

Supplementary information

Title: Synergistic effects of plasma-catalyst interactions for CH₄ activation

Author(s): Jongsik Kim,^a David B. Go,^{a,b} and Jason C. Hicks*^a

^a Department of Chemical and Biomolecular Engineering, University of Notre Dame, 182, Fitzpatrick Hall, Notre Dame, Indiana, 46556, United States

^b Department of Aerospace and Mechanical Engineering, University of Notre Dame, 372, Fitzpatrick Hall, Notre Dame, Indiana, 46556, United States

Table of Contents

Table S1 **S2**

Fig. S1-S3 **S3-S5**

Table S1 Kinetic parameters obtained during plasma-assisted catalysis after correction and thermal catalysis.

| plasma-assisted catalysis (| | | | $-r_{CH4,f,corr} = \frac{k_{plasma-cat} \times P_{CH4}}{(1 + K_{CH4, plasma-cat} \times P_{CH4})^2}$ | $\ln(k_{plasma-cat})$ VS. 1/power _{DBD} | | R ² |
|-----------------------------|---|---|--|--|--|--------------------|----------------|
| temperature (K) | total flow rate (mL min ⁻¹) | DBD power (power _{DBD} , W) | k _{plasma-cat} (s ⁻¹ kPa ⁻¹) | K _{CH4, plasma-cat} (kPa ⁻¹) | slope | y-intercept | |
| 790 | 120 | 1 | 1.35 (± 0.05) | 0.019 | | | |
| | | 3 | 2.48 (± 0.10) | 0.022 | -0.85 | 1.15 | |
| | | 5 | 2.31 (± 0.05) | 0.018 | (± 0.19) | (± 0.10) | 0.91 |
| | | 7 | 3.11 (± 0.14) | 0.026 | | | |
| 790 | 130 | 1 | 0.64 (± 0.02) | 0.004 | | | |
| | | 3 | 0.89 ($\leq \pm 0.01$) | 0.011 | -0.72 | 0.26 | |
| | | 5 | 1.26 (± 0.01) | 0.015 | (± 0.18) | (± 0.10) | 0.89 |
| | | 7 | 1.72 ($\leq \pm 0.01$) | 0.007 | | | |
| 790 | 140 | 1 | 0.45 (± 0.02) | 0.037 | | | |
| | | 3 | 0.82 (± 0.01) | 0.058 | -0.83 | 0.05 | |
| | | 5 | 0.94 ($\leq \pm 0.01$) | 0.017 | (± 0.09) | (± 0.05) | 0.98 |
| | | 7 | 0.87 (± 0.01) | 0.012 | | | |
| 790 ^b | 120 ^b | 1 ^b | 1.51 (± 0.02) | 0.024 | | | |
| | | 2 ^b | 2.10 (± 0.08) | 0.035 | -0.70 | 1.12 | |
| | | 3 ^b | 2.71 (± 0.09) | 0.033 | (± 0.17) | (± 0.10) | 0.89 |
| | | 4 ^b | 2.36 (± 0.11) | 0.037 | | | |
| 810 | 120 | 1 | 0.95 (± 0.02) | 0.017 | | | |
| | | 3 | 1.59 (± 0.03) | 0.018 | -0.82 | 0.75 | |
| | | 5 | 1.73 (± 0.01) | 0.013 | (± 0.07) | (± 0.04) | 0.99 |
| | | 7 | 1.99 (± 0.01) | 0.008 | | | |
| 840 | 120 | 1 | 0.66 (± 0.04) | 0.001 | | | |
| | | 3 | 1.39 (± 0.13) | 0.011 | -1.54 | 1.07 | |
| | | 5 | 1.98 (± 0.11) | 0.018 | (± 0.37) | (± 0.20) | 0.90 |
| | | 7 | 3.03 (± 0.12) | 0.028 | | | |
| 850 | 120 | 5 | 2.00 (± 0.01) | 0.005 | - | - | - |
| 865 | 120 | 1 | 1.26 (± 0.03) | 0.017 | | | |
| | | 3 | 1.61 (± 0.01) | 0.007 | -0.49 | 0.71 | |
| | | 5 | 1.73 (± 0.02) | 0.010 | (± 0.15) | (± 0.08) | 0.84 |
| | | 7 | 2.11 (± 0.03) | 0.009 | | | |
| 880 | 120 | 3 | 1.41 (± 0.01) | 0.006 | - | - | - |
| | | 5 | 2.73 (± 0.03) | 0.006 | | | |
| 890 | 120 | 1 | 0.98 (± 0.03) | 0.013 | | | |
| | | 3 | 2.24 (± 0.04) | 0.018 | -1.33 | 1.31 | |
| | | 5 | 3.15 (± 0.16) | 0.028 | (± 0.14) | (± 0.07) | 0.98 |
| | | 7 | 2.88 (± 0.08) | 0.024 | | | |
| 890 | 140 | 1 | 0.38 ($\leq \pm 0.01$) | 0.019 | | | |
| | | 3 | 0.69 (± 0.01) | 0.023 | -1.43 | 0.40 | |
| | | 5 | 1.06 (± 0.01) | 0.016 | (± 0.43) | (± 0.23) | 0.85 |
| | | 7 | 1.60 ($\leq \pm 0.01$) | 0.015 | | | |
| thermal catalysis (| | | | $-r_{OBS} = k_{therm-cat} \times P_{CH4}$ | $\ln(k_{therm-cat})$ VS. 1/T | | |
| temperature (K) | total flow rate (mL min ⁻¹) | k _{therm-cat} (s ⁻¹ kPa ⁻¹) | | | slope | y-intercept | R ² |
| 790 | 120 | 0.84 (± 0.04) | | | | | |
| 840 | 120 | 1.94 (± 0.07) | | -8.9 (± 1.5) | | 11.1 (± 1.7) | 0.97 |
| 890 | 120 | 2.92 (± 0.07) | | | | | |

