

Fast pulsed non-thermal plasmas for catalyst-free and catalytic CH₄ activation

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The CH₄ pyrolysis needs very high temperature due to the strong C-H bands of 435 kJ/mol. Non-oxidative CH₄ conversion to value-added chemicals generally requires specific catalytic condition, whereas electricity-driven technology is supposed to be highly promising to realize these processes with basic ambient.^{1,2} In this paper, CH₄ activation by high-energy electron collision, fast gas heating process, or energy pooling of Ar metastable particles were verified and regulated in fast pulsed non-thermal plasmas (dielectric barrier discharge (DBD), spark discharge, CH₄/Ar discharge, respectively).³⁻⁵

In DBD plasma, abundant of CH₃ radicals formed by electron-induced reaction ($e + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H} + e$) could couple to C₂H₆ at low temperature (even near room temperature, shown as Fig. 1), while would also enhance the free radical chain reaction ($\text{CH}_3 + \text{CH}_4 \rightarrow \text{C}_2\text{H}_6 + \text{H}$) in plasma-catalytic CH₄ activation at high temperature (1253 K). The effects of pulse parameters (polarity, frequency, rising/falling time and width) on CH₄ conversion and C₂H₆ yield were understood and optimized by combined utilizations of experiment, diagnosis and simulation.

In spark discharge plasma, CH₄ gas molecules could be heated to ~2000 K within dozens of nanoseconds, bringing out very high CH₄ conversion, C₂H₂/H₂ yield and energy utilization efficiency, and then C₂H₂ will be adequately hydrogenated to C₂H₄ when adding 0.5% Pd/CeO₂ catalyst after plasma area. Within single pulse, vibrational temperature drops dramatically from over 6000 K to 2000 K (shown as Fig. 2), which indicates that the vibrational-rotational energy relaxation may play an important role in the electrical-thermal energy transfer process.

In CH₄/Ar discharge plasma, except for the direct electron impact dissociation during the pulse-on period, both the charge transfer between Ar⁺ and CH₄ and the quenching of Ar metastable species by CH₄ contribute to a further increase of CH₄ dissociation degree during the pulse-off period (i.e. the Ar⁺ and Ar metastable species can function as an energy pooling for the formation of H and hydrocarbon radicals). Specially, the evolution of the absolute density of the hydrogen atom at the ground state, as a real-time and *in-situ* indicator of the CH₄ dissociation degree, is measured using the two-photon absorption laser induced fluorescence (TALIF) method (shown as Fig. 3). The innovative approaches proposed in this work may contribute to the catalyst-free and catalytic CH₄ activation by non-thermal plasmas.

This work was supported by the National Science Fund for Distinguished Young Scholars (Grant No. 51925703), the National Natural Science Foundation of China (Grant Nos. 51637010, 51807190 and 51707186).

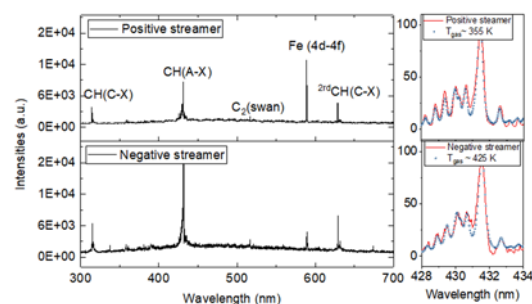


Fig. 1. Typical OES and simulation of gas temperatures in the two form microsecond pulsed CH₄ DBD plasmas.³

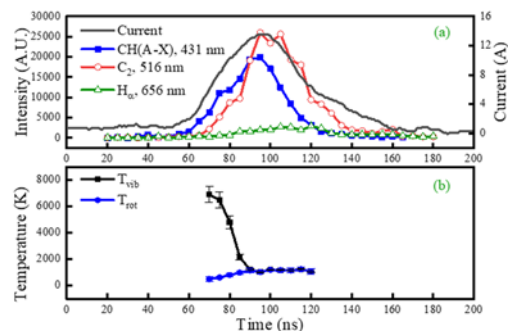


Fig. 2. Time evolution of (a): current and typical OES and (b): vibrational and rotational temperatures in the pulsed spark discharge plasma.⁴

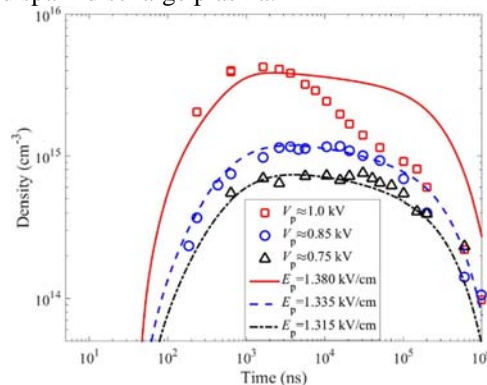


Fig. 3. Dots: the measured temporal evolution of the H atom density using the TALIF. Curves: the calculated temporal evolution of the H atom density using the reaction kinetic model.⁵

References

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