Multi-Modal In-Situ/Operando Spectroscopy Combining PM-IRAS, OES, and MS for Observing Plasma-Stimulated Activation of Surface Species

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Introduction

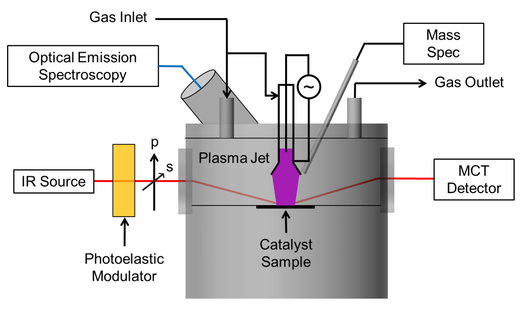
- There has been a growing interest in integrating atmospheric pressure non-thermal plasmas (NTPs) into heterogeneous catalysis to promote catalytic activities and/or selectivities, and even novel chemical transformations[1]
- Plasma catalysis is related to the interactions between the plasma and a surface catalytic material
- To improve plasma catalytic system, it is essential to understand the fundamental behavior of the underlying plasma-catalytic surface interactions[1]
- In conventional catalysis, there has been an extensive number of mechanistic studies using model surfaces with reduced complexity and heterogeneity[2] but still mimic the catalytic properties of the real catalysts
- To date, there has been no model surface studies in plasma catalysis
- For model surface studies, it is desirable to utilize surface-specific Infrared spectroscopic techniques in conjunction with plasma-phase characterization to better understand the fundamental interactions of the plasma with a surface

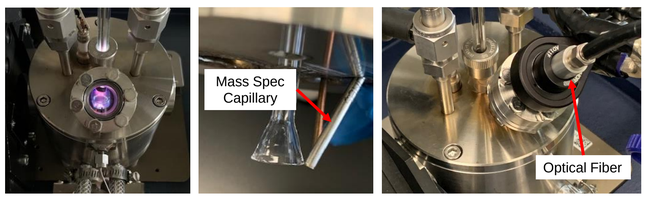
Research Objective

- Design a multi-modal spectroscopy instrument combining polarization-modulation infrared reflection-absorption spectroscopy (PM-IRAS), mass spectrometry (MS), and optical emission spectroscopy (OES)
- Investigate how plasma-induced reactive species influence deposition and activation of the carbonaceous species in non-oxidative coupling of methane via NTPs with different surface materials at 1 atm and 298 K

Design of a Multi-Modal Spectroscopy Instrument

Modification of Harrick Refractor™ Reactor

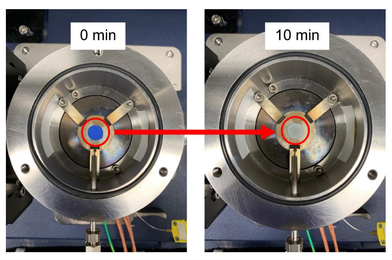




- The spectroscopic cell lid was modified to implement three components: (1) a flared quartz tube for generating the plasma jet, (2) an optical window for OES, and (3) a MS capillary sniffer

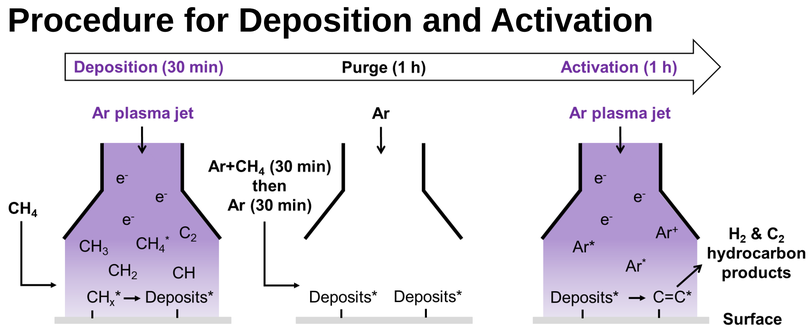
Plasma Jet Operational Test

- Filter paper was dyed with brilliant blue G dye solution and treated with an Ar plasma jet into 20% O_2 in N_2
- After Ar plasma jet exposure, the color of the dyed filter paper faded away uniformly



