Nonthermal Plasma Decomposition of Methane in an RF Flow Reactor

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Abstract: An RF flow reactor is used for direct decomposition of methene , The reactor operates at 13.56 MHz and achieves 99% decomposition rate at 5% CH_4 in Ar or Kr with C_2H_2 as the main gas product and carbon black. The addition of He or Ne to CH_4 does not achieve similar results. Plasma parameters, plasma stability, and the concentration of Ar_m^*. metastable excited states are measured to understand the mechanisms of these effects.

1. Introduction

Direct decomposition of methane using plasma is attractive because with the use of green electrical power, it doesn't result in generation of CO_2 and has the potential to produce value added products such as carbon black or carbon nanotubes. But plasma pyrolysis does not differ significantly from thermal pyrolysis and does not capture the non-equilibrium properties of nonthermal plasma. Modeling and simulations have proposed that metastable excited states of argon, for example, can play a role in more efficient decomposition and better product selectivity[1]. Here we use an RF flow reactor with a variety of mixtures of CH4 with He, Ne, Ar, and Kr to test these hypotheses.

2. Methods

The experimental setup is essentially the same as described in [2]. It is flow through reactor that consists of a quartz tube with two copper electrodes wrapped over the tube 35 mm apart and a total gas flow of 50 sccm. The reactor was operated at 2.4 torr and input power of 30 W – 200 W at 13.56 MHz. Optical emission spectroscopy was used to estimate rotational and vibrational excitation temperature using C_2 swan band at 516 nm. Ar line emission was used to estimate trends in the concentrations of metastable excited states of Ar, $1s^3$ and $1s^5$ using a Branching method. Fourier Transform Infrared Spectroscopy was used to monitor the gas composition including the detection of C_xH_y products. Solid products were tested for pure CH_4 and compared with those produced in mixtures of He, Ar, and Kr with 5% CH_4 at 150 W. Fast imaging was used to examine the stability of the discharge for these conditions (Figure 1).

3. Results and Discussion

FTIR absorption spectroscopy of Ar/CH_4 showed that percent decomposition CH_4 decreases from ~99% at 5% CH_4 in Ar to ~30% for 100% CH_4 at the same input power of 100 W. The main gas product is C_2H_2 as may be expected thermodynamically but C_2H_4 and C_2H_6 are also present at methane >15% of the total flow rate. Solid products also change with percent methane in Ar. At 5% CH_4, the solid product is graphitized carbon or carbon black while at higher concentrations, the solid product is mostly amorphous. Hence, the presence of Ar appears to play an important role in the decomposition of CH_4 which, we hypothesize is due to the presence of excited argon metastable states, Ar_m^*. The concentrations of Ar_m^* estimated by the Branching method decrease with the increase in CH_4 concentration from 1% to 5% supporting the hypothesis. Other inert gases were also tested and the results are summarized in Table 1. Notably, Kr, with metastable levels of higher energy than Ar produces similar decomposition products. Ar and Kr with 5% CH_4 also have higher gas rotational excitation temperatures.

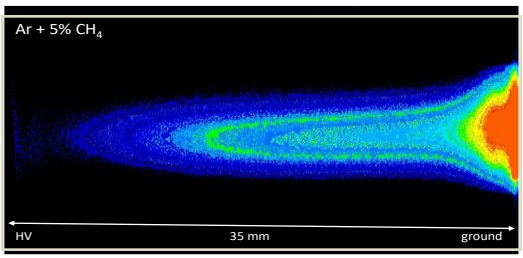

Fig. 1. Fast frame imaging at 3000 fps of the discharge in Ar/CH4 mixture at 100 W.

Table. 1. Results summary for all gas mixtures tested.

Gas	Instabilities 95% + 5% CH4	Trot, K	Product: solid/gas
CH4	no	~900 K	amorphous
He	no	600 K	Amorphous
Ne	no	900 K	amorphous
Ar	Yes	1500 K	Carbon black, C_2H_2
Kr	Yes	2000 K	Carbon black, C_2H_2

4. Conclusion

RF flow reactor achieves a high rate of decomposition of CH4 for low concentrations of CH4 in Ar and Kr. We are currently conducting laser induced fluorescence measurements in Ar and Ar/CH4 mixtures to potentially resolve the role of Ar and Ar_m^*

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References

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