

Surface chemistry at a plasma-surface interface for N₂ fixation

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Abstract: The chemistry on a surface in direct contact with a plasma is studied in-situ on an iron foil with infrared reflectance absorption spectroscopy. The surface composition notably changes when igniting the plasma in various gas mixtures, e.g. N₂/H₂. This is inferred from a change in the reflectance of the foil.

1. Introduction

Plasma catalysis received much attention because it promised to replace heterogeneous catalysis in the chemical industry. However, recent results indicate that in-plasma catalysis cannot deliver on its promise in some cases because the highly energetic plasma environment is very different from thermal catalysis, and any desired reaction product might also be destroyed by the plasma.

Yet, kinetic modelling shows the importance of surface chemistry on the overall formation, e.g. for NH₃ [1, 2]. These models, however, include surface reactions as they are described in heterogeneous catalysis although the plasma reaction steps and the impact of radicals and excited species on the surface can only be guessed.

In this contribution, we present our recent experimental findings about the surface chemistry at a plasma-surface interface. The chemical composition of an iron foil is measured in-situ with infrared reflection absorption spectroscopy (IRRAS). The foil is in direct contact with a low-pressure RF plasma. A N₂/H₂ or N₂/O₂ gas mixture is used to study the processes related to either NH₃ or NO_x synthesis.

IRRAS is comparable to absorption spectroscopy, which is a widely used diagnostic of plasmas. The measured reflectance relies on the presence of surface-bound species, instead of IR active vibrational transitions of gaseous species. However, unlike absorption spectroscopy, the adsorbed species do not have an intricate rotational structure. Rather, each vibration absorbs light at a given frequency, which has a much larger linewidth due to the various bonding configurations of the surface groups.

2. Methods

A capacitive coupled plasma is ignited using a planar electrode configuration. The grounded electrode is covered from the plasma using an iron foil, which is replaced for each measurement. The plasma is ignited between 8 and 10 mbar with a continuous flow. Before each measurement, the foil is cleaned using a helium plasma. Afterwards, a N₂/H₂ or N₂/O₂ mixture is used to study nitrogen fixation.

The foil is probed by the IR light of a Fourier Transform IR (FTIR) spectrometer (Vertex 70, Bruker). The light is reflected on the sample under an angle of 70° to the normal of the surface.

3. Results and Discussion

The pure H₂ plasma alters the surface composition on two different timescales: short and long timescale. The former occurs too fast given the temporal resolution of our

technique, which is roughly a minute. The long timescale, however, occurs over several minutes and it is attributed to atomic hydrogen penetrating the material. Also, igniting the plasma in nitrogen only shows an abrupt change, i.e. on a short timescale. This is expected as nitrogen atoms cannot diffuse into the metal as atomic hydrogen.

Furthermore, igniting in a N₂/H₂ gas mixture shows the dominance of hydrogen on the surface chemistry. When igniting in a N₂/H₂ gas mixture after pre-dosing the surface with a H₂ plasma, the reflectance of the iron foil is unaffected. This effect is also observed in the current kinetic plasma-surface models [1], where the surface coverage of H is orders of magnitude larger than N and NH_x.

Preliminary measurements with a N₂/O₂ gas mixture show the formation of O₃(g) and adsorbed NO₂. The O₃(g) density decreases with increasing N₂/O₂ gas ratio, whereas NO₂(s) increases with this ratio. However, a closer look at the results is required for more detailed conclusions.

4. Conclusion

We measured in-situ the surface composition of an iron foil in direct contact with a plasma. Changes in the reflectance spectra indicate how the surface is altered by the plasma. Also, distinct processes are identified by the time scale at which certain changes in the reflectance occur.

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References

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