9	10.3	0.370
25wt.% NiO/γ-Al_2O_3	27.7	22.1	125.2	10.1	0.331

6.2 N_2-physisorption and XRF

Nitrogen physisorption was conducted on a Micromeritics ASAP 2020 instrument at -196 ºC to obtain textural information. As shown in Table S6 and Figure S14, the surface area, average pore size and pore volume of the catalysts decreases with increasing Ni loading, possibly due to occupying of the porosity channels by NiO particles. For the spent catalysts, the BET surface area and pore volume both declined slightly. In addition, the practical loadings were a little higher than the theoretical values indicated by X-ray fluorescence (XRF).

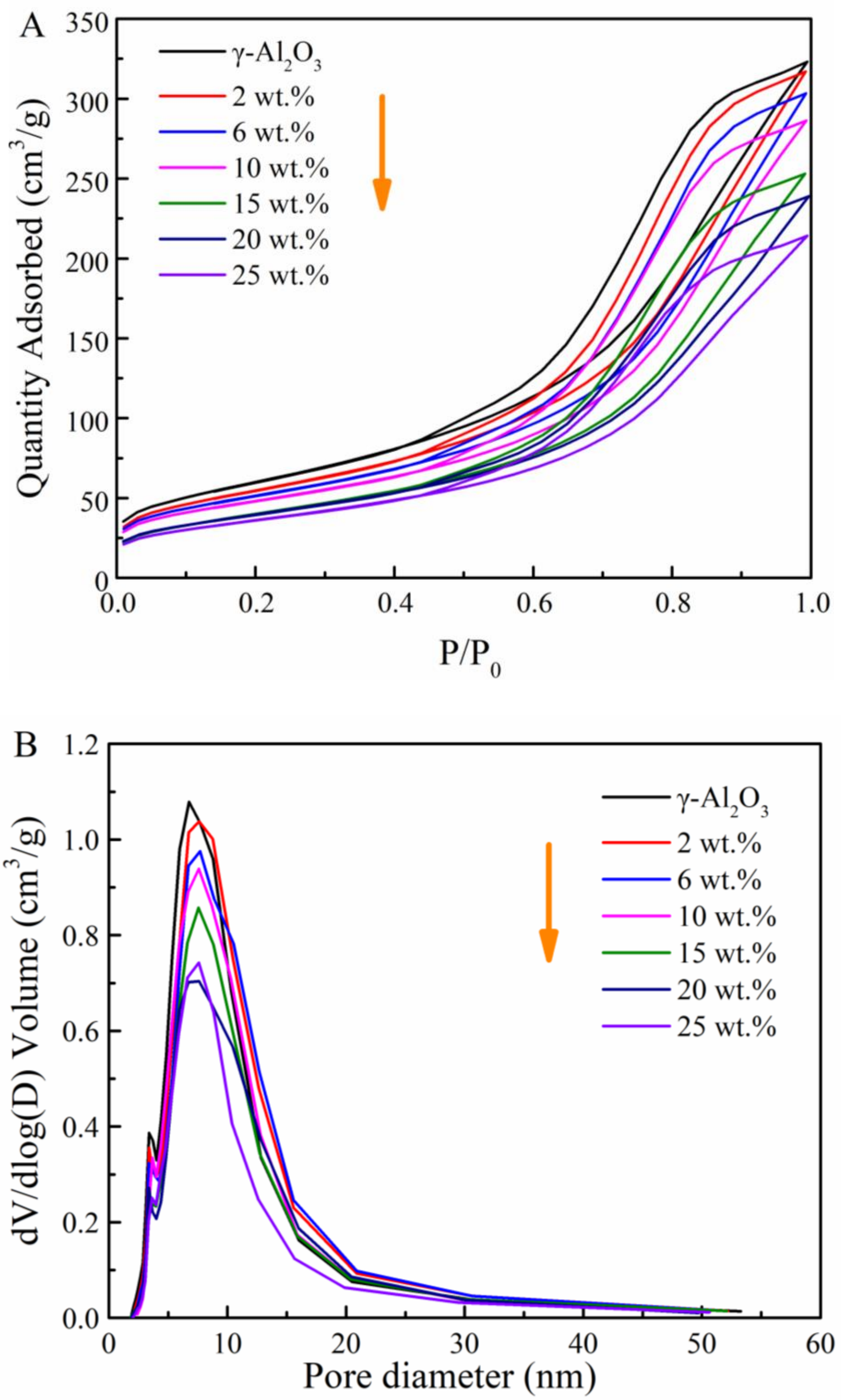


Figure S14. (A) N_2 adsorption-desorption isotherms and (B) Pore size distribution of γ-Al_2O_3 and NiO/γ-Al_2O_3 catalysts with varied Ni metal loading.

6.3 HAADF-STEM and HRTEM

High angle annular dark field scanning transmission electron microscopy (HAADF-STEM) was performed by Titan^{3TM} G2 60-300 with Cs-corrector configuration.

