Species and Pathways in a He/NO Plasma

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Abstract: We quantify the stable and radical species present in a radiofrequency (RF) atmospheric pressure He/NO plasma based on molecular beam mass spectrometry (MBMS) measurements. Our findings show that NO is mainly reduced to form N_2 and O_2 but may also be oxidized to form small amounts of NO_2, depending on the initial NO density. NO_2 formation is expected to occur via reactions involving short-lived species such as O.

1. Introduction

Fossil-fuel-powered vehicles contain catalytic aftertreatment systems for remediation of NO_x pollutants, however, selective catalytic reduction of NO_x is kinetically limited below 473 K [1]. Such limitations lead to the "cold-start" problem, where temperatures are not high enough for effective NO_x reduction during vehicle start-up. We plan to employ low-temperature plasma in series with a catalyst to allow NO_x reduction to proceed at non-equilibrium conditions.

As a precursor to studying NO_x reduction via plasma catalysis, we have focused on identifying and quantifying the species produced in the plasma phase. Here, we report how varying the initial concentration of NO impacts the species formed in a He/NO plasma.

2. Methods

An RF atmospheric pressure plasma jet is used to generate the He/NO plasma. MBMS measurements are taken at the outlet of the plasma jet. Species densities are quantified for NO, NO_2, N_2, O_2, and O with reference to calibration [2]. N, N_2O, and O_3 were detected as well but were not present in measurable quantities. NO concentration is varied from 20-200 ppm.

3. Results and Discussion

Figure 1 shows that as initial NO density increases, NO consumption and N_2 and O_2 production increase. This trend is expected because higher NO densities are expected to increase the rate of reactions that decompose NO. Figure 1 shows a discrepancy between the amount of N_2 and O_2 produced, which would be approximately equal if N_2 and O_2 were the only products formed. For each of the conditions shown, O was quantified; and for the 50, 100, and 200 ppm NO cases, NO_2 was quantified. The formation of O and NO_2 can account for the difference between N_2 and O_2 densities. The increase in NO_2 density with increasing initial NO density implies that increasing initial NO concentration increases the rate of NO_2 formation pathways until detectable levels of NO_2 are formed. Two potential pathways leveraging non-charged reactive species for NO_2 formation are as follows [3]:

$$O + NO + He \rightarrow NO_2 + He \quad k_1 = 1\times10^{-43}\,(300/T_g)^{1.6}\ m^6s^{-1}$$
$$NO + O_3 \rightarrow NO_2 + O_2 \quad k_2 = 1\times10^{-}18\,\exp(-1370/T_g)\ m^6s^{-1}$$

The gas residence time in the plasma and afterglow is 1.2 ms, therefore, stables species like O_3 are unlikely to contribute to NO_2 formation due to the lower reactivity of such species. Rather, short-lived species like O are expected to contribute to NO_2 formation. Future work will include varying gas flow rates in the reactor to determine the range of timescales over which NO_2 formation occurs. These timescales will be compared with timescales of NO_2 formation reactions from the literature, including reactions with charged species, to determine reaction pathways.

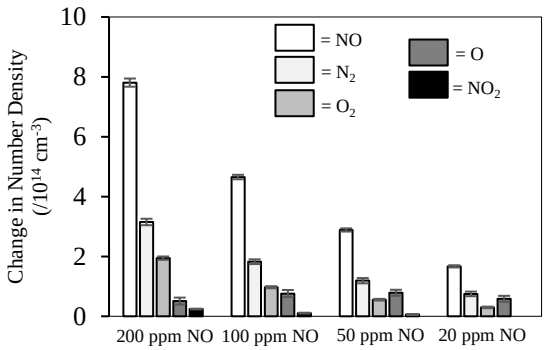

Fig. 1. Change in number density of NO, N_2, O_2, O, and NO_2 for varying initial NO densities in an He/NO plasma. 13.56 MHz, 2.34 slm, 2 mm ID, 6.2 W, 50 Hz 50% duty cycle, 5 mm plasma region, measured 10 mm in the afterglow.

4. Conclusion

The stable and radical species formed and consumed in a He/NO plasma were quantified, and potential NO_2 formation pathways were presented. N_2 and O_2 were the main products formed, while NO_2 was generated in small amounts for conditions with a higher initial NO density. NO_2 formation is expected to occur via reactions involving short-lived species like O with lifetimes on the same scale as the gas residence time in the reactor.

Acknowledgement
This work is supported by the National Science Foundation under award number CBET 2234270.

References

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