Packed bed reactor for in situ study of the catalyst surface during plasma assisted catalysis

S. Gershman[1], V. Storr[2], M.Carreon[2]
[1]*Princeton Plasma Physics Laboratory, Princeton, NJ*
[2]*Department of Chemical Engineering, University of Arkansas, Fayetteville, AR*

Abstract: In this contribution, we report the design, construction, and testing of a plasma reactor suitable for in situ measurements of surface changes of the catalyst/support under realistic operational conditions. Plasma synthesis of ammonia is used as a model reaction. The reactor is able to provide in situ information on surface modification in previously inaccessible packed bed reactors.

1. Introduction

Packed bed reactors are commonly used in chemical industry for large-scale production of chemicals and for the removal of pollutants from liquids and gases. This configuration has been studied extensively [1-4] but the in-situ studies of the catalyst have not been hindered by lack of access. In situ and operando studies of the bulk and surface species are essential for mechanistic understanding of the reactions and for the study of catalyst selectivity, activity, and fouling. Diffuse reflectance infrared Fourier Transform spectroscopy (DRIFTS) is used for in situ studies in thermal catalysis. In plasma catalysis the in situ studies have plasma conditions that vary significantly from the PBR plasma type and operational parameters [1-4]. The main goal of this work was to design, build, and validate the operation of a PBR with operational parameters, that match closely the commonly used tubular packed bed dielectric barrier discharge (DBD) reactors.

2. Methods

A PBR is designed to be used with PIKE DRIFTS cell (PIKE Technologies, Inc.). It is comprised of two disk flanges with ZnSe window(s) and a compressible gasket between (Figure 1.a). The 1 mm gap between the center high voltage electrode and the ZnSe window is packed with a catalyst support/catalyst powder. The reactor operates at 48 kHz, 12 – 14 kV p-p, 8 – 10 W, parameters typical for AC driven DBD reactors [2-4]. The reactor was tested for operation with Ag and Fe catalysts on micro and meso porous silica and SBA-15 used for ammonia synthesis from 1:1 N_2:H_2 plasma at atmospheric pressure. NH_3 production was verified using FTIR gas absorption spectroscopy.

3. Results and Discussion

Spectra showed immediate changes due to plasma exposure for all powders as for example, in Figure 1.b for SBA-15. The most notable is the immediate decrease in the Si-O-Si peak at 1053 cm^{-1} and a growth/shift to 1010 cm^{-1}. Changes in this region can indicate attached N-H vibrations, Si-NH_x, or Si-N N-H vibrations These changes persist after treatment. There is also a consistent appearance of two bands, 1600 cm^{-1} and 1630 cm^{-1} that may be attributed to attached –N vibrations, ex. Si-N. These peaks are only present during plasma possibly due to nitrogen desorption.

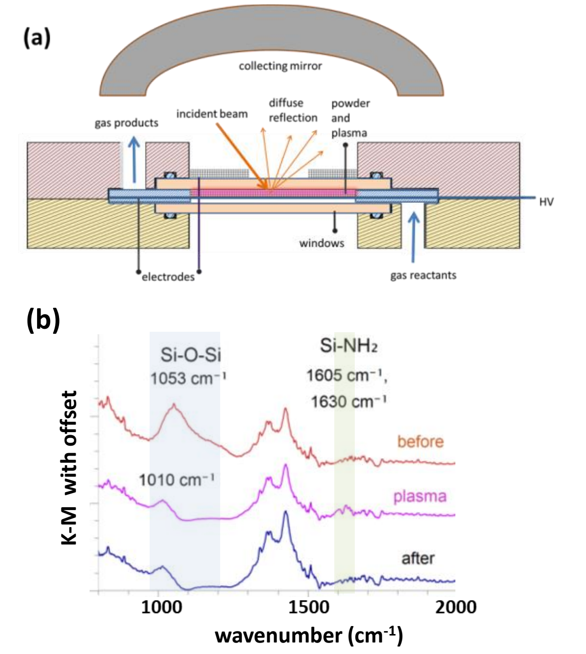

Fig. 1. a. Plasma PBR for in situ DRIFTS analysis of a solid catalyst. b. A sample spectrum of silica SBA-15 showing persistent (blue) and temporary surface changes (green).

4. Conclusion

The new reactor gives access to areas difficult to reach. The reactor demonstrated its ability to provide information on temporary and persistent changes in the surface of a catalyst.

Acknowledgement
This material is based upon work supported by the Princeton Collaborative Research Facility, supported by DOE under Contract No. DE-AC02-09CH11466

References

(1) Carreon, M. L. *J. Phys. Appl. Phys.* **2019**, *52* (48),
(2) Gershman, S. Plasma Chem Plasma Process 2022 42
(3) Winter, R. *ACS Catal. 2020, 10, 24, 14763–14774*
(4) Gorky, F.; *J. Phys. Appl. Phys.* **2021**, *54* (26),