From CO_2 dissociation to dry reforming of methane in microwave discharges: Importance of the chemical kinetics in the afterglow

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Abstract: In this contribution we present an investigation of methane addition to CO_2 microwave discharges. Experimental results include the effluent gas composition, core plasma temperature and optical emissions. Addition of only 1% CH_4 is found to diminish the CO_2 conversion and decrease the energy efficiency significantly, while barely changing discharge characteristics. A quasi-1D chemical kinetic model is implemented for the afterglow, which shows that the overall chemistry is nearly completely controlled by hydrogen radical reactions in the cooling trajectory.

1. Introduction

The dry reforming of methane (DRM) has promising uses in the context of methane valorisation, carbon capture and utilisation, and biogas reforming. Methane is reacted with CO_2 to directly produce synthesis gas, a useful feedstock for the chemical industry. Especially warm plasmas (i.e. microwave, gliding arc and atmospheric pressure glow discharge) have shown promising results in terms of energy efficiency and conversion [1-3], showing great improvement in comparison to direct CO_2 dissociation. Additionally, previous experimental work has shown complete oxygen removal from the effluent with only 5% CH_4 addition (oxygen separation is a major challenge for CO_2 dissociation) [1]. This work investigates the effects of methane addition to CO_2 discharges, by coupling experimental results with simple chemical kinetic modelling.

2. Methods

The addition of 0-30% methane to a CO_2 vortex-stabilised 2.45 GHz microwave discharge is studied. Three pressure are tested (150, 400 and 900 mbar). The power and total flow are kept constant at 1000 W and 9.4 SLM.

The effluent composition is measured using gas chromatography. The plasma core gas temperature is determined from the Doppler broadening of the atomic oxygen emission triplet at 777 nm. The same emission line is used to determine the plasma size.

A quasi-1D chemical kinetic model is implemented for the afterglow. The model is initialized by taking the chemical equilibrium at a given temperature, and a constant cooling rate is assumed.

3. Results and Discussion

Figure 1 shows the conversion of CH_4 and CO_2 as a function of CH_4 addition. CO_2 conversions of 45% are reached, with a related energy efficiency of 70%.

Starting at pure CO_2, the CO_2 conversion diminishes with only 1% CH4 addition, while it is found that the discharge characteristics (i.e. gas temperature and optical emissions) show nearly no changes.

Additionally, the CO_2 conversion appears insensitive to pressure variations, while the gas temperature in the core, and plasma size have a strong pressure dependence.

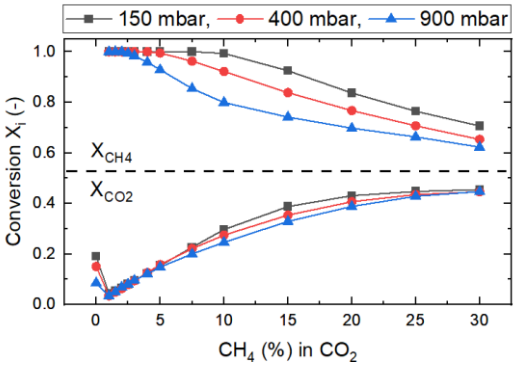

Fig. 1. Conversion of CO_2 and CH_4 as a function of CH_4 addition to CO_2 plasmas.

The afterglow model shows that hydrogen-containing radicals catalyse the recombination of CO and O_2 for small CH_4 additions. Additionally, they are found to drive the water gas shift (WGS) reaction in the afterglow for higher methane additions (10-30%).

The afterglow model can accurately reproduce the experimentally obtained selectivity. A sensitivity analysis on the selectivity shows no influence of the initial temperature, and minimal influence of the cooling rate and pressure.

4. Conclusion

It is shown that the overall chemistry of discharges with 1% to 30% methane is nearly completely controlled by the chemical kinetics of the afterglow. These chemical kinetics are driven by hydrogen-containing radicals. They are found to both catalyse the recombination of CO and O_2, as well as drive the WGS equilibrium reaction.

Acknowledgement

This work is partially funded by NXTGEN HT under the Energy domain, project 03: Plasma conversion of methane

References

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