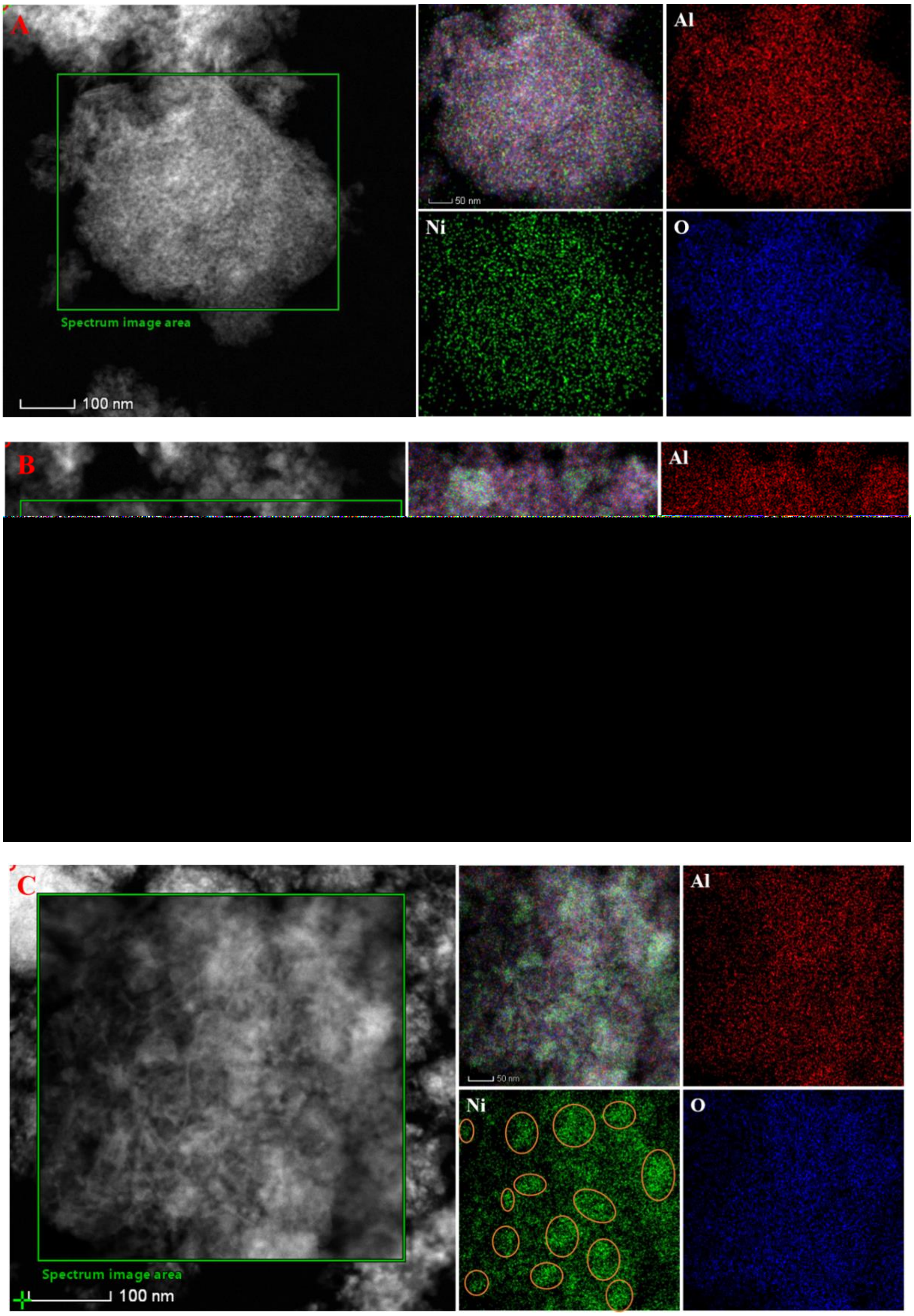


Figure S15. HAADF-STEM Mapping results. A: 6 wt.% NiO/γ-Al_2O_3; B: 15 wt.% NiO/γ-Al_2O_3; C: 20 wt.% NiO/γ-Al_2O_3.

High-resolution transmission electron microscopy (HRTEM) was conducted on Tecnai G2 F30 S-Twin with 300 kV accelerating voltage. The HRTEM images of the NiO/γ-Al_2O_3 catalysts with loading of 2, 6, 10, 15, 20, and 25 wt.% are shown in Figure S11.