[a] 1Ni of 5 mg; SiO₂ diluent of 100 mg; P_{CH4} of ≤ 25.3 kPa and P_{CO₂} of 25.3 kPa (balanced by He); 1 atm. [b] 1Ni of 5 mg; BaTiO₃ diluent of 100 mg; P_{CH4} of ≤ 25.3 kPa and P_{CO₂} of 25.3 kPa (balanced by He); 1 atm.

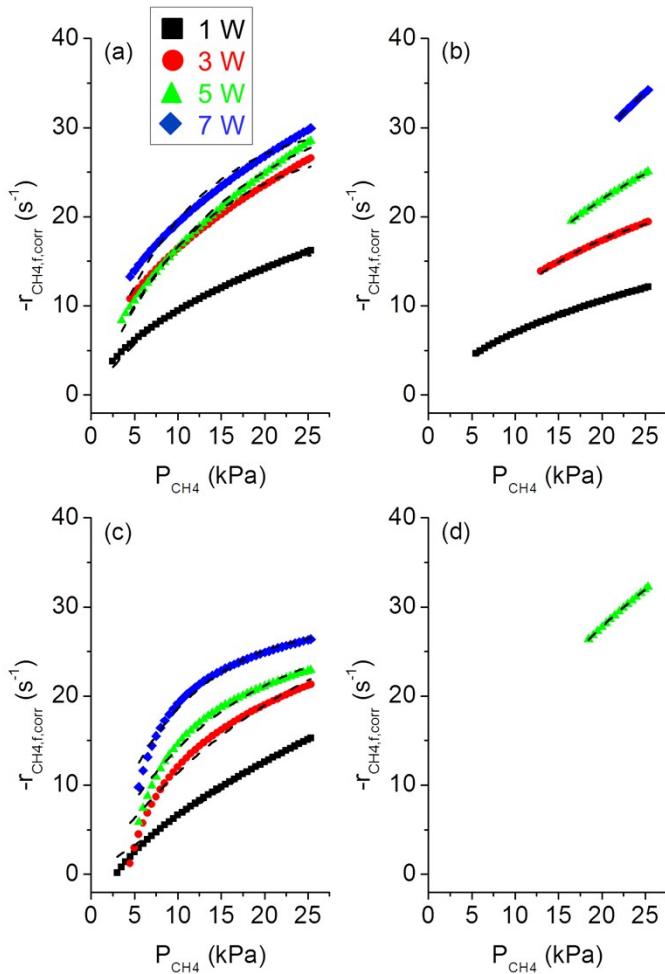


Fig. S1 Change in corrected forward CH_4 consumption rate ($-r_{\text{CH}_4,\text{f},\text{corr}}$) in a response to a change in partial pressure of CH_4 (P_{CH_4}) at constant partial pressure of CO_2 of 25.3 kPa (balanced by He) for plasma-assisted catalysis at different DBD plasma powers with a total flow rate of 120 mL min⁻¹: (a) at 790 K, (b) at 810 K, (c) at 840 K, and (d) at 850 K. All curve fits using Eqn. 21 show regression factors of ≥ 0.96 (dashed lines). Kinetic parameters are shown in Table S1.

