The chemistry of plasma-assisted dry reforming of methane

N. Hansen[1], E. C. Litzer[1], L. Sheps[1], H. Chen[2], B. Yang[2]

[1]*Combustion Research Facility, Sandia National Laboratories, Livermore, CA, USA*
[2]*Center for Combustion Energy, Tsinghua University, Beijing, China*

Abstract: We report molecular-beam mass spectrometry measurements of the plasma-assisted dry reforming of methane. We conducted $^{13}CO_2$ experiments in a tubular configuration of an atmospheric pressure dielectric barrier discharge (DBD) to follow the chemistry of the CO_2 in detail. We combined our experimental work with the development of a kinetic model and provide new kinetic insights into the formation of organic acids.

1. Introduction

Dry reforming of methane is a chemical process that converts two greenhouse gases, methane (CH_4) and carbon dioxide (CO_2), into a syngas mixture of carbon monoxide (CO) and hydrogen (H_2). Because low-temperature plasmas can initiate chemical conversion through the generation of charged species, radicals, and excited-state species, plasma-assisted reforming is considered a promising alternative to the conventional thermal catalytic reforming.

In this work, we studied the chemistry of plasma-assisted dry-reforming of methane in a dielectric barrier discharge (DBD) plasma flow reactor activated by a nanosecond repetitively pulsed discharge.

2. Methods

We have studied the plasma-assisted dry reforming of methane using a tubular configuration of an atmospheric pressure dielectric barrier discharge (DBD) followed by molecular-beam mass spectrometry. We measured the species pool formed in CH_4/CO_2 plasmas, including positive ions, radicals, and molecules. To trace the individual contributions of CH_4 and CO_2 to the observed products, we conducted experiments using isotopically labeled $^{13}CO_2$. The experiments were conducted over a range of different plasma powers (~0.5-15 W) and residence times (0.5-4 s).

A chemical kinetic model (135 species, 1239 reactions) was constructed to provide insight on the key reaction steps that drive the plasma reformation of methane.

3. Results and Discussion

Figure 1 shows how isotope labeling experiments can be used to extract mechanistic insights into complex reaction networks. For example, the $^{13}CO_2$ experiments allows for the distinction of CO from CH_4 oxidation *vs.* CO_2 decomposition.

Furthermore, we can show that the formation of C_{2+} hydrocarbons (ethane, propane, …) is (not surprisingly) dominated by CH_4 chemistry. The oxidation products of methane include CH_2O, CH_3O, CH_4O, and CO_2. C_2H_4O is also exclusively formed through oxidation of hydrocarbons that are traceable back to CH_4.

The mass spectra also provide clear experimental evidence for ^{13}CO- or $^{13}CO_2$-driven formation of double-oxygenated species. Based on the modeling results, the reaction CO+OH leads to the formation of HOCO, a main intermediated species contributes to the formation of acids. The ion chemistry initiated by the protonation of CO_2 also plays a role in formic acid formation.

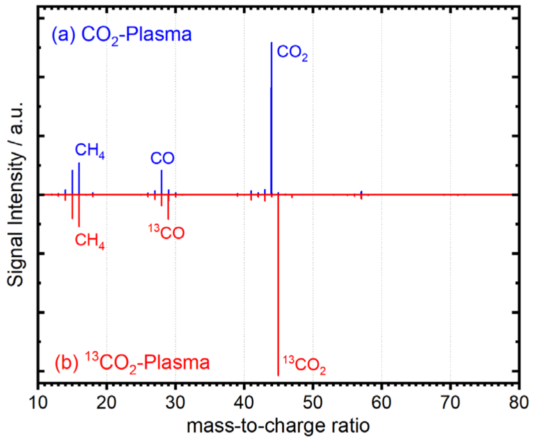

Fig. 1. Comparison of (a) a sampled mass spectrum following CH_4/CO_2 experiments and (b) a sampled mass spectrum following isotopically labeled $^{13}CO_2$ experiments.

4. Conclusion

We performed $^{13}CO_2$ labeling to gain experimental insights into plasma-assisted dry reforming of methane. Using molecular-beam mass spectrometry, we provide evidence for ^{13}CO- or $^{13}CO_2$-driven formation of double-oxygenated species. A zero-dimensional plasma kinetic model has been developed to include this newly observed chemistry. The reaction path analysis shows that HOCO is the main intermediate driving the formation of double-oxygenated species.

Acknowledgement

This material is based upon work supported by the Low-Temperature Plasma Research Facility at Sandia National Laboratories, which is a collaborative research facility supported by the U.S. Department of Energy, Office of Science, Office of Fusion Energy Sciences.