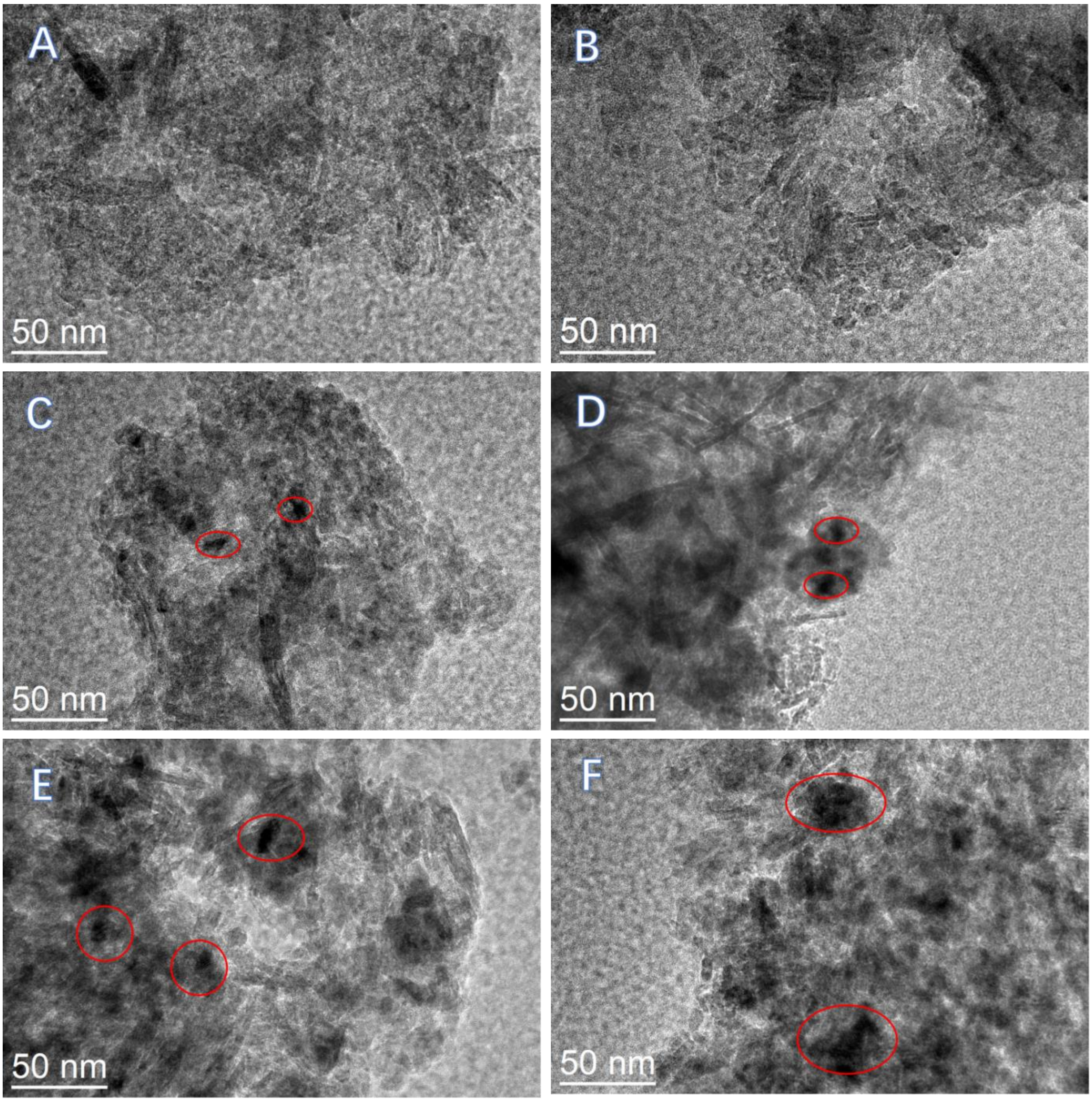


Figure S16. HRTEM images of NiO/γ-Al_2O_3 catalysts with varying loading (the images of A – F correspond to Ni loading of 2, 6, 10, 15, 20, 25 wt.%)

