

On the role of sheath layer in nonthermal plasma catalysis

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Nonthermal plasma (NTP) is the unique means for process intensification of catalytic chemical conversions at the molecular level, being the promising electrified technology for producing chemicals/fuels sustainably using renewable energy. The hybrid NTP catalytic systems are very complex, and hence fundamental understanding of them is necessary [1]. For a conventional thermal catalytic system with solid catalyst and gaseous reactants, the boundary layers around solid catalyst particles play a key role in determining the catalytic performance, and this aspect was commonly overlooked by current studies in plasma catalysis. Also, plasma sheath exists in a system of gas discharge around solid phases (**Figure 1**) [2], and the relationship between boundary layers and plasma sheath in plasma catalytic systems is not yet investigated, neither its effects on the performance of plasma catalytic reactions.

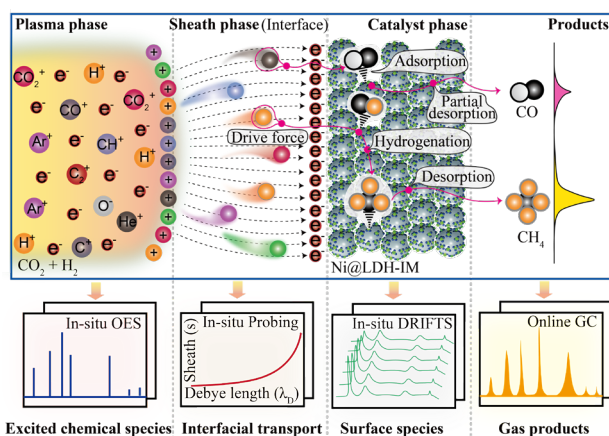


Figure 1. Conceptual illustration of sheath in plasma catalysis and relevant diagnostic methodologies.

In this study, we found that varying relevant process parameters (such as excitation modes, alternating current, AC, and radio frequency, RF) could change sheath thickness of heterogeneous plasma catalytic systems of CO₂ methanation, methanol synthesis (via CO₂ hydrogenation) and ammonia synthesis, and the reduced sheath thickness significantly enhances gas conversion rates and target product selectivity with improved energy efficiency. As shown in Figure 2, by changing applied voltage under either AC or RF excitation mode, CO₂ conversion and CH₄ selectivity change rather significantly. Based on the OES data, we calculated the sheath thickness of different systems, which is correlated with the activity data, showing a generally decreased sheath thickness leading to the improved catalytic efficiency.

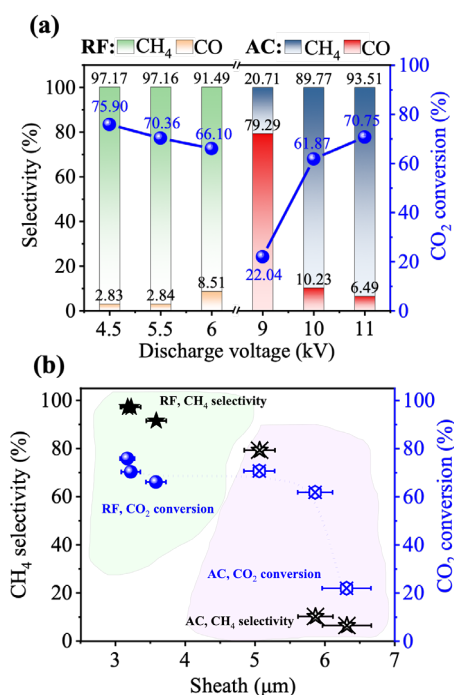


Figure 2. (a) effect of applied voltage under excitation of AC and RF on CO₂ conversion and CH₄ selectivity in CO₂ methanation; (b) effect of sheath thickness of AC and RF conditions on CO₂ conversion and CH₄ selectivity.

Comparative DRIFTS characterization of the systems suggests that thin sheath layer under RF excitation enhances the flux of active species, particularly hydrogen, to the catalyst surface, facilitating surface hydrogenation reactions. Our findings 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. 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.

References

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- [2] E.C. Neyts et al., *Chem. Rev.*, 115 (2015): 13408-13446.