Role of sheath layer in nonthermal plasma catalysis

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Abstract: Plasma sheath plays a crucial role in mediating interactions between the plasma and the catalyst surface. Here, we systematically study the generic influence of sheath thickness on nonthermal plasma catalysis, showing that thinner sheaths significantly enhance gas conversion rates and target product selectivity with improved energy efficiency, exemplified by CO_2 methanation and supported by in situ characterization data.

1. Introduction

Non-thermal plasma (NTP) catalysis, powered by renewables, can be a promising electrified sustainable technology for energy storage and chemical/fuel production, yet fundamental understanding of the systems is limited due to their very complex natures [1]. In NTP catalysis, the sheath layer plays a crucial role in mediating interactions between the plasma and the catalyst surface. This thin, nonneutral region near the catalyst surface, similar to the boundary layers in thermal heterogeneous catalysis, significantly impacts electron, ion, and radical dynamics, which in turn affect reaction mechanisms and rates [2], yet this aspect was not carefully investigated till now. Here, we quantify the sheath thickness in different NTP catalytic systems (e.g., CO_2 hydrogenation) and investigate its generic influence on the hybrid systems.

2. Methods

A dielectric barrier discharge (DBD) system was used for the investigation, and alternating current (AC) sinusoidal and radio-frequency (RF) pulsed power sources were used to change the sheath thickness. In-situ diffuse reflectance infrared Fourier transform spectroscopy-mass spectrometry (DRIFTS-MS) was employed to investigate surface-adsorbed species during NTP catalysis reactions, employing a Thermo Scientific Nicolet iS50 FTIR spectrometer, a Hidden QGA mass spectrometer and a specially designed flow cell.

3. Results and Discussion

Our findings demonstrate that RF-induced thinner sheaths were beneficial to NTP catalysis, as exemplified in CO_2 methanation, where CO_2 conversion reached 70.36% and CH_4 selectivity 97.16% at 5.55 W discharge power (Fig. 1). *In-situ* DRIFTS-MS revealed that thinner sheaths activate additional reaction pathways, broadening reaction networks and increasing pathway throughput. Complementary Monte Carlo particle-tracking simulations and density functional theory (DFT) calculations highlighted the role of sheath-induced electric fields in enhancing reactive species flux, as demonstrated by the increased surface adsorption ratio of H from 25.79% under AC conditions to 94.09% under RF conditions, while also modulating adsorption energies of intermediates and facilitating dual reaction pathways on catalyst surfaces.

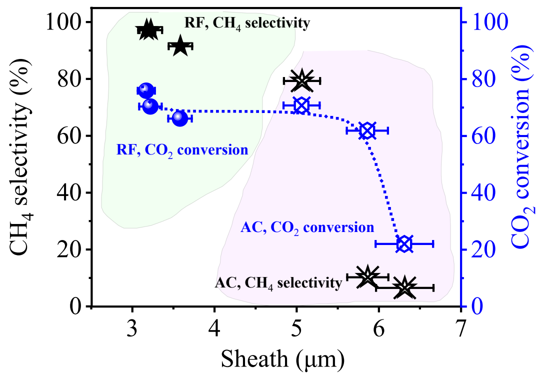

Fig. 1. Impact of sheath thickness of AC and RF conditions on CO_2 conversion and CH_4 selectivity.

4. Conclusion

Findings of the work establish the correlation between the plasma sheath thickness and NTP catalytic performance, being one of the fundamental reasons explain the measured better performance by the RF-driven DBD systems. The reduced sheath thickness could improve the flux of plasma-induced species through it arriving at the catalyst surface to encourage multiple conversion pathways. These findings advance our mechanistic understanding of NTP catalysis and pave the way for the rationale design and optimization of the hybrid systems with the much-enhanced energy efficiency.

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References

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