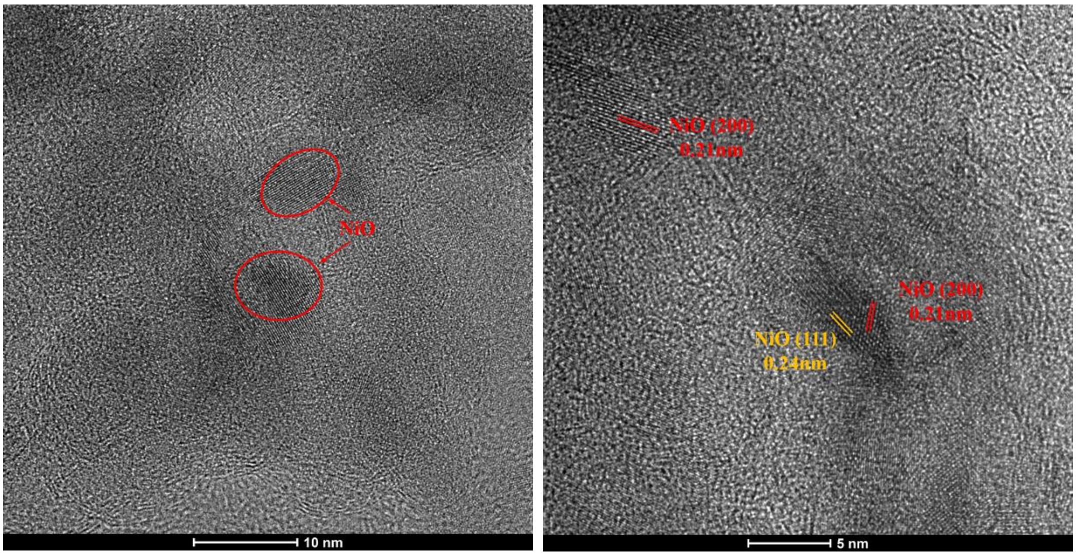


Figure S17. HRTEM results of the 10 wt.% NiO/γAl_2O_3 catalysts.

6.4 H_2-TPR

The TPR results, presented in Figure S12 and Table S7, provide quantitative information of nickel oxide species in the catalysts. Each hydrogen consumption peak can be deconvoluted by Gaussian-type functions.

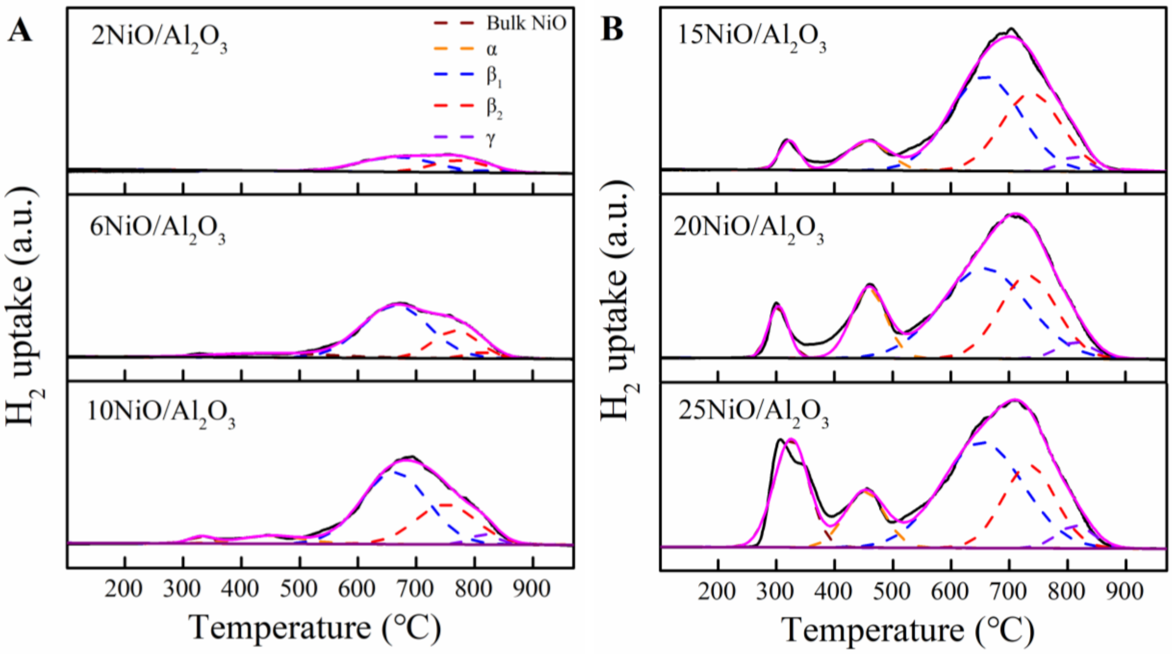


Figure S18. TPR quantitative analysis of the NiO/γ-Al_2O_3 catalysts with varied Ni metal loading

Table S7. TPR quantitative data of the $NiO/\gamma-Al_2O_3$ catalysts with varied Ni metal loading

Ni loading	Temperature (°C)					Area				
	Bulk NiO	α	β_1	β_2	γ	Bulk NiO	α	β_1	β_2	γ
2wt.%	/	/	667	773	817	/	/	2049	1182	158
6wt.%	/	452	664	767	815	/	931	6490	2317	368
10wt.%	330	452	662	750	816	307	939	8800	4421	512
15wt.%	322	456	658	738	812	1087	2239	12504	8649	767
20wt.%	303	458	657	732	813	1924	4436	14441	8767	1121
25wt.%	325	451	653	733	813	6897	4463	15321	8593	1533

6.5 XPS

X-ray photoelectron spectroscopy (XPS) was conducted by Thermo Fisher ESCALAB XI^+ with Al Kα X-ray source. The C 1s binding energy value (284.8 eV) was taken as a reference level. We present the XPS data in the Al (2p), O (1s) and Ni (2p) regions to provide information about the chemical environment of the nickel present on the catalyst surface.