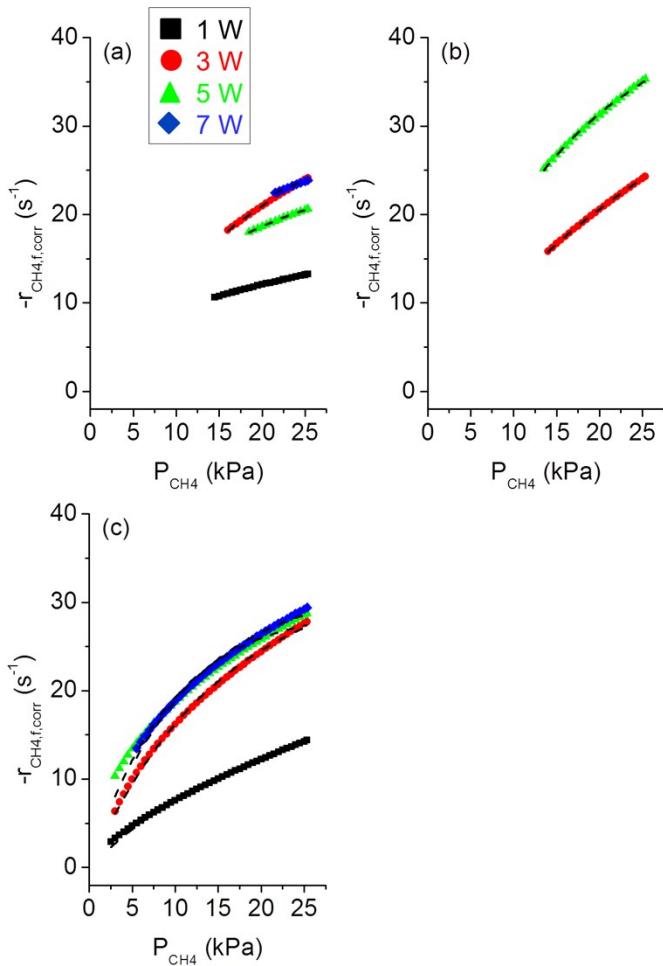


Fig. S2 Change in corrected forward CH₄ consumption rate ($-r_{\text{CH}_4,\text{f},\text{corr}}$) in a response to a change in partial pressure of CH₄ (P_{CH_4}) at constant partial pressure of CO₂ (P_{CO_2}) of 25.3 kPa (balanced by He) for plasma-assisted catalysis at different DBD plasma powers with a total flow rate of 120 mL min⁻¹: (a) at 865 K, (b) at 880 K, and (c) at 890 K. All curve fits using Eqn. 21 show regression factors of ≥ 0.97 (dashed lines). Kinetic parameters are shown in Table S1.

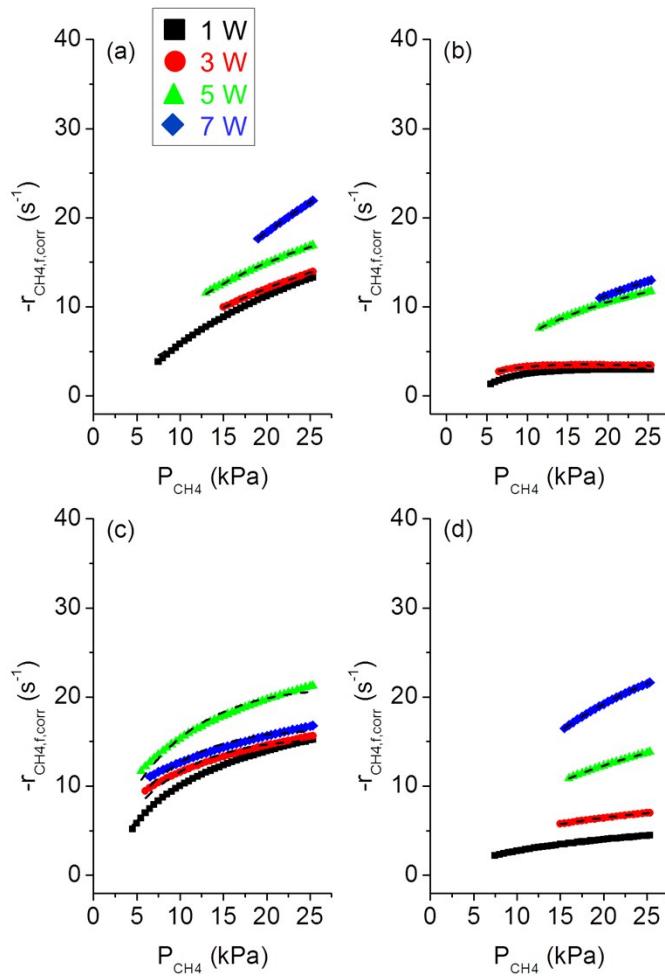


Fig. S3 Change in corrected forward CH₄ consumption rate ($-r_{\text{CH}_4,\text{f},\text{corr}}$) in a response to a change in partial pressure of CH₄ (P_{CH_4}) at constant partial pressure of CO₂ (P_{CO_2}) of 25.3 kPa (balanced by He) for plasma-assisted catalysis at different DBD plasma powers: (a) at 790 K and 130 mL min⁻¹, (b) at 790 K and 140 mL min⁻¹, (c) at 790 K and 120 mL min⁻¹ with the use of BaTiO₃ diluent, and (d) at 890 K and 140 mL min⁻¹. All curve fits using Eqn. 21 show regression factors of ≥ 0.94 (dashed lines). Kinetic parameters are shown in Table S1.