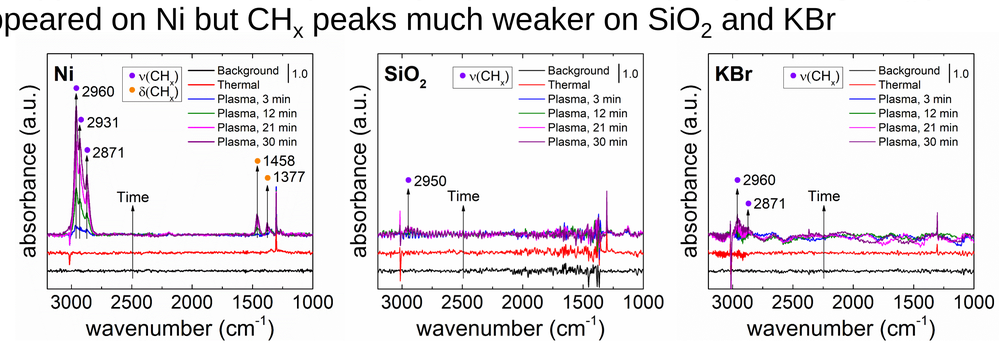
Experimental Procedure and Results

Sequential Procedure for Deposition and Activation



Surface-dependent Carbonaceous Species Deposition

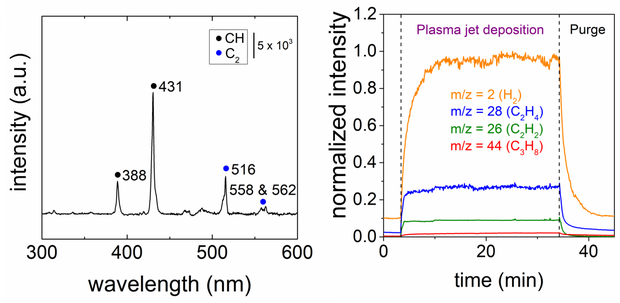
- On application of the Ar plasma jet (7 kV, peak-to-peak), strong CH_x peaks appeared on Ni but CH_x peaks much weaker on SiO_2 and KBr



Results

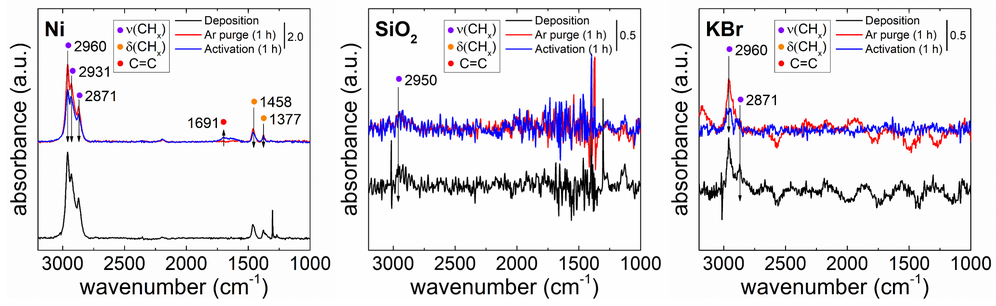
Surface-dependent Carbonaceous Species Deposition

- Different surfaces didn't affect the plasma production of key CH_4-derived radical species
- No clear difference in the gas-phase product with different surfaces

