How Plasma Sheaths Govern Activity, Selectivity, and Energy Efficiency in Plasma Catalysis

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Highlights

- Plasma sheath dynamics govern activity, selectivity, and energy efficiency in NTP catalysis
- Pulsed excitation creates thinner, stronger-field sheaths that enhance ion flux and hydrogenation
- Sheath engineering links plasma physics with catalyst design for efficient plasma catalysis

1. Introduction

Nonthermal plasma assisted-heterogeneous catalysis (plasma catalysis) has emerged as a transformative technology for distributed energy storage and sustainable production of fuels and chemicals utilizing renewable resources (e.g., solar and wind energy), carbon dioxide (CO_2), green hydrogen and etc. [1] In such hybrid systems, plasma-catalyst interactions are governed by incident fluxes of neutral/excited species, ions, electrons, and photons, together with local electric fields, ultimately dictating adsorption and surface reactions, and plasma sheath is the key interfacial structure that mediates plasma-solid surface interactions. Although the critical role of sheath in plasma catalysis has been recognized by previous studies [2], relevant studies on the interrelation between plasma bulk parameters, sheath dynamic, and plasma catalytic performance remain unexplored. In this work, we investigate the generic role of plasma sheath dynamics in plasma catalysis using three representative reactions of CO_2 methanation, ammonia (NH_3) synthesis, and methanol (CH_3OH) via CO_2 hydrogenation. Sheath thickness under sinusoidal (SIN) and pulsed (PUL) excitation was quantified using optical emission spectroscopy (OES) and correlated with surface mechanistic events and reactor-scale catalytic performance.

2. Methods

For the plasma catalysis experiments, SIN excitation was provided using a sinusoidal power supply (CTP-2000K, Nanjing Suman Plasma Technology Co., Ltd., China), while PUL excitation was driven by a pulsed power supply (MPP04-A10A-100, Kurita Co., Ltd., Japan). The applied voltage and current were monitored in real-time using a high-voltage probe (P6015A, Tektronix, USA) and current transformer (Model 4418, Pearson Electronics, USA), with data recorded on an oscilloscope (TBS1102C, Tektronix, USA). The discharge power was calculated from the typical Q-U Lissajous method based on the measurement with a capacitor of 22 nF. Plasma emission spectra were captured using an optical emission spectrometer (Maya2000Pro, Ocean Optics, USA) with an exposure time of 100 ms and a spectral resolution of approximately 1 nm. The experimental plasma parameters were derived from OES measurements and subsequent calculations based on emission from Balmer Hydrogen Lines, Argon Lines, and Nitrogen Lines.

3. Results and discussion

Catalytic performance was evaluated as a function of excitation mode (sinusoidal, SIN, versus pulsed, PUL) and applied voltage, with representative results shown in **Figure 1**. For NH_3 synthesis, PUL excitation at 6.7 kV achieved 3.4 g NH_3 kWh^{-1} for PUL at 6.7 kV (NH_3 yield = 4.2 %), compared with 0.6 g NH_3 kWh^{-1} under SIN excitation at 9.4 kV (~5.9× improvement).

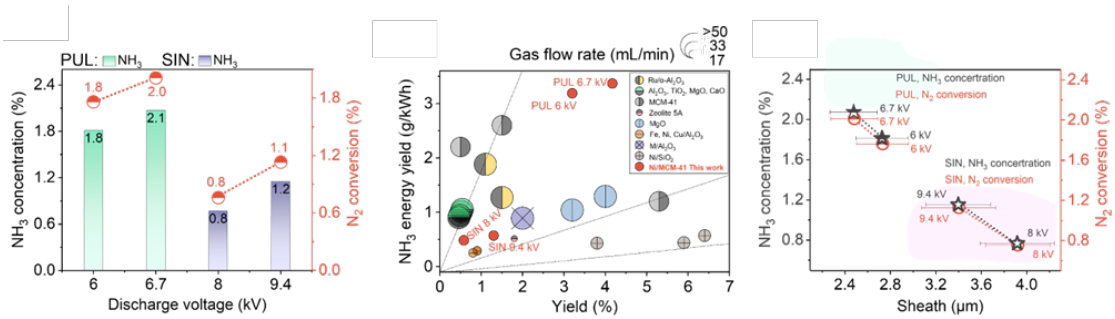

Figure 1. Effect of excitation mode and applied voltage on plasma catalytic NH_3 synthesis.

To elucidate the role of sheath-mediated transport, time-resolved particle-tracking simulations coupled with Monte Carlo processes were employed to capture the dynamics of charged and neutral species at the plasma-catalyst interface (**Figure 2**). The simulations reveal a sharp divergence between neutral and ionic dynamics. Neutral species exhibit low probability of adsorption on catalyst surface, and their motion is independence on excitation mode, e.g., CO_2 adsorption ratios (fraction of particles adsorbing on the surface) are 0.96% (SIN) and 0.90% (PUL), consistent with thermal diffusion control. By contrast, ionic flux responds strongly to sheath thickness and field strength. Surface adsorption ratio of H^+ increases markedly from 26.2% under SIN excitation to 92.1% under PUL excitation.

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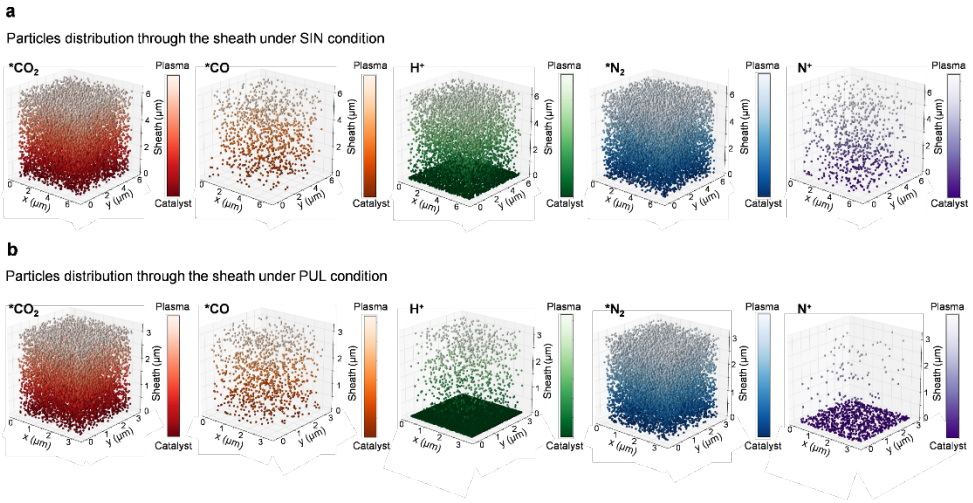

Figure 2. Simulated spatial distributions of key reactive species across the plasma sheath under **(a)** SIN and **(b)** PUL excitation conditions.

4. Conclusions

This study establishes plasma sheath dynamics as a general, mechanistically grounded descriptor for plasma catalysis, linking electron-scale field behavior to macroscopic activity and selectivity. By identifying sheath thickness and electric field as tunable levers, our findings provide a framework for rational control of plasma-catalyst coupling, guiding the development of next-generation plasma reactors capable of higher efficiency, selective product formation, and reduced energy consumption. the conclusions here.

References

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Keywords
Plasma catalysis, sheath, excitation, mechanism