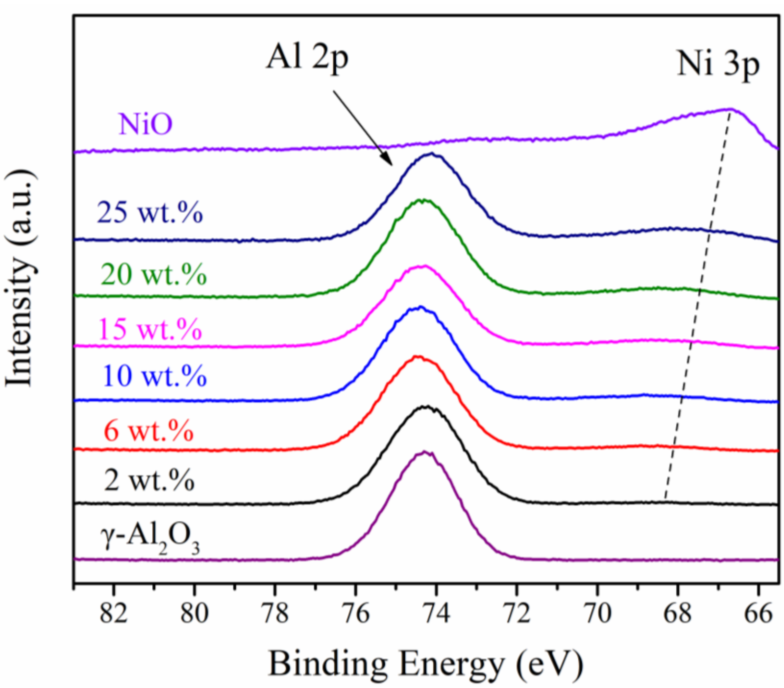


Figure S19. XPS profile of Al2p of the $NiO/\gamma-Al_2O_3$ catalysts with varying Ni loading

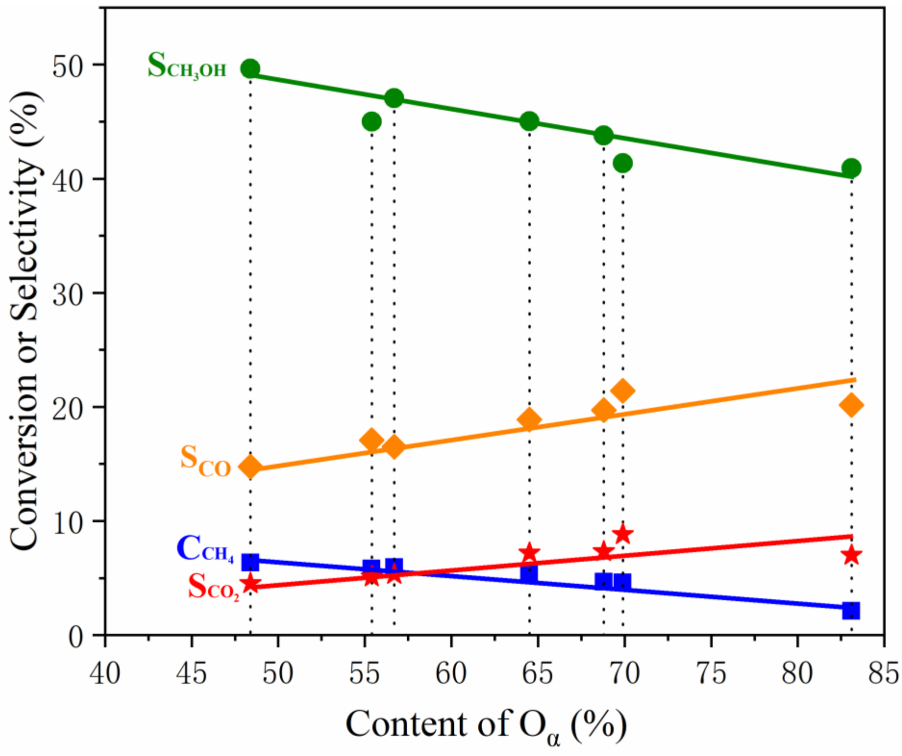


Figure S20. Linear relationship between content of lattice oxygen species (Oα) and reaction performance.

6.6 Compare of fresh and spent NiO/γ-Al_2O_3 catalyst

Thermogravimetry was conducted by Netzsch STA 449 F3 connected to a Balzers QMG 403D mass spectrometer. Before TG-MS analysis, 0.02 g sample was pretreated under 110 °C for 90 min, and the TG-MS experiment was carried out in a O_2/He mixture (20% O_2) with a flow rate of 50 mL/min and a heating rate of 10 °C /min. The carbon deposition test of fresh and spent NiO/γ-Al_2O_3 catalysts are shown in Figure S19, in which the continuous weight loss above 300 °C may be caused by the interaction of two OH groups on γ-Al_2O_3, leading to desorption of H_2O. As some OH groups are strongly bound to the surface, this dehydration process can continue to very high temperature.