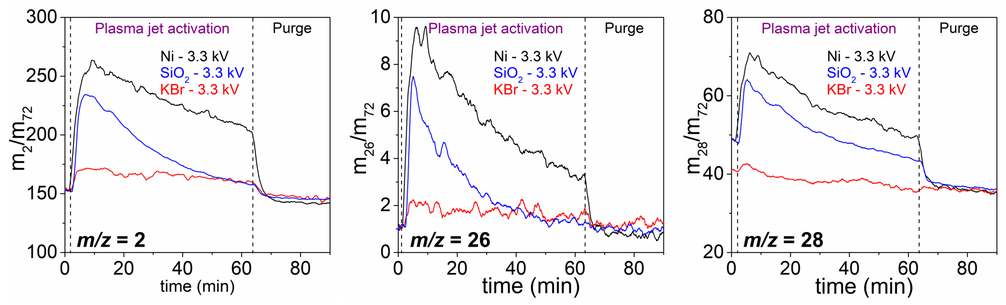


Activation of Carbonaceous Deposits by an Argon Plasma Jet

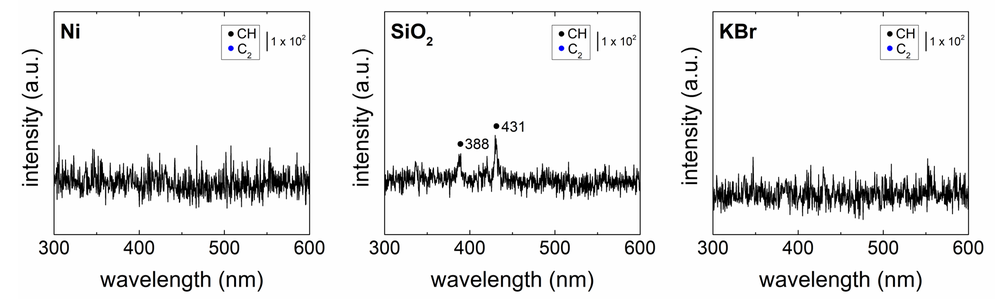
- On application of the Ar plasma jet (3.3 kV, peak-to-peak), formation of C=C species (1691 cm^{-1}) was observed on Ni, but not on SiO_2 and KBr



- Comparable amount of H_2 and C_2 hydrocarbons formation observed with Ni and SiO_2 during the activation

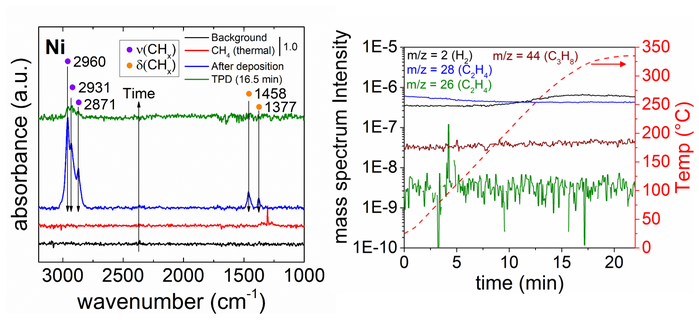


- Ar plasma jet activation with Ni (no CH radicals in the plasma-phase) is most likely to be a surface phenomenon while activation with SiO_2 (CH radicals in the plasma-phase) is possibly a plasma-phase recombination



Temperature-Stimulated or Plasma-Stimulated Activation?

- Temperature programmed desorption (TPD) after the deposition to confirm the plasma-stimulated activation
- No surface C=C formation
- No H_2 and C_2 hydrocarbons production



Conclusions

- Multi-modal spectroscopy was designed and its capabilities were verified in a model system (non-oxidative coupling of methane via NTPs)
- Transition metal Ni was found to be much more interactive with the CH_4 plasma radicals than SiO_2 and KBr in both deposition and activation
- The appearance of C=C species on Ni but not on SiO_2 and the absence of CH radicals with Ni but the presence of CH radicals with SiO_2 during the activation step indicated that the activation possibly takes place through two different mechanisms

References

(1) Bogaerts, A. et. al., *J. Phys. D Appl. Phys.* 53 (2020) 443001.
(2) Henry, C. R., *Surface Science Reports* 31 (1998) 231-325.

Acknowledgements

This work is based on support from the National Energy Technology Laboratory (NETL) under Award No. DE-FE0031862.