Kinetic and thermodynamic insights into plasma-based gas conversion

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Abstract: Plasma-based gas conversion has enabled a wide range of innovations, like ozone production and VOC decomposition. Unlocking its full potential in chemical processing—particularly for carbon and nitrogen valorization—requires a deeper insight into kinetics and thermodynamics. Such understanding is crucial to optimize efficiency, enhance selectivity, and facilitate scalability, ensuring the advancement of this transformative technology.

1. Introduction

Plasma-based gas conversion typically falls into two broad categories. (i) Transformation of gas mixtures into value-added chemicals, such as C_2 and C_3 from CH_4, CH_3OH from CO_2, and NH_3 from N_2 and H_2, for direct use in the chemical industry. (ii) Decomposition of gases into smaller molecules or atoms, such as CO_2 into CO and O_2, and CH_4 into C(s) and H_2, which typically requires further processing (e.g. Fischer-Tropsch and methanol synthesis).

The first category primarily involves plasma-catalysis, combining plasma reactors with catalysts at elevated gas temperatures (400–800 K). In contrast, the second category is mostly driven by non-equilibrium "warm" discharges, operating at 1000–5000 K and dominated by thermal reactions rather than electron-induced reactions.

These observations raise two fundamental questions. (i) How do elevated temperatures affect reaction kinetics in plasma processes? (ii) If thermal effects appear dominant, does plasma still offer unique thermodynamic benefits, or is it simply an efficient heat source? Resolving these questions is essential for improving our understanding and optimizing plasma-based gas conversion applications.

2. Results and Discussion

2.1 Temperature-Dependent Kinetics

Temperature-dependent studies [1–3] reveal that reaction pathways and conversion in plasma-based gas processing are strongly influenced by the gas temperature (Fig. 1). In plasma-catalytic systems, for instance, elevated temperatures not only accelerate reaction rates but also influence reaction selectivity, shifting the balance among competing pathways.

While electron-induced reactions often dominate at low temperatures, thermal reactions play a more prominent role as the temperature increases. In some scenarios, thermal chemistry reinforces electron-driven pathways, while in others, it competes with them. Hence, developing temperature-dependent plasma-chemical reaction models is essential to accurately understand conversion rates and selectivities across different temperature regimes. These mechanistic insights help identify the optimal operating window for plasma-based gas conversion processes, maximizing the synergy between thermal and electron-driven effects for improved performance.

2.2 Non-Equilibrium Thermodynamics

Recently, an effective (average) energy input related to the entropy change under non-equilibrium conditions—at (constant) temperature—was proposed as a key parameter controlling plasma reactions [4]. At high gas temperatures, certain plasma processes that seem governed by thermal chemistry, still deviate from classical expectations. This is manifested as enhanced conversions and energy efficiencies relative to thermal equilibrium benchmarks.

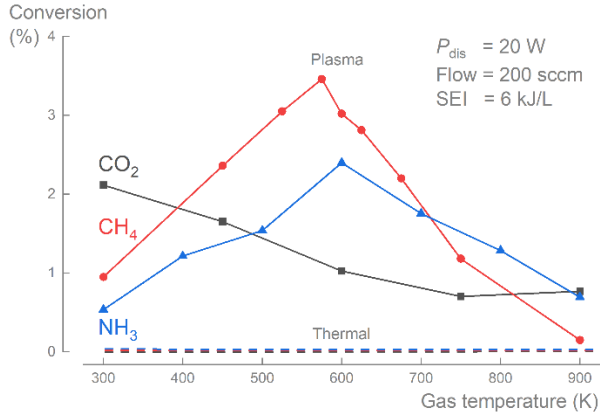

Fig. 1. CO_2, CH_4, and NH_3 conversion for thermal (dashed lines) and plasma (solid lines) conditions in a temperature-controlled DBD. Data taken from [1–3].

Such behavior suggests additional non-equilibrium contributions. The contribution of entropy (at a constant temperature), that is $T_e\Delta S_{m,e}$ and $T_{gas}\Delta S_{m,T}$, as the fundamental parameter in plasma gas conversion thus becomes integral to characterize the system.

3. Conclusions

In summary, plasma-based gas conversion is governed by an intricate balance of temperature-sensitive kinetics and non-equilibrium thermodynamics. Even under conditions where thermal chemistry appears dominant, plasma can modulate reaction pathways in ways that remain inaccessible under strict thermal equilibrium. A more fundamental understanding would open up the route to further enhancements in plasma-based gas conversion.

References

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