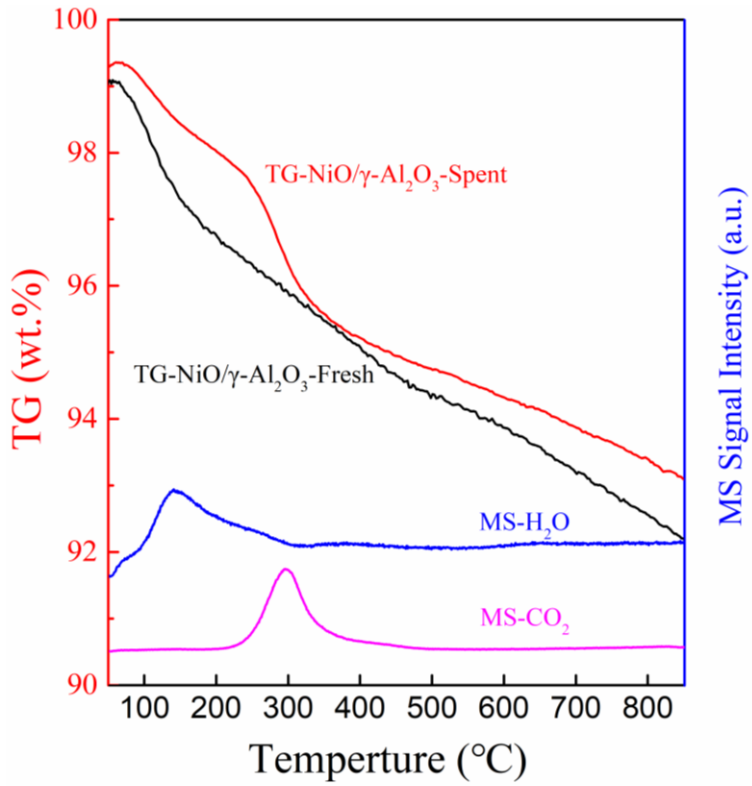


Figure S21. TG-MS of the fresh (black color) and spent (red color) NiO/γ-Al_2O_3 catalyst (fresh catalyst was used as a contrast)

