A new double dielectric barrier discharge (DDBD) reactor to prevent carbon deposition in plasma-assisted non-oxidative methane coupling

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Significance and Relevance

An alternative plasma double dielectric barrier discharge (DDBD) reactor utilizing water as the ground electrode is proposed to prevent coke formation in the anaerobic methane upgrading. This approach achieves nearly 100% selectivity for alkanes using a micrometric gap (0.5 mm) while ensuring long-term stability, offering an effective solution for electrified and clean methane upgrading.

Preferred and 2nd choice for the topic:

- *Preferred:* **Advanced process with electrocatalysis and plasma utilization**
- *2nd choice:* **Catalysis to electrify the chemical production**

Preferred presentation: **Oral preferred or Short Oral / Poster**

Introduction and Motivations

The non-oxidative conversion of methane (NOCM) is a dream reaction to directly convert methane into higher hydrocarbons to avoid the formation of oxygenate intermediates or undesired CO_2. Nevertheless, the controlled and selective activation of the C-H bond(s) represents a major challenge, to prevent the total dehydrogenation to coke, leading to catalyst deactivation[1]. While only a few materials have shown promising results with the traditional thermo-catalytic approach[2], operating conditions remain harsh. The rise of greener catalytic approaches such as plasma technologies offers an alternative path for activating the methane C-H bond under mild conditions while entering the frame of the chemical industry electrification[3]. Cold plasmas provide a rich environment of reactive species able to activate small molecules[4]. However, controlled activation remains challenging, and coke formation is inevitable in traditional configurations. Here, we propose a novel reactor, using two dielectric barriers (in quartz) and circulating water as the ground electrode, effectively preventing carbon deposition with very high selectivity towards alkanes. The effects of power, water temperature, and gap size have been investigated, analyzing energy efficiency, product and hydrocarbon selectivity, and carbon balances.

Results and Discussion

The proposed reactor has first been compared to a traditional DBD reactor made of alumina, and, while the effective plasma power to conversion is almost equal, differences are observed in the gaseous products, as well as in solid deposits. The tubular reactor, using water as the ground electrode, effectively helped to prevent the formation of black carbon by reducing the intensity of the micro-discharges, however, a yellowish film was formed. The effects of varying the water temperature did not significantly alter the performances; however, this parameter could play a fundamental role in preventing the condensation of heavier hydrocarbons, potentially resulting in the development of a polymeric film through a gelling mechanism. The influence of gap modification, through adjustments to the diameter of the internal electrode, was also studied. When the gap was narrowed to the micrometric range (0.5 mm), the plasma chemistry was completely modified resulting in a selectivity near 100% towards alkanes. Furthermore, after a brief plasma modification (wetting) of the quartz reactor wall, the carbon balance was almost equal to 100% and no carbon deposits were observable after the reaction. Moreover, the direct visualization of plasma has allowed an interpretation of its dynamic character. In conclusion, we have demonstrated an alternative plasma technology as an

effective method for non-oxidative methane conversion to hydrocarbons, preventing coke formation, while offering a very high control of product selectivity.

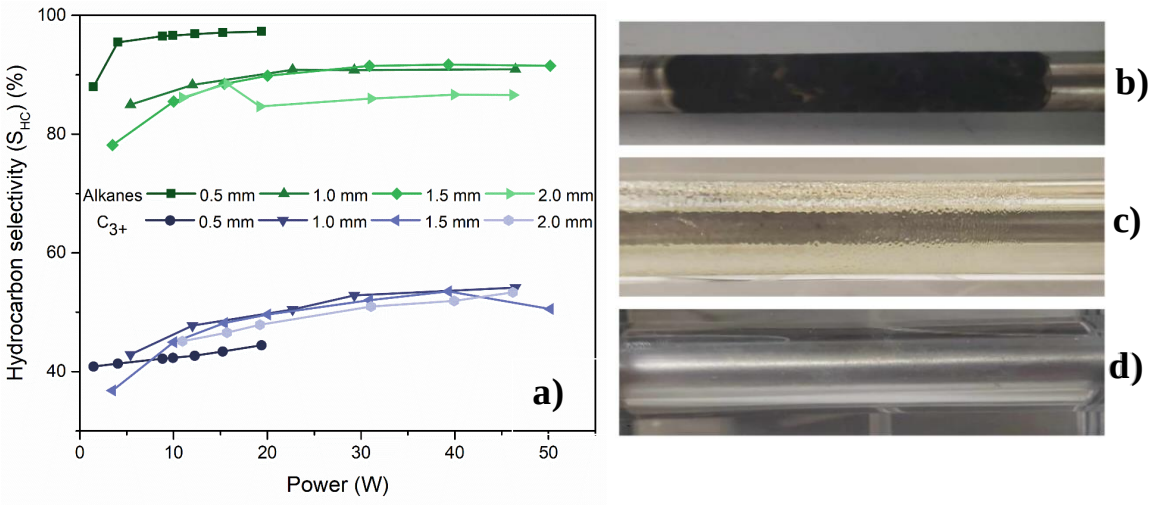

Figure 1. (a) Effect of gap size on hydrocarbon selectivity to alkanes and C_{3+} hydrocarbons with the water-electrode reactor. Reaction conditions: frequency 35kHz, water temperature 50°C, feed flow 50 mL min^{-1} (50% CH_4, bal. Ar), plasma length 10 cm. Optical pictures after reaction of **(b)** inner electrode of traditional DBD reactor with a gap of 1.5 mm **(c)** water electrode reactor with a gap of 1.5mm, and **(d)** water electrode reactor with a 0.5 mm gap.

References

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