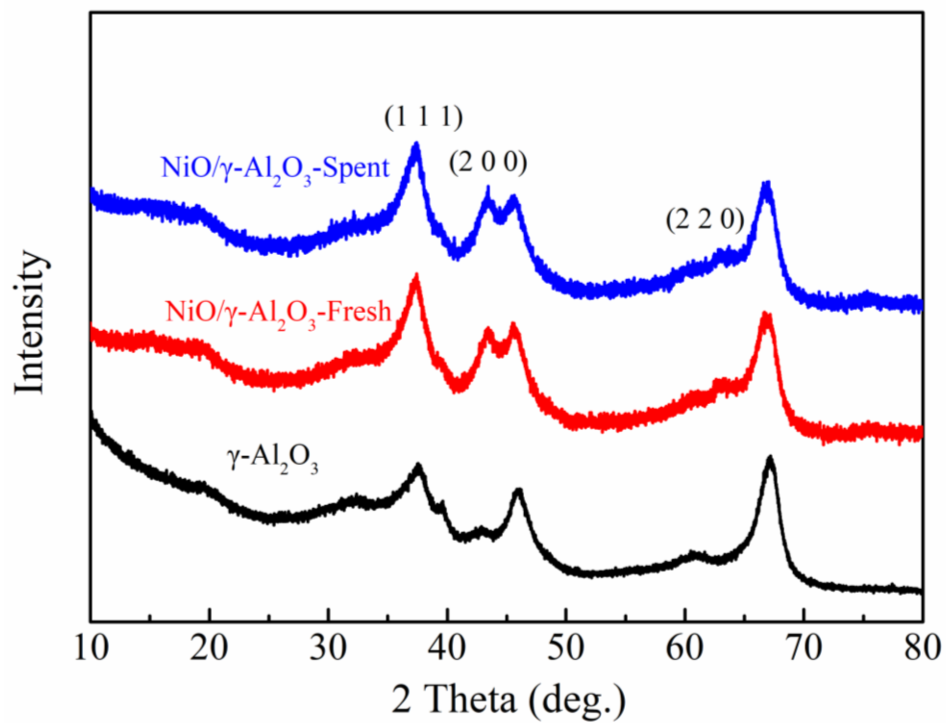


Figure S22. XRD spectra of the fresh and spent NiO/γ-Al_2O_3 catalyst

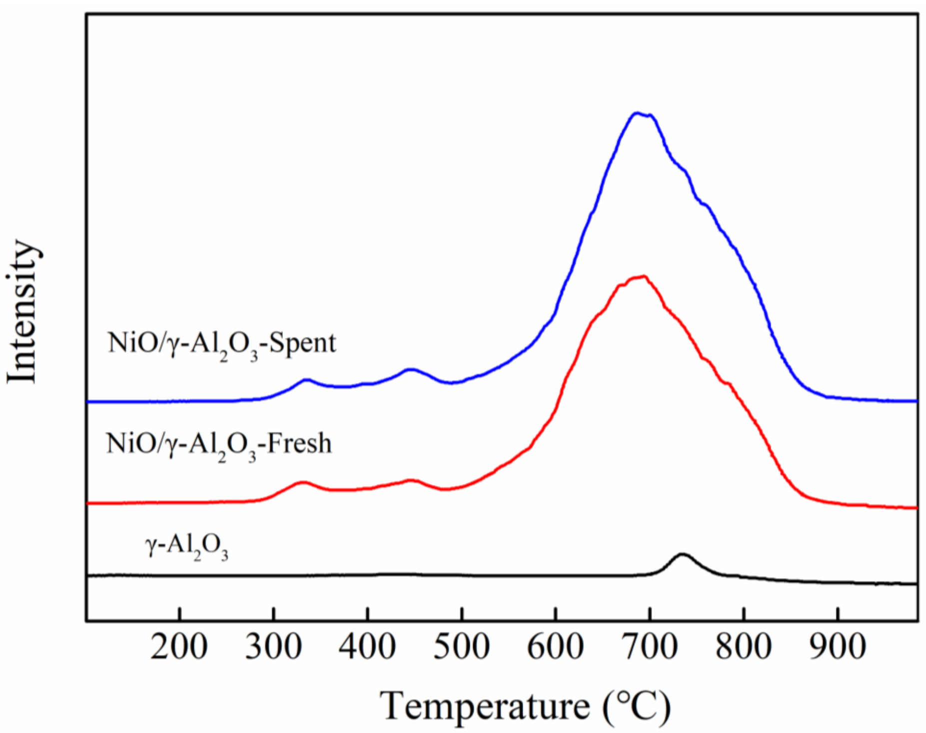


Figure S23. TPR profile of the fresh and spent NiO/γ-Al_2O_3 catalyst

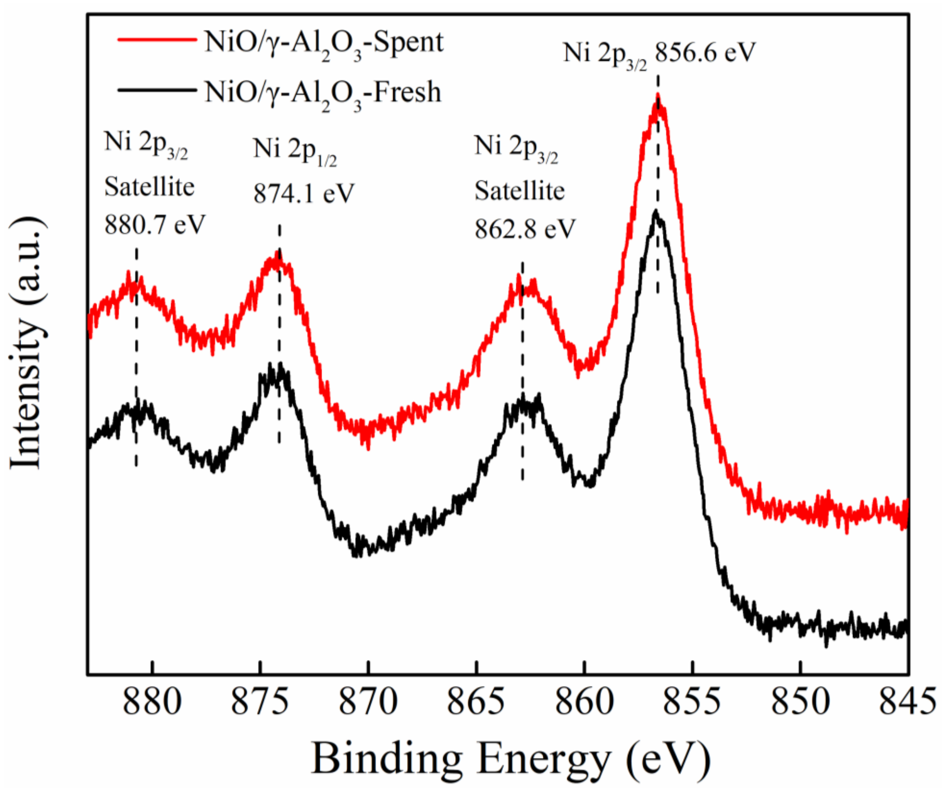


Figure S24. XPS profile of the fresh and spent NiO/γ-Al_2O_3 catalysts

7 Optical emission spectroscopy (OES) diagnostics of the CH_4/O_2 plasma

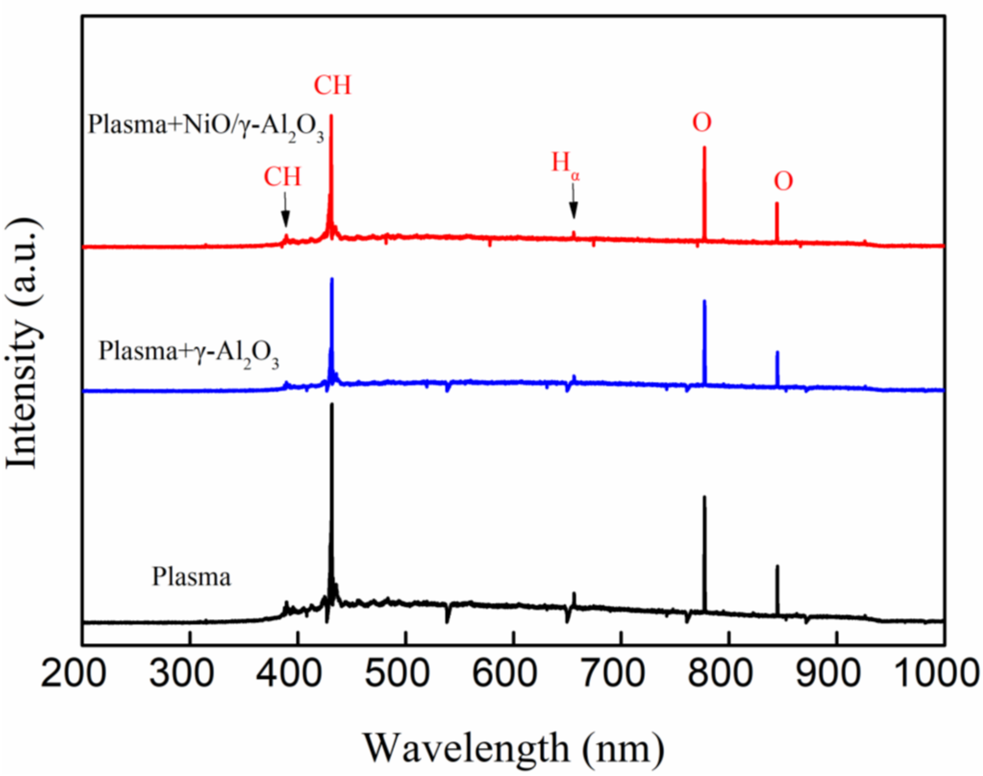


Figure S25. Optical emission spectra for plasma only, plasma+γ-Al_2O_3 and plasma+NiO/γ-Al_2O_3

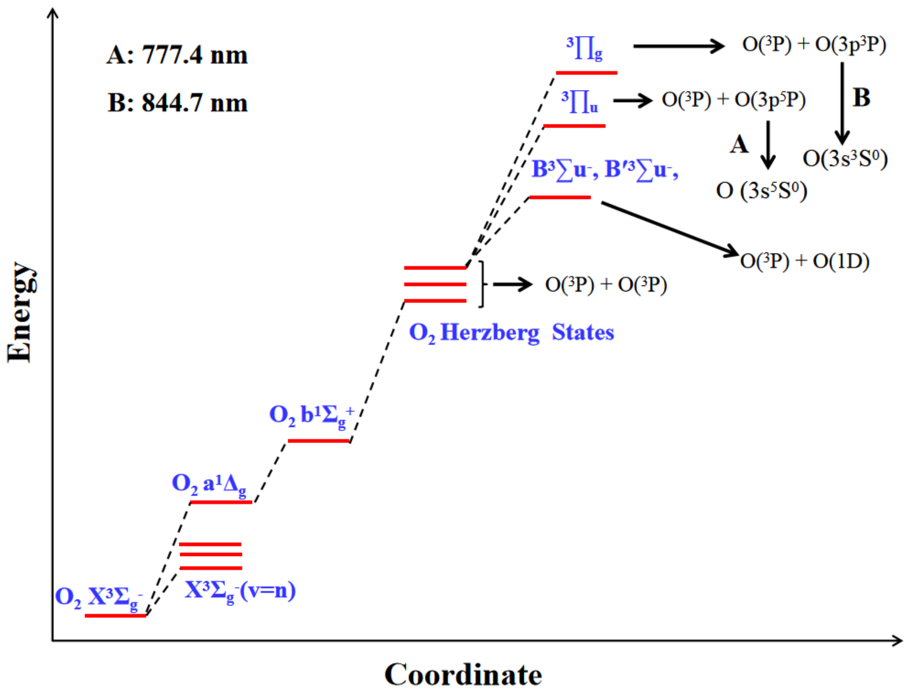


Figure S26. Activation paths of O_2 through inelastic collision with energetic electrons in DBD plasma, based on literature